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FIRST REPORT OF THE COMMITTEE ON ATOMIC WIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY

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In September, 1930, at the meeting of the International Union of Chemistry at Liege, the Committee on Elements which has functioned since 1923 was replaced by three committees, on Atomic Weights, Atoms, including isotopy and atomic structure, and Radioactive Constants. Hereafter the function of the first of these committees will be to prepare annually a table of atomic weights on the basis of the most recent evidence. National Committees on Atomic Weights are requested by the International Union to refrain from publishing tables of their own.

While it was impossible for the new committee to issue a report earlier this year. it is the intention of the committee normally to issue its report so far as possible in the first (January) number of current chemical and physical periodicals. These reports will cover the twelve months from October to September preceding.

Authors of papers bearing on the subject are requested to send copies to each of the five members of this committee at the earliest possible moment.[1]

Since the reports of the German and American committees[2] adequately cover the ground of progress during 1929, only investigations published since January 1, 1930, are reviewed in this report.

Batuecas, Schlatter and Maverick[3] have published new determinations

	I	II
N_2	1 0040	
NH_3	1.01543	1.01515
HCl	1.00787	1.00737
CO	1.00048	
H_2S	1.01031	1.01035

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[1] Prof. G. P. Baxter, Coolidge Laboratory, Harvard University, Cambridge. Mass.. U. S. A.; Mme. M. Curie, Institut du Radium, 1 Rue Pierre Curie, Paris 5, France; Prof. O. Honigschmid, Arcisstrasse 1, Munich, Germany; Prof. P. Le Beau. École Superieure de Pharmacie, 4 Avenue de l'Observatoire, Paris 5, France; Prof. R. J. Meyer, Meinekestrasse 8, Berlin W. 15, Germany.

[2] *Ber.*, 63B, 1 (1930); THIS JOURNAL, 52, 857 (1930).

[3] Batuecas, Schlatter and Maverick, J. *chim. phys.*, 27, 36, 45 (1930).

of $(PV)_0/(PV)_1$ by the expansion method. In Column I the assumption is made that the quantity varies lineally with the pressure; in Column II an equation of the second degree is used.

Nitrogen.—Moles and Batuecas[4] have redetermined the density of ammonia at various pressures. The gas was prepared (1) from ammonium oxalate and potassium hydroxide, (2) by synthesis (technical) from the elements, (3) by hydrolysis of magnesium nitride. After chemical purification the gas was fractionally distilled and in most cases was dried finally with phosphorus pentoxide. Correction for adsorption on the walls of the

Method of preparation	Globe N-3 773 ml.	Globe N-2 647 ml. Preliminary	Globe G, 1007 ml.	Average
		1 Atmosphere		
1	0.77167	0.77196		0.7718
	.77234	.77184		.7721
	.77226	.77207		.7722
	.77137	,77219		.7718
Average	.77191	.77202		.7720
	.77174	.77130		.77152
	.77168	.77190		.77179
	.77113	.77158		.77136
	.77160	.77168		.77164
		.77166		77166
	.77170	.77149		.77160
	.77184	.77212		,77198
Average	,77162	.77168		.77165
2	.77118	,77185		.77152
	.77153	,77207		,77180
	.77180	.77119		,77149
	.77144	,77188		,77166
	.77161	.77193		.77177
Average	.77151	.77178		.77165
3			0.77169	.77169
			.77165	.77165
	.77195		,77193	,77194
	.77168		,77170	77169
	.77187		,77206	.77197
Average	.77183		,77181	,77179
Average of all	.77163	.77172	.77181	.77169

Method of preparation	Globe N_3	Globe N_2	Globe G	Average
		$^2/_3$ Atmosphere		
1	0.76758		0.76763	0.76761
	,76734		,76773	.76754
	.76839		,76842	.76841
	.76803		.76844	.76824
Average	.76784		.76806	,76795

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[4] Moles and Batuecas, *Anales soc. españ. fís. quím.*, *28*, 871 (1930).

Method of preparation	Globe N_3	Globe N_2	Globe *G*	Average
2	0.76754	0.76770		0.76762
	.76770			.76770
	.76752	.76769		.76761
Average	.76759	.76770		.76764
3	.76743		.76729	.76736
	.76737		.76758	,76748
Average	.76740		.76744	.76742
Average of all	.76766	.76770	.76785	.76773
		$^1/_2$ Atmosphere		
1	0.76511		0.76624	0.76568
	.76623		.76597	.76610
	.76586		.76557	.76572
Average	.76573		.76593	.76583
2	.76592		.76606	.76599
	.76582		.76592	.76587
Average	.76587		.76599	.76593
3		0 76539		.76539
	.76641			.76641
	.76577	.76561		.76569
	.76610	.76593		.76602
	.76605	.76541		.76573
Average	.76608	.76559		.76585
Average of all	,76592	.76559	.76595	.76585
		$^1/_3$ Atmosphere		
1	0.76328		0.76321	0.76325
	.76378		.76341	.76360
	.76395		.76434	.76415
Average	.76367		.76365	.76366
2	.76424		.76314	,76369
			.76348	.76348
	.76400		.76403	.76402
	.76416		(76260)	.76416
	.76444		.76387	.76416
	.76387		.76360	.76374
Average	.76418		.76362	.76390
3	.76391			
	.76438			
	.76342			
	.76350			
	.76405		.76426	.76416
Average	.76385		.76426	.76392
Average of all	.76392		.76370	.76383

globes was made. The results are expressed in the weight of the liter at 0° and 760 mm.

From the densities at various pressures the limiting density of ammonia is calculated by the method of differences to be 0.75990. The corresponding molecular weight of ammonia is then 17.032, and the atomic weight of nitrogen 14.009.

Phosphorus.—Ritchie[5] has determined the density of phosphine at different pressures. The gas was prepared from phosphonium iodide by means of potassium hydroxide and was fractionated.

P, atmospheres	Globe I, 336 ml.	Globe II, 341 ml.	Average
1	(1.5311)	1.5308	1.5308
	1.5308	1.5307	1.5308
	1.5307	1.5305	1.5306
	1.5307	1.5307	1.5307
	1.5308	1.5308	1.5308
	1.5306		1.5306
Average	1.5307	1.5307	1.5307
0.75	1.5274	1.5272	1.5273
		1.5273	1.5273
	1.5271	1.5272	1.5272
Average	1.5273	1.5272	1.5272
0.50	1.5241	1.5237	1.5239
	1.5242		1.5242
	1.5237	1.5236	1.5237
	1.5233	1.5238	1.5236
	1.5238	1.5238	1.5238
Average	1.5238	1.5237	1.5238
0.25	1.5204	1.5202	1.5203
	1.5202	1.5203	1.5203
		1.5201	1.5201
	1.5205	1.5205	1.5205
Average	1.6204	1.5203	1.5203

Assuming a linear relation between P V and pressure, $(PV)_0/(PV)_1$ is calculated to be 1.0091.

If the normal liter of oxygen weighs 1.4290 g. and the coefficient of deviation from Boyle's Law per atmosphere is —0.00096, then $PH_3 = 34.000$ and $P = 30.977$. This value for phosphorus is appreciably lower than the chemical value.

Sulfur.—Hönigschmid and Sachtleben[6] have completed a synthesis of silver sulfide from its elements. The compound was found to be stable up to 300° but to lose sulfur by decomposition above this temperature. When reheated in sulfur vapor, partially decomposed sulfide takes up quantitatively the deficiency in sulfur. Excess sulfur is given up at 300°. To carry out a synthesis weighed quantities of the purest silver were heated in sulfur vapor until the reaction was complete and then the excess of sulfur was eliminated in a current of pure nitrogen at 280°. Constancy in weight of the sulfide was readily attained. The sulfur was prepared by precipita-

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[5] Ritchie, *Proc. Roy. Soc.* (*London*), **A128**, 551 (1930).

[6] Hönigschmid and Sachtleben, *Z. anorg. Chem.*, 195, 207 (1931).

tion from thiosulfate and double distillation in vacuum. Weights are corrected to vacuum. In the twelfth analysis the materials of the eleventh were reweighed in exhausted receptacles.

THE ATOMIC WEIGHT OF SULFUR

Wt. of Ag, g.	Wt. of Ag_2S, g.	Ratio $Ag_2S:2Ag$	Atomic weight of sulfur
7.90291	9.07742	1.148617	32.066
9.42181	10.82209	1.148621	32.066
9.74522	11.19355	1.148620	32.066
9.59836	11.02489	1 148622	32.067
9.20378	10.57166	1.148622	32 067
10.75224	12.35021	1.148617	32.066
8.28317	9.51424	1.148623	32.067
9.86327	11.32913	1.148618	32.066
10.43748	11.98871	1.148621	32.066
7.21091	8.28265	1 148627	32.068
9.84440	11.30749	1.148621	32.067
9.84439	11.30748	1.148622	32.067
	Average	1.148621	32.066

Since all recent determinations of the atomic weight of sulfur have yielded a value not far from 32.06, this value has been adopted for the table.

Chlorine.—Scott and Johnson,[7] call attention to an error in the solubility of silver chloride at 0° assumed by Honigschmid and Chan[8] in their syntheses of silver chloride, which amounts to 0.002% in the weight of silver chloride.

Calcium.—Honigschmid and Kempter[9] purified calcium nitrate from marble by ten recrystallizations, and converted the product to chloride by precipitation of the carbonate and solution of the latter in hydrochloric acid (Sample I). Sample II was prepared from commercial nitrate by fifteen crystallizations. After recrystallization of the chloride it was prepared for weighing by dehydration and fusion in hydrogen chloride, and allowed

ATOMIC WEIGHT OF CALCIUM

Sample	Wt. of $CaCl_2$, g.	Wt. of Ag, g.	Ratio $CaCl_2:2Ag$	Atomic weight of calcium
I	1.84526	3.58692	0.514441	40.082
I	1.62314	3.15509	.514451	40.084
I	1.42216	2.76444	.514447	40.083
I	2.21933	4.31400	.514448	40.083
I	1.03950	2.02064	.514441	40.082
I	1.45783	2.83364	.514472	40.088
II	2.93786	5 71052	.514464	40.086
II	2.45368	4.76952	.514451	40.084
II	2.11276	4.10689	.514441	40.082
		Average	.514451	40.084

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[7] Scott and Johnson, THIS JOURNAL, 52, 3586 (1930).

[8] Honigschmid and Chan, *Z. anorg. Chem.*, 163,315 (1927).

[9] Honigschmid and Kempter, *ibid.*, 195, 1 (1931).

ATOMIC WEIGHT OF CALCIUM *(Concluded)*

Sample	Wt. of $CaCl_2$, g.	Wt. of AgCl, g.	Ratio $CaCl_2:2AgCl$	Atomic weight of calcium
I	1.97942	5.11225	0.387191	40.083
I	2.35393	6.07937	.387199	40.086
I	1.67385	4 32284	,387210	40.089
I	1.62314	4.19217	.387183	40.082
I	1.42216	3.67297	.387196	40.085
I	2.21933	5.73153	.387214	40.090
II	1.03950	2.68467	.387198	40.086
II	1.45783	3.76499	.387206	40.088
		Average	.387200	40.086

to solidify in nitrogen. The solutions of the weighed chloride were corrected for deviations from the neutral point by titration with $N/100$ solutions of acid and base and then were compared with silver in the usual way, and the silver chloride was collected and weighed. Weights are corrected to vacuum.

The average of both series, 40.085, is slightly higher than that found earlier by Richards and Honigschmid, 40.071. For the present 40.08 is recommended.

A. V. and O. Frost[10] claim to have discovered a concentration of Ca^{41} by beta-ray emission from K^{41} in a potassium feldspar containing 0.042% of calcium oxide. Only 0.15 g. of calcium oxide was available. From the ratio $CaCl_2:CaBr_2$ the atomic weight of calcium was found in two experiments to be 40.23. Similar experiments with ordinary calcium which had been purified in the same way gave 40.10.

Honigschmid and Kempter[11] attacked the same problem with calcium extracted from sylvin by von Hevesy. After preliminary purification the average atomic weight through the chloride was found to be 40.22. Spectroscopic investigation, however, revealed the presence of strontium. After removal of this impurity by fractional precipitation of the oxalate, the observed atomic weight was lowered to 40.093. The material still contained 0.015 atom per cent. of strontium so that the value to be expected is 40.091. Since the sylvin is a geologically younger mineral than the feldspar, a smaller concentration of Ca^{41} is to be expected, so that the question as to appreciable variation of Ca^{41} in nature is still an open one.

Vanadium.—Scott and Johnson,[12] have analyzed vanadyl trichloride. This was made by heating purified vanadium trioxide in a current of chlorine, and the product was purified by vacuum distillation, after removal of excess chlorine with mercury and sodium. Portions for analysis were removed in sealed glass bulbs in the later stages of the distillation. After being weighed the bulbs were broken under either nitric acid or ammonia.

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[10] Frost and Frost, *Nature*, 125, 48 (1930).

[11] Hönigschmid and Kempter, Z. *anorg. Chem.*, 195, 9 (1931).

[12] Scott and Johnson. THIS JOURNAL, 52, 2638 (1930).

In the former case the glass was washed with nitric acid and collected on a filter. In the latter, after the supernatant liquid had been filtered, the precipitate was dissolved in nitric acid and the glass was washed and collected. The solutions were then compared with silver in the usual way, and in some cases the silver chloride was collected. The analyses are arranged in the order of decreasing volatility of the chloride samples. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF VANADIUM

Acid Hydrolysis

wt. of $VOCl_3$, g.	Wt of Ag, g	Ratio $VOCl_3$ 3Ag	Atomic wt. of vanadium	Wt of AgCl, g	Ratio $VOCl_3$ 3AgCl	At. wt of vanadium
8.15697	15 23143	0.535535	50 950	20 23483	0 403115	50.973
8.29538	15 48986	.535536	50.950	20 57872	403105	50 969
7.60527	14 20111	535541	50 951	18 86755	403087	50.961
7.01143	13 09218	535543	50 952			
	Average	535539	50 951		403102	50 968

Alkaline Hydrolysis

wt. of $VOCl_3$, g.	Wt of Ag, g	Ratio $VOCl_3$ 3Ag	Atomic wt. of vanadium	Wt of AgCl, g	Ratio $VOCl_3$ 3AgCl	At. wt of vanadium
7.75120	14 47384	0 535532	50.949			
7.88453	14 72386	535493	50 936	19.56218	403050	50 945
9.19783	17.17614	535500	50.938	22 81924	,403073	50 955
6.69572	12 50344	535510	50 941			
8.04970	15.03136	,535527	50.947	19 96976	.403094	50 964
7.62984	14.24666	535553	50 955			
	Average	.535519	50 945		.403072	50 955

Experimental evidence was found that the nephelometric end-point was slightly affected by the presence of vanadic acid, but the effect on the atomic weight of vanadium is less than 0.005. The average of the comparisons with silver, 50.948, agrees almost exactly with the recent results obtained by McAdam, and by Briscoe and Little.

Chromium.—Gonzales[13] has applied to chromyl chloride the recently developed method of preparing volatile inorganic compounds by fractional distillation in vacuum. The compound was prepared by the action of concentrated sulfuric acid on a mixture of sodium chloride and potassium bichromate and after fractional distillation under low pressure was collected in sealed glass bulbs. The bulbs were broken under water and the halogen was determined by comparison with silver in the usual way. Ultimately the silver chloride was determined. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF CHROMIUM

Wt. of CrO_2Cl_2, g.	Wt. of Ag, g.	Ratio CrO_2Cl_2:2Ag	Atomic wt. of chromium	Wt. of AgCl, g.	Ratio CrO_2Cl_2:2AgCl	At. wt. of chromium
9.56543	13.32143	0.718049	52.012	17.69786	0.540485	52.029
9.54415	13.29120	.718080	52.019	17.65929	.540460	52.022
	Average	.718065	52.016		.540473	52.026

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[13] Gonzales, *Anales soc. españ. fís. quím.*, *28,* 579 (1930).

The average result 52.02 is only 0.01 unit higher than the current one and no change is recommended for the present.

Arsenic.—Krepelka[14] has published details of the analysis of arsenic trichloride noted earlier.[15] Recrystallized arsenic trioxide was reduced with sugar charcoal and the metal resublimed. Conversion of the metal to chloride was followed by repeated vacuum distillation of the latter. Samples were collected for weighing in sealed evacuated bulbs. Hydrolysis with ice water was followed by comparison with silver in the usual way. In two cases the silver chloride was collected and weighed. Vacuum weights are given.

THE ATOMIC WEIGHT OF ARSENIC

Wt. of $AsCl_3$, g.	Wt. of Ag, g.	Ratio $AsCl_3$:3Ag	At. wt. of arsenic[a]	Wt. of AgCl, g.	Ratio $AsCl_3$:3AgCl	At. wt. of arsenic[a]
3.98710	7.11681	0.560237	74.944			
4.81766	8.59961	.560218	74.938			
6.27437	11.20020	560201	74.933			
2.42721	4.33242	.560244	74.946	5.75672	0.421631	74.934
3.86442	6 89796	.560227	74.941			
5.09819	9.10041	.560215	74.937			
5.46890	9.76222	.560211	74.936			
5.10039	9.10415	.560227	74.941			
5.71146	10.19540	.560200	74.932			
3.05992	5.46180	.560240	74.945			
1.49994	2.67755	.560191	74.929	3.55734	.421646	74.941
	Average	.560219	74.938		.421638	74.938

[a] Calculated with Cl = 35.457. The figures given by the authors are calculated with Cl = 35.458.

This value is slightly lower than the value which has been in use for some time, and slightly higher than that found by Aston with the mass spectrograph after correction for the presence of O^{18}, 74.927. The value 74.93 is adopted in the table of atomic weights.

Tantalum.—Krishnaswami[16] has analyzed the chloride and bromide of tantalum. Metallic tantalum was first obtained by reducing purified potassium tantalum fluoride with sodium in an atmosphere of argon. When examined spectroscopically the metal appeared to be free from impurities, although it contained a small percentage of oxide. The metal was converted to halides by the action of pure dry halogens and the halides were twice distilled in vacuum and collected in sealed glass bulbs. After being weighed the bulbs were broken under ammonia and the solutions filtered to remove glass and tantalic acid. To find the weight of the glass the tantalic acid was dissolved in oxalic acid and the glass was collected on a weighed crucible. The solutions were then compared with silver, and

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[14] Krepelka, *Collect. trav. chim. Tchecoslovaquie*, 2, 255 (1930).

[15] Krepelka, *Nature*, 123,944 (1929).

[16] Krishnaswami, *J. Chem. Soc.*, 1277 (1930).

the silver halides were collected and weighed. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF TANTALUM

Wt. of $TaBr_5$, g.	Wt. of Ag, g	Ratio $TaBr_5:5Ag$	Atomic wt. of tantalum	Wt. of AgBr, g.	Ratio $TaBr_5:5AgBr$	At. wt. of tantalum
3.07127				4.96415	0.61869	181.36
3.72095				6.01413	.61870	181.37
3.81890	3.54594	1.07698	181.34	6.17267	.61868	181.35
3.59654	3.33939	1.07700	181.36	5.81303	.61870	181.37
2.69071	2.49831	1.07701	181.37	4.34926	.61866	181.33
2.61163	2.42488	1.07702	181.37	4.22133	.61868	181.35
3.92094	3.6464064	1.07699	181.35	6.33750	.61869	181.36
204583	1.89956	1.07700	181.36	3.30681	.61867	181.34
	Average	1.07700	181.36		.61868	181.35

Wt. of $TaCl_5$, g.	Wt of Ag, g	Ratio $TaCl_5:5Ag$	Atomic wt. of tantalum	Wt. of AgCl, g.	Ratio $TaCl_5:5AgCl$	At. wt. of tantalum
3.15350	4.74301	0.66488	181.35	6 30152	0.50044	181.37
2.96215	4.45549	.66483	181.33	5.91874	.50047	181.40
4.08061	6.13756	.66486	181.34	8.15438	.50042	181.36
3.21073	4.82972	.66479	181.30	6.41613	.50042	181.36
3.49922	5.26278	.66490	181 36	6 99201	.50046	181.39
	Average	,66485	181.34		.50044	181.37

The average value, 181.36, is lower than that found by Balke in 1910, 181.50. Balke's method, in which the ratio $TaCl_5:Ta_2O_5$ was determined, has been found to be unreliable because of the uncertain composition of most oxides. The new value therefore has been adopted.

Rhenium.—Hönigschmid and Sachtleben[17] have taken advantage of the increased quantities of rhenium now available by analyzing silver perrhenate. Three specimens of material were prepared. (I) Potassium perrhenate was recrystallized and the silver salt precipitated. Retained potassium was removed by reprecipitation and crystallization. (II) Metallic rhenium was burned to heptoxide in oxygen, and after solution of the oxide in water, silver perrhenate was precipitated with silver nitrate. (III) The third sample was prepared by dissolving silver oxide in perrhenic acid.

THE ATOMIC WEIGHT OF RHENIUM

Sample	Wt. of $AgReO_4$, g.	Wt. of AgBr, g.	Ratio $AgReO_4:AgBr$	Atomic weight of rhenium
I	5.36365	2.81186	1.90751	186.34
11	7.83577	4.10795	1,90747	186.33
11	8.55829	4.48684	1.90742	186.33
II	6.34973	3.32894	1.90743	186.33
III	8.90918	4.67111	1.90729	186.30
III	6.95494	3.64684	1.90712	186.27
III	7.85704	4.11955	1.90726	186.30
		Average	1.90735	186.31

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[17] Hönigschmid and Sachtleben, Z. *anorg. Chem.*, 191,309 (1930).

The silver salt was prepared for weighing by fusion in air of a mixture of the perrhenate with an excess of acid. Weighed amounts of salt were dissolved in water and the silver was precipitated as silver bromide. Weights are corrected to vacuum.

This result is 2.4 units lower than the preliminary value found by W. and I. Noddack by analysis of the disulfide, but in view of the inferiority of the latter method and the small quantities weighed, the new value 186.31 is adopted for the table.

Thallium.—Honigschmid and Striebel[18] prepared thallous bromide by precipitation from a solution of the purified sulfate. After distillation in nitrogen the salt was weighed in a quartz tube. Solution in hot water was followed by hot precipitation with a nearly equivalent amount of silver The end-point was found with a nephelometer in the usual way. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF THALLIUM

Preliminary Series

Wt. of TlBr, g.	Wt. of Ag, g.	Ratio TlBr:Ag	Atomic weight of thallium
3.86281	1.46582	2.63526	204.38
3.78429	1.43583	2.63561	204.41
3.96949	1.50639	2.63510	204.36
3.94471	1.49669	2.63562	204.42
	Average	2.63540	204.39

Final Series

Wt. of TlBr, g.	Wt. of Ag, g.	Ratio TlBr:Ag	Atomic weight of thallium
4.01222	1.52251	2.63527	204.377
3.97142	1.50692	2.63546	204.397
3.90498	1.48170	2.63547	204.399
4.07193	1.54509	2.63540	204.391
3.68886	1.39974	2.63539	204.390
4.04739	1.53580	2.63536	204.387
	Average	2.63539	204.390

This value agrees exactly with that found earlier by Honigschmid, Berckenbach and Kothe through the analysis of thallous chloride.

Lead.—Baxter and Bliss[19] have determined the atomic weight of two specimens of RaG. The first was extracted from Swedish kolm, the second from uraninite from Wilberforce, Ontario, Canada. Purification was effected by precipitation as chromate and sulfate and crystallization as nitrate and chloride. After resublimation the chloride was fused preparatory to weighing, Comparison with silver was carried out as usual. Weights are corrected to vacuum.

The kolm lead has a lower atomic weight than any other specimen yet examined and seems to consist almost entirely of the isotope Pb^{206}.

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[18] Honigschmid and Striebel, Z. *anorg. allgem. Chem.*, 194, 293 (1930)

[19] Baxter and Bliss, THIS JOURNAL, 52, 4848, 4851 (1930).

International Atomic Weights

1931

	Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.93
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.00
Cerium	Ce	58	140.13
Cesium	Cs	55	132.81
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium	Cb	41	93.3
Copper	Cu	29	63.57
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.64
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.002
Holmium	Ho	67	163.5
Hydrogen	H	1	1.0078
Indium	In	49	114.8
Iodine	I	53	126.932
Iridium	Ir	77	193.1
Iron	Fe	26	55.84
Krypton	Kr	36	82.9
Lanthanum	La	57	138.90
Lead	Pb	82	207.22
Lithium	Li	3	6.940
Lutecium	Lu	271	175.0
Magnesium	Mg	1	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61

	Symbol	Atomic Number	Atomic Weight
Molybdenum	Mo	42	96.0
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	190 8
Oxygen	O	8	16 0000
Palladium	Pd	46	106.7
Phosphorus	P	15	31 02
Platinum	f't	78	195.23
Potassium	K	19	39 10
Praseodymium	Pr	59	140.92
Radium	Ra	88	225.97
Radon	Rn	86	222
Rhenium	Re	76	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.44
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	79.2
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.06
Tantalum	Ta	73	181.4
Tellurium	Te	52	127.5
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169 4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	184.0
Uranium	U	92	238.14
Vanadium	V	23	50.95
Xenon	Xe	54	130.2
Ytterbium	Yb	70	173.5
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	9122

THE ATOMIC WEIGHT OF LEAD

Sample	Wt. of $PbCl_2$, g.	Wt. of Ag, g.	Ratio $PbCl_2$:2Ag	Atomic weight of lead
Common	2.74332	2.12809	1.28910	207.222
	3.60741	2.79852	1,28904	207.209
	3.07537	2.38565	1.28911	207.224
	2.81471	2.18351	1.28908	207.218
			1.28909	207.218
Kolm	1.61294	1.25678	1.28339	205.990
	1.60407	1.24983	1.28343	205.999
	2.56499	1.99842	1.28351	206.016
	1.83748	1.43167	1.28345	206.003
	3.32075	2.58729	1.28349	206.011
	3.07451	2.39530	1.28356	206.027
			1.28347	206.008
Uraninite	3.74779	2.91808	1.28433	206.194
	5.63102	4.38436	1.28434	206.196
			1.28434	206.195

Aston[20] has extended the usefulness of the mass spectrograph to the determination of the chemical atomic weight of complex elements by microphotometric measurements of the intensities of the isotopic lines in a mass spectrogram. The following table gives the percentages of the components, as well as the packing fractions and the atomic weights calculated on the basis of chemical oxygen.

	Isotopic weights and percentages											Packing fraction	Atomic wt. 0 = 16.0000
Chromium	50	52	53	54									
	4.9	81.6	10.4	3.1								-10×10^{-4}	52.011
Zinc	64	65	66	67	68	69	70						
	48.0	2.5	25.9	5.3	17.1	0.85	0.38					$-9\ 9 \times 10^{-4}$	65.380
Molybdenum	92	94	95	96	97	98	100						
	14.2	10.0	15.5	17.8	9.6	23.0	9 8					-5.5×10^{-4}	95.97
Krypton	78	80	82	83	84	86							
	0.42	2.45	11.79	11.79	56.86	16.70						-8.8×10^{-4}	83.77
Tin	112	114	115	116	117	118	119	120	121	122	124		
	1.07	0.74	0.44	14.19	9.81	21.48	11.02	27.04	2.96	5.03	6.19		
												-7.3×10^{-4}	118.72
Xenon	124	126	128	129	130	131	132	134	136				
	0.08	0.08	2.30	27.13	4.18	20.67	26.45	10.31	8.79				
												-5.3×10^{-4}	131.27
Mercury	196	198	199	200	201	202	204						
	0.10	9.89	16.45	23.77	13.67	29.27	6.85					$+0.8 \times 10^{-4}$	200.62

The close agreement of the calculated atomic weights with those found by chemical means in the case of chromium, zinc, molybdenum, tin and mercury, indicates that the method is capable of giving results of a high

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[20] Aston, *Proc. Roy. Soc.* (London), **A126,** 511 (1930); **A130,** 302 (1931); *Nature,* **126,** 200, 348 (1930).

degree of accuracy. In the cases of krypton and xenon the calculated and experimental (density) values are discrepant and, as pointed out by Aston, new determinations of the densities and compressibilities of these gases should be made.

[CONTRIBUTION FROM THE DEPARTMENT OF BOTANY AT LOS ANGELES AND THE DIVISION OF PLANT NUTRITION AT BERKELEY, UNIVERSITY OF CALIFORNIA]

THE CRYSTAL STRUCTURE OF SOME FORMS OF GLUCOSE. A PRELIMINARY PAPER

BY O. L. SPONSLER AND W. H. DORE

RECEIVED JUNE 18, 1930 PUBLISHED MAY 6, 1931

In anticipation of throwing more light upon the atomic arrangement of the cellulose unit, several crystalline forms of glucose have been under investigation. The structural relationship between cellulose and the beta modification of the amylene oxidic ring form of glucose has been pointed out by the authors.[1] In order to gain a clearer conception of cellulose it has seemed desirable to determine the structure of the crystals of the beta form and also of other forms of glucose. The present report deals with some preliminary results on the alpha and the beta forms of d-glucose ($C_6H_{12}O_6$) and on the alpha glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$).

The first two forms were prepared[2] by the method of Hudson and Dale[3] and the monohydrate by that of Hudson and Yanovsky.[4] The fine crystals so obtained were examined by the powder method of x-ray crystal analysis. Radiation from a molybdenum target Coolidge tube was employed for obtaining the diffraction patterns. The existence of crystallographic data for the two alpha forms made it possible to determine the lattice dimensions and to assign space groups to these forms. The absence of similar data for beta glucose precluded those deductions regarding its structure, but the diffraction patterns made it evident that the alpha and beta forms have different crystal structures.

After this paper was written Hengstenberg and Mark[6] reported a lattice for "d-glucose" without stating whether the alpha or beta form was used. They employed a single crystal rotation method. The agreement of their data with those appearing in this paper, together with the method they used for preparing their material, makes it clear that they were working with alpha d-glucose.

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[1] Sponsler and Dore, "Fourth Colloid Symposium Monograph," The Chemical Catalog Co., New York, 1926, pp. 174–202; Meyer and Mark, *Ber.*, 61, 593–614 (1928).

[2] The thanks of the authors are due to Mr. T. C. Broyer, of the Plant Nutrition Laboratory, for preparing these two forms.

[3] Hudson and Dale, THIS JOURNAL, 39,320 (1917).

[4] Hudson and Yanovsky, *ibid.*, 39, 1013 (1917).

[5] Hengstenberg and Nark, *Z. Krist.*, 72, 301 (1929).

Alpha d-Glucose.—Taking 130decker's[6] value of 1.5384 for the specific gravity, 180 for the molecular weight and Avogadro's constant as 6.062 X 10^{23}, the molecular volume of alpha d-glucose is

$$\frac{180}{1.54} \times \frac{1}{6.062 \times 10^{23}} = 193 \times 10^{-24} = 193 \text{ cu. Å.}$$

Groth[7] described d-glucose as orthorhombic bisphenoidal with axial ratios: $a : b : c = 0.794 : 1.000 : 0.335$. The determination of these ratios by Becke[8] was made on material which, from the method of its preparation, was clearly the alpha modification.

Assuming four asymmetric molecules in the elementary cell (the minimum for the rhombic bisphenoidal class), the volume is 4 × 193 or 772 cu. Å., corresponding to cell dimensions: a = 10.45 Å., b = 14.85 Å., c =

TABLE I

INTERPLANAR SPACINGS FOR ANHYDROUS ALPHA d-GLUCOSE

Observed spacing	Relative intensities	Calculated spacings	and indices
..	......	14.85	(010)
..	......	10.45	(100)
8.65	V. v. weak	8.55	(110)
7.44	V. weak	7.43	(020)
6.07	Mod	6.05	(120)
5.23	Mod.	5.23	(200)
..	......	4.97	(001)
4.72	V. strong	4.72	(011)
4.48	Tr.	4.49–7	(101)(130)
4.31	V. v. strong	4.30	(111)
3.87	V. weak	3.84	(121)
3.60	Tr.	3.60	(201), 3.59 (230)
3.51	Mod.	3.51	(031), 3.50 (211)(140)(300)
3.34	Tr.	3.33	(131)
3.16	V. strong	3.15	(320)
2.98	Tr.	2.98	(041), 2.97 (050)
2.88	Weak	2.91	(231), 2.86–5 (141)(330)(301)(150)
2.60	Weak	2.61–59	(400)(241)(250)
2.48	V. strong	2.48	(002)(420)
2.28	Tr.	2.30–28	(122)(411)(251)
		2.31–28	(401)(350)(341)
2.25	V. strong	2.24–26	(202)(260)(350)(341)
2.06	Mod.	2.06	(042)
1.95	Weak	1.96–7	(441)(270)(242)
1.81	Weak	1.81	(402)(460)
1.68	V. v. weak	1.68	(461)(352)
1.59	V. weak	1.60	(123), 1.58 (203)
1.34	V. weak	1.34	(670)
1.29	V weak	1.29	(810)(820)

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[6] Bödecker, Ann., 117, 111 (1861).

[7] Groth, "Physikalische Krystallographie," 1910, Vol. III, p. 437.

[8] Becke, Z. Kryst. Mineral. 20, 297 (1892).

4.97 Å. Interplanar spacings calculated to these dimensions are compared with the observed spacings in Table I. The axial values are represented by the half values in the column of observed spacings; lines for the full values are absent from the diffraction pattern.

	Calcd.	Obsd.
a =	10.45	5.23
b =	14.85	7.44
c =	4.97	2.48

Of the nine possible space groups[9] included in the rhombic bisphenoidal class, only one, V^4 (or Q^4), fits the data presented. In that group four asymmetric molecules are required; and the face planes are interleaved so that only their half values will appear in the diffraction pattern.

TABLE II

INTERPLANAR SPACINGS FOR ALPHA d-GLUCOSE MONOHYDRATE

Observed spacing	Relative intensities	Calculated spacing	and indices
9.70	Mod.	9.50	(001)
7.00	Strong	6.88	(101)
6.00	V. weak	5.99	(101)
4.52	V. v. strong	4.45	(102)
4.30		4.31	(200)
4.10	V. v. weak	4.05	(111)
3.85	V. strong	3.87	(111)
3.50	Weak	3.44	(202)
3.30	V. v. weak	3.33	(112), 3.27 (210)
3.20	Strong	3.20	(211), 3.17 (003)
3.10		3.12	(103), 3.11 (112)
3.00'	V. v. weak	3.00	(211)(202)
2.85	Mod.	2.87	(300), 2.84 (212)(103)
2.63	Weak	2.66	(301)
2.50	Strong	2.51	(020), 2.50 (310)
2.42	Mod.	2.41	(120)
2.24	V. weak	2.22	(104)
2.17	Strong	2.18	(122), 2.17 (220)(401), 2.16 (400)(014)
2.04	V. weak	2.04	(401), 2.02 (222)
1.99	Mod.	2.00	(303), 1.99 (410)(222), 1.98
1.90	V. v. weak	1.90	(005), 1.89 (320)
1.85	Mod.	1.86	(402)
1.72	V. v. weak	1.72	(500)(404)(024)
1.65	V. weak	1.65	(130)
1.59	V. weak	1.60	(422), 1.58 (006)
1.52	V. v. weak	1.52	(025)
1.39	V. v. weak	1.39	(603)
1.32	V. v. weak	1.32	(430)
1.28	V. v. weak	1.29	(333)(022)(424)
1.21	V. v. weak	1.21	(240)
1.17	V. v. weak	1.18	(242), 1.16 (242)
1.14	V. v. weak	1.15 .	(340)(036)

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[9] Astbury and Yardley, *Phil. Trans. Roy. Soc. London,* **224A,** 221 (1924)

Alpha d-Glucose Monohydrate.—Taking Bodecker's value of 1.5714 for the specific gravity and 198 for the molecular weight, the molecular volume of alpha glucose monohydrate is

$$\frac{198}{1.5714} \times \frac{1}{6.062 \times 10^{23}} = 207.9 \times 10^{-24} \text{ or } 207.9 \text{ cu. Å.}$$

Groth[7] describes alpha glucose monohydrate as monoclinic sphenoidal with axial ratios: $a:b:c = 1.735:1:1.908$, with the angle between inclined axes, $\beta = 97'59'$. An elementary cell containing two molecules as a minimum has dimensions: a = 8.72 Å. b = 5.03 Å., and $c = 9.59$ Å., $\beta = 97°59'$, when based on the volume and axial ratios given. A comparison of the interplanar spacings from those dimensions and from the x-ray data is presented in Table II. From crystallographic data the crystal is shown to be monoclinic; from chemical data the molecule is known to be asymmetric. In the absence of x-ray data from a single crystal, those two considerations would place the structure in space group C_2^2. That space group[8] demands two molecules per unit cell and requires that the (010) spacing be halved. Our interpretation is in agreement with both requirements.

TABLE III

INTERPLANAR SPACINGS FOR BETA d-GLUCOSE AND ALPHA d-GLUCOSE OBSERVED VALUES

Beta *d-glucose*		Alpha d-glucose	
Å. units	Intensity	Å. units	Intensity
5.47[a]	V. v. st.[a]	8.65	V. v. w.
5.27		7.44	V. w.
4.63	V. v. st.	6.07	M.
4.34	V. st.	5.23	M.
4.11	W.	4.72	V. st.
3.86	V. v. w.	4.48	V. v. w.
3.81	V. v. st.	4.31	V. v. st.
3.62	M.	3.87	V. w.
3.35	M.	3.60	V. v. w.
3.17	St.	3.51	M.
2.83	V. st.	3.34	V. v. w.
2.78	V. v. w.	3.16	V. st.
2.48	W.	2.98	V. v. w.
2.45		2.88	W.
2.30	W.	2.60	W.
2.27		2.48	V. st.
2.14	W.	2.28	V. v. w.
2.09		2.25	V. st.
1.85	V. w.	2.06	M.
1.78	W.	1.95	W.
1.68	V. w.	1.81	W.
1.56	V. v. w.	1.68	V. v. w.
		1.59	V. w.
		1.34	V. w.
		1.29	V. w.

[a] Bracketed figures indicate outer limits of a broad band which may represent a composite of several lines. V. = Very. W. = Weak. St. = Strong. M. = Medium.

Beta d-Glucose.—The powder data for beta glucose are not capable of interpretation without the support of crystallographic data, but the observed interplanar spacings are here placed on record in Table III in order to point out a difference between the crystals of the beta and alpha forms.

Summary

The crystal structures of three forms of glucose (alpha and beta anhydrous glucose and alpha glucose monohydrate) have been studied by the x-ray powder method. The interplanar spacings of the three forms are given. The data for anhydrous alpha glucose correspond to an orthorhombic unit cell having dimensions: $a = 10.45$ Å., $b = 14.85$ Å., $c = 4.97$ Å., and meet the requirements of space group V^4. The data for alpha glucose monohydrate agree with the requirements of a monoclinic unit cell having dimensions: $a = 8.72$ Å., $b = 5.03$ Å., $c = 9.59$ Å., $\beta = 97°59'$ and correspond to space group c_2^2.

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[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OR THE STATE UNIVERSITY OF IOWA]

OXIDATION–REDUCTION POTENTIALS.
IV. THE DETERMINATION FROM EQUILIBRIUM DATA.
B. FERRIC–FERROUS ELECTRODE

BY STEPHEN POPOFF, VERNON B. FLEHARTY AND EDWIN L. HANSON

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The determinations of oxidation–reduction potentials from equilibrium data are considered to be more reliable[1] than those from e. m. f. measurements because in the former one attains true equilibrium, while in the latter one cannot always be certain that an inert electrode will always record the true potential, especially in dilute solutions. E. m. f. measurements are further complicated by liquid junction potentials, which cannot, theoretically at least, always be entirely eliminated. In equilibrium data it is also possible to work with the more dilute solutions in which the principle of ionic strength can be considered to hold—thus the activity coefficients of the ions can be calculated from the limiting case of the Debye–Hückel equation.

When metallic mercury comes in contact with ferric perchlorate solution, the following reaction takes place

$$2Fe(ClO_4)_3 + 2Hg \rightleftharpoons 2Fe(ClO_4)_2 + Hg_2(ClO_4)_2$$

This reaction is of special interest because, at equilibrium, the substances are present in comparable amounts which can be suitably analyzed. It is therefore possible to determine the equilibrium constant by purely

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 411.

chemical means, to calculate the oxidation–reduction potential of the ferric–ferrous electrode, and to compare the latter with that obtained from e. m. f. measurements.

The equilibrium of this particular reaction has not been studied chemically, although Noyes and Brann[2] determined the equilibrium constant of the reaction

$$Ag + Fe(NO_3)_3 \rightleftharpoons AgNO_3 + Fe(NO_3)_2$$

The perchlorates, mercury and perchloric acid were considered to be better suited for the determination of the equilibrium constant than the nitrates, silver and nitric acid, because in the latter case it is difficult to prepare pure metallic silver in a fine and suitable state of subdivision possessing the same energy content, and because of the possible oxidizing action of nitric acid.

In our investigation sufficiently dilute solutions were employed to be able to use the principle of ionic strength in the calculation of the equilibrium constant. The equilibrium constant was also calculated from total concentration by suitable mathematical and graphical treatments.

As a result of this experimental study the oxidation–reduction potential of the ferric–ferrous electrode was calculated to be —0.7473 v. Popoff and Kunz[3] obtained —0.7477 v. by e. m. f. measurements.

Preparation of Materials

(1) All water was redistilled from an alkaline permanganate solution.

(2) Ferric perchlorate was prepared by treating J. T. Baker c. p. ferric chloride with successive portions of G. Frederick Smith perchloric acid, and heating until no test for chloride ion was obtained. It was then recrystallized four times from 0.1 M perchloric acid.

(3) Mercury was purified by passing it through a column of dilute nitric acid six times; through redistilled water six times; distilling, filtering and passing through nitric acid and water as before.

(4) Potassium permanganate, silver nitrate, preventive, hydrochloric acid and perchloric acid solutions were made from the best chemicals obtainable.

Analytical Methods

All analyses were made using weight pipets and burets.

(1) The potassium permanganate solution was standardized electrometrically against Bureau of Standards sodium oxalate using McBride's conditions.[4]

(2) The silver nitrate solution was standardized electrometrically using a silver–silver chloride electrode with recrystallized potassium chloride as the standard.

(3) The total iron in the ferric perchlorate solution was determined electrometrically by the Zimmerman–Reinhardt method making the solution 0.5 *M* with respect to perchloric acid.

(4) The concentration of perchloric acid in the ferric perchloric solution was determined volumetrically using methyl orange as the indicator, by adding an excess of sodium hydroxide, filtering, and titrating the excess base with a standard acid solution.

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[2] Noyes and Brann, THIS JOURNAL, 34, 1016 (1912).

[3] Popoff and Kunz, ibid., 51, 382 (1929).

[4] McBride, *ibid.*, 34, 393 (1912).

(5) and **(6)** The weight ratio between the silver nitrate and sodium chloride solutions was determined electrometrically using silver-silver chloride electrodes.

(7) The perchloric acid solution was standardized volumetrically using phenolphthalein as the indicator, against a carbonate-free solution of sodium hydroxide which had been standardized against constant boiling hydrochloric acid solution.

(8) Analysis of the equilibrium mixture.

(a) The ferrous iron was determined by precipitating the mercurous ion with an excess of sodium chloride, filtering, adding **20** cc. of preventive solution and enough perchloric acid to make the acid concentration approximately **0.5** M. The solution was then titrated electrometrically with potassium permanganate.

(b) The mercurous mercury was determined by adding an excess of sodium chloride and titrating the excess electrometrically with the silver nitrate, using a silver–silver chloride electrode.

(c) The ferric iron was obtained by difference between the total iron and ferrous iron found.

Table I expresses the results of these analyses. Concentration (*C*) is expressed in moles per thousand grams of water in vacuum in all tables.

TABLE I

ANALYTICAL METHODS

Solution	*C*	Solution	*C*
1. $KMnO_4$	0.020254	4. $HClO_4$ in $Fe(ClO_4)_3$	0.079275
	.020252		.079176
	.020257		.079076
	.02025		.07918
Two months later	0.02017	5. Concentrated NaCl	0.11058
			.11062
2. $AgNO_3$	0.027343		.11052
	.027357		.11064
	.027352		.1106
	.027352		
	.02735	6. Dilute NaCl	0.064346
			.064302
3. $Fe(ClO_4)_3$	0.23844		.064316
	,23826		.064297
	.23838		.06432
	.23796		
	.2384	7. $HClO_4$ Soln.	0.36087
			.36116
			.36107
			.36137
			.3611

The Relation between Equilibrium Constant and Oxidation–Reduction Potential.—The reaction

$$2Fe^{+++} + 2Hg \rightleftharpoons 2Fe^{++} + Hg_2^{++} \qquad (A)$$

occurs in the cell

$$Pt \mid Fe(ClO_4)_3, Fe(ClO_4)_2 \mid Hg_2(ClO_4)_2 \mid Hg$$

The equations for the potentials at each electrode at 25° are

$$E_{\mathrm{Fe}} = E_{0\mathrm{Fe}} - 0.05915 \log \frac{a_{\mathrm{Fe}^{+++}}}{a_{\mathrm{Fe}^{++}}}$$

$$E_{\mathrm{Hg}} = E_{0\mathrm{Hg}} - \frac{0.05915}{2} \log a_{\mathrm{Hg_2}^{++}}$$

At equilibrium, the potential of the cell will be zero, and

$$E_{0\mathrm{Hg}} - \frac{0.05915}{2} \log a_{\mathrm{Hg_2}^{++}} = E_{0\mathrm{Fe}} - \frac{0.05915}{2} \log \frac{a^2_{\mathrm{Fe}^{+++}}}{a^2_{\mathrm{Fe}^{++}}}$$

Transposing, one gets

$$E_{0\mathrm{Hg}} - E_{0\mathrm{Fe}} = \frac{0.05915}{2} \log a_{\mathrm{Hg_2}^{++}} - \frac{0.05915}{2} \log \frac{a^2_{\mathrm{Fe}^{+++}}}{a^2_{\mathrm{Fe}^{++}}}$$

$$- \frac{0.05915}{2} \log \frac{a^2_{\mathrm{Fe}^{++}} \times a_{\mathrm{Hg_2}^{++}}}{a^2_{\mathrm{F_2}^{+++}}}$$

However, $a^2_{\mathrm{Fe}^{++}} \times a_{\mathrm{Hg_2}^{++}}/a^2_{\mathrm{Fe}^{+++}}$ is the equilibrium constant of reaction (A)

$$E_{0\mathrm{Hg}} - E_{0\mathrm{Fe}} = \frac{0.05915}{2} \log K$$

in which K is the equilibrium constant.

The value for $E_{0\mathrm{Hg}}$ has been determined by Lewis[6] and if the value for the equilibrium constant of the reaction shown is determined precisely, one can calculate the oxidation–reduction potential of the ferric--ferrous electrode.

Experimental Methods

(1) Attainment of equilibrium was accomplished by approaching the equilibrium of the reaction from both sides at a temperature of 25°. One set of runs was allowed to come to 25° in the water thermostat, approaching the equilibrium from the "cold side," so to speak. Another set of the same concentration was heated to 30–35° in an air thermostat, then brought to the equilibrium at 25° in the water-bath. This can be termed as approaching the equilibrium from the "hot side." These mixtures were continually rotated and shaken in a constant temperature bath at 25 ± 0.01". The solutions were analyzed for the ferrous iron and the mercurous mercury by withdrawing a weighed amount of the solution, approximately 100 g. being used for each analysis.

(2) The ease of reversibility of the reaction was determined by varying the mercury content, the temperature and the time of rotation (for both "hot" and "cold"). It was finally decided to use 40 cc. of mercury in about *500* cc. of solution and to rotate the mixtures for both "hot" and "cold" for at least forty-eight hours at 25° before any analyses were attempted. It had been determined previously that twenty-four hours of rotation at 30–35° was more than sufficient to shift the equilibrium and that twenty-four hours of rotation at 25° was more than sufficient to obtain the same equilibrium as that established from the "cold" side. Special

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[6] **Lewis** and Randall, **Ref. 1**, p. **433.**

Pyrex bottles were made (holding about 500 cc.) which could be glass sealed. Ordinary glass-stoppered bottles, which were sealed with paraflin, failed to give reproducible and identical results for both "hot" and "cold" equilibrium mixtures at 25°. At the present time no explanation will be offered.

(3) Variation of Acid and Salt Concentrations.—In each of the five series the acid concentration was kept constant but the concentration of the ferric perchlorate (starting mixture) was varied down to 0.001 *C*. The acid concentration **was** varied from 0.02 to 0.002 C. The latter was found to be the lowest concentration at which no hydrolysis took place when 0.001 *C* iron solution was used. Lower concentration of ferric perchlorate than 0.001 C was not employed because the errors in the analyses would have been too great. In the 0.003 C perchloric acid series, 0.004 C iron was the upper limit. **A** starting solution containing 0.001 *C* of iron and 0.001 C of perchloric acid hydrolyzed.

Experimental Data and Calculations

Table II gives the experimental results obtained in 0.02, 0.01, 0.005, 0.003 and 0.002 *C* perchloric acid concentrations, respectively, with vary-

TABLE II

EFFECT ON THE EQUILIBRIUM CONSTANT CALCULATED AS THOUGH MERCURY WAS MONOVALENT AND DIVALENT AS DESIGNATED, PROM TOTAL CONCENTRATIONS, ON VARIATION OF CONCENTRATIONS OF ACID AND SALTS

Total C_{Fe}	$C_{Fe^{++}}$	$C_{Hg_2^{++}}$ or $\frac{1}{2}C_{Hg^+}$	$C_{Fe^{+++}}$	$K'_{C_{Hg_2^{++}}}$	$K'_{C_{Hg^+}}$
		Series I, 0.02 C $HClO_4$			
0.006	0.004788	0.002456	0.001207	0.03868	0 01949
.003	.002533	.001262	.0004598	.03828	.01390
.001	.0009015	.0004588	.00009521	.04113	.008688
		Series II, 0.01 C $HClO_4$			
.008	.006109	.002992	.001891	.03124	.01933
.006	.004685	.002288	.001302	.02965	.01647
.003	.002513	.001244	.0004802	.03408	.01302
.002	.001731	.0008607	.0002692	.03557	.01107
		Series III, 0.005 C $HClO_4$			
008	.005789	.002897	.002239	.01938	.01499
006	.004514	.002229	.001475	.02094	.01364
.004	.003151	.001581	.0008488	.02179	.01174
.003	.002415	.001215	.0005779	.02122	.01015
.002	.001677	.0008255	.0003232	.02222	.008565
.001	.0008819	.0004526	.0001158	.02624	.006762
		Series IV, 0.003 C $HClO_4$			
.004	.003028	.001503	.0009720	.01459	.009365
.002	.001610	.0008053	.0003902	.01371	.006645
.001	.0008526	.0004453	.0001474	.01490	.005152
		Series V, 0.002 C $HClO_4$			
.002	.001546	.0007712	.0004542	.008930	.005248
.001	.0008301	.0004153	.0001698	.009920	.004060

ing concentration of iron. $K'C_{Hg_2^{++}}$ represents the equilibrium constant calculated from total concentration by the equation

$$K'C_{Hg_2^{++}} = \frac{C_{Fe^{++}}^2 \times C_{Hg_2^{++}}}{C_{Fe^{+++}}^2}$$

It was discovered that if the equilibrium constants were calculated upon the assumption that mercurous ion were monovalent, interesting results were obtained. If mercurous ion were monovalent

$$K'C_{Hg^+} = \frac{C_{Fe^{++}} \times C_{Hg^+}}{C_{Fe^{+++}}}$$

No attempt is made to draw any conclusions from the values of $K'C_{Hg^+}$.

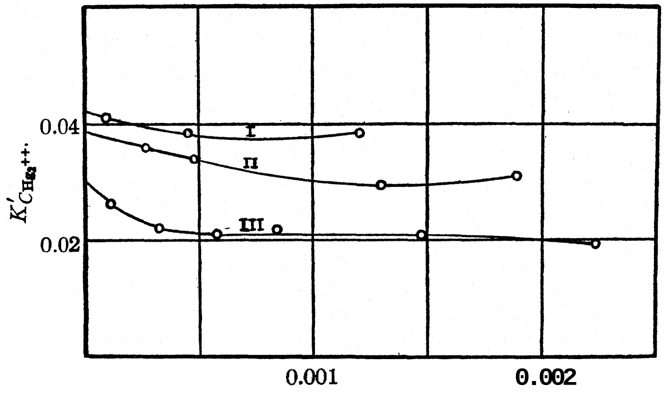

Fig. 1.—The apparent equilibrium constants from total concentration in varying acid and salt concentrations.

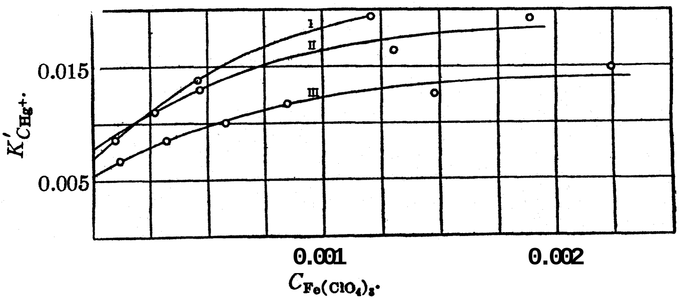

Fig. 1a.—The apparent equilibrium constants from total concentration in varying acid and salt concentrations.

In an analysis of a typical equilibrium mixture the percentage mean error was 0.1 for the determination of ferrous iron and 0.15 for mercurous mercury.

The Equilibrium Constant from Total Concentration.—The values of $K'C_{Hg_2^{++}}$ and $K'C_{Hg^+}$ in 0.02, 0.01, 0.005 (corresponding to I, II, III, respectively) C perchloric acid were plotted (Figs. 1 and 1a, respectively) against the C of the ferric perchlorate (at equilibrium) and the curves extrapolated to zero concentration of ferric perchlorate. The extrapolated values, Table III, were plotted (Figs. 2 and 2a, respectively) against the C of the perchloric acid and the curves again extrapolated to zero concentration of the acid.

Table III

Equilibrium Constant in Varying Acid Concentration

$C_{\mathrm{HClO_4}}$	$K''C_{\mathrm{Hg_2^{++}}}$	$K''C_{\mathrm{Hg^+}}$
0.020	0.0421	0.00706
.010	.0386	.00796
.005	.0310	.00556
.000	.0188	.00126

Due to the uncertainty of graphical extrapolation the data were extrapolated mathematically using the principle of moments and zero sum. A

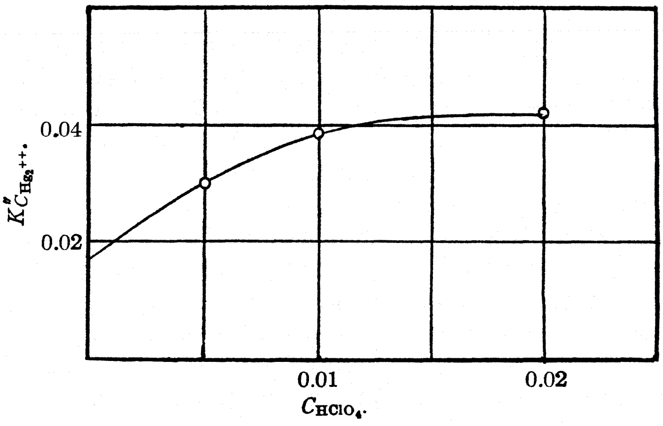

Fig. 2.—The equilibrium constants in varying acid against the acid concentration.

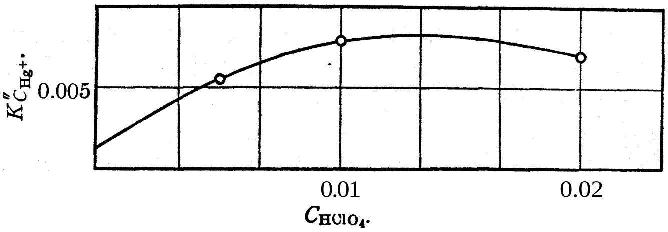

Fig. 2a.—The equilibrium constants in varying acid against the acid concentration.

value of 0.0188 was calculated for the true equilibrium constant ($K'C_{\mathrm{Hg_2^{++}}}$) and 0.00126 for the true equilibrium constant ($K'C_{\mathrm{Hg^+}}$) from total concentration.

The Equilibrium Constant from Ionic Strength.—It was possible in Series V, 0.002 *M* acid, 0.002 and 0.001 M ferric perchlorate, to calculate the activity coefficients in

$$K_f = \frac{C_{Fe^{++}}{}^2 \times f_{Fe^{++}}{}^2 \times C_{Hg_2^{++}} \times f_{Hg_2^{++}}}{C_{Fe^{+++}}{}^2 \times f_{Fe^{+++}}{}^2}$$

by the equation[6]

$$-\log f = 0.5z^2\sqrt{\mu}$$

The latter equation holds for most solutions whose ionic strengths are not greater than 0.01. Table IV gives the values obtained.

TABLE IV

THE EQUILIBRIUM CONSTANT FROM IONIC STRENGTH IN 0.002 M $HClO_4$

Total C_{Fe}	μ	f^{++}	f^{+++}	K_f
0.002	0.0117	0.608	0.326	0.01884
.001	.0068	.685	.427	.01751

Although the ionic strengths of the solutions containing 0.001 M ferric perchlorate (starting solution) and either 0.005 M or 0.003 M perchloric acid are 0.0097 and 0.0078, respectively, the equilibrium constants, using activity coefficients, calculate to be 0.0510 and 0.0274, respectively. It may be concluded that the equation used to calculate the activity coefficients does not hold for the foregoing solutions.

One may also calculate the equilibrium constants for all the solutions in Series III and IV, using activity coefficients, and then plot the values thus obtained against the square root of the ionic strength and extrapolate to zero ionic strength, assuming that the points lie on a straight line. The latter assumption, however, can hardly be justified, although the final extrapolated values agree closely among themselves and are not very far from 0.0184, the true equilibrium constant, since the equilibrium constant in each acid is different, although the ionic strengths of the solutions are the same and less than 0.01.

The true equilibrium constant may be taken as the average of the equilibrium constants obtained from total concentration and from (average) ionic strength in 0.002 M perchloric acid. The average value is 0.0184 or 0.018 ± 0.0005.

The Oxidation–Reduction Potential of the Ferric–Ferrous Electrode.—Using the equation

$$E_{0_{Fe}} = E_{0_{Hg}} - \frac{0.05915}{2}\log K$$

and Lewis's[5] value for E_{0Hg} (—0.7986 v.), the value for E_{0Fe} calculates to be −0.7473 v. Noyes and Brann[2] found from equilibrium data −0.7467 v., while Popoff and Kunz[3] report —0.7477 v. from e. m. f. measurements.

[6] Bronsted and La Mer, THIS JOURNAL. 46, 555 (1924).

Summary

1. The following reaction was studied chemically and found to be a truly and easily reversible reaction

$$2Fe^{+++} + 2Hg \rightleftharpoons 2Fe^{++} + Hg_2^{++}$$

2. The equilibrium constant of the reaction was calculated either from total concentration by suitable graphical and mathematical treatments or from ionic strength of dilute solutions, and was found to be 0.0180 ± 0.0005.

3. The principle of ionic strength may not be considered to hold even in solutions as low as 0.01 when there is too much acid present as compared with the other salts.

4. The oxidation-reduction potential of the ferric–ferrous electrode, calculated from the equation

$$E_{0_{Fe}} = E_{0_{Hg}} - \frac{0.05915}{2} \log K$$

was found to be −0.7473 v. This value agrees very closely with −0.7477 v. obtained from our former e. m. f. measurements.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OP THE UNIVERSITY OF WISCONSIN]

METHODS OF CALCULATING AND AVERAGING RATE CONSTANTS[1]

BY W. E. ROSEVEARE

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Introduction

In order to obtain a more probable value of the rate of a chemical reaction, for temperature coefficients, etc., it has been customary to take the simple arithmetical average of individual calculated values. Due to the nature of the rate function, such an arithmetical average may possibly be as far from the true value as that calculated from the two least accurate measurements. This applies only to the average of rate constants which are calculated*from measurements made on a single sample of reacting material and not to the average of those found under identical conditions of time and concentration. Most rates of reaction have been calculated by the interval method or the method of integrating from the zero of time using the formulas: $k = \frac{1}{t_n - t_{n-1}} \ln\left(\frac{a - x_{n-1}}{a - x_n}\right)$ and $k = \frac{1}{t_n} \ln \frac{a}{a - x_n}$. The arithmetical averages of the rates calculated by these methods give quite different results and both are incorrect.

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[1] This paper was presented in preliminary form by the author before the Mid-west Regional meeting of the American Chemical Society, May 9, 1930.

Present Incorrect Methods of Averaging

Error of the Interval Method Average.—It can be shown that the simple arithmetical average of the interval rate constants, when calculated for equal time intervals, is equal to the rate constant as calculated from the initial and final observed values of the concentration and is independent of all intermediate ones. If $k_{0,1}$, $k_{1,2}$, $k_{2,3}$ . . . k, $_{-1,n}$ are the interval rate constants for n intervals, then the arithmetical average will be: $(1/n)$ $(k_{0,1} +$ $k_{2,3}+\ldots$ k, $_{-1,n})$. For a unimolecular reaction $k_{0,1} = (1/At) \ln (C_0/C_1)$, where At is the time interval during'which the concentration changes from C_0 to C_1. If all the time intervals are the same and k_a is the arithmetical average, then

$$k_a = \frac{1}{n}\left[\frac{1}{\Delta t}\ln\frac{C_0}{C_1} + \frac{1}{\Delta t}\ln\frac{C_1}{C_2} + \ldots \frac{1}{\Delta t}\ln\frac{C_{n-1}}{C_n}\right]$$

$$k_a = \frac{1}{n\,\Delta t}\ln\left[\frac{C_0\,C_1\,C_2\,\ldots\,C_{n-1}}{C_1\,C_2\,C_3\,\ldots\,C_n}\right]$$

All the values of C cancel out except the first and the last and since $n\,At =$ $t,,$ then

$$k_a = \frac{1}{t_n}\ln\left(\frac{C_0}{C_n}\right)$$
$$k_a = k_{0,n}$$

Thus the arithmetical average is independent of all values except the first and last. This proof may be extended to a reaction of any order. It can be shown by very simple analytic geometry that, for points whose abscissas are equally spaced, the arithmetical average of the slopes of straight lines drawn through adjacent points is equal to the slope of the straight line drawn through the first and last points and is independent of the ordinates of the intermediate points. Wagner[2] showed this to be true in the case of a second order reaction.

Error of the Second Method.—When each value of k is calculated by integrating from the zero time, each value of $a - x$ is combined with a single value of the initial concentration which may rest on a single measurement. Guggenheim[a] pointed out that this gave undue weight to the initial concentration. Even though the initial concentrations were known with absolute accuracy, this method gives too much weight to the points near the zero of time.

Methods Applicable to Unimolecular Reactions

Rate measurements may be divided into two classes, depending on whether one analyzes for the concentration $(a - x)$ or the amount which has reacted, x.

When x is Measured Directly.—Guggenheim[3] developed a method

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[2] C. Wagner, *Z. physik. Chem.*, *115*, 132 (1925).

[3] E. A. Guggenheim, *Phil. Mag.*, [7] *2*, 538 (1926).

which eliminates the use of the initial concentration. He plotted the common logarithm of the amounts reacting in a chosen interval of time against the time. The slope multiplied by **2.303** gave the rate constant.

The rate may also be determined analytically from three values of x, provided the time intervals between them are the same. If x_1, x_2 and x_3 are the amounts which have reacted at times t_1, t_2 and t_3, then

$$k(t_2 - t_1) = \ln \frac{(a - x_1)}{(a - x_2)} \qquad (1)$$

$$k(t_3 - t_2) = \ln \frac{(a - x_2)}{(a - x_3)} \qquad (2)$$

If we impose the condition that $(t_3 - t_2) = (t_2 - t_1)$, *i. e.*, the time intervals are the same, then

$$\frac{a - x_1}{a - x_2} = \frac{a - x_2}{a - \quad x\ a}$$

and

$$a = \frac{x_1x_3 - x_2^2}{x_1 - 2x_2 + x_3}$$

If t_1 was taken as the zero of time, then this equation would reduce to that obtained by Smith[4] for the initial concentration in terms of the concentrations at two times, one twice the other. Substituting a from Equation **3** in either Equation 1 or 2 we obtain

$$k = \frac{1}{\tau} \ln \frac{(x_2 - x_1)}{(x_3 - x_2)} \qquad (3)$$

where τ is the time interval between the x_1 and x_2 as well as between the x_2 and x_3. For a gaseous reaction followed by the change in volume at constant pressure or the pressure change at constant volume, the x's may be replaced, respectively, by the volume or pressure. This method and Guggenheim's are alike in that the initial concentrations are eliminated. Even though one finds a perfectly straight line using the former method or a constant value of k using the second method, it does not follow that the reaction obeys the simple unimolecular law. A straight line and a constant value of k will be obtained when and only if the rate is given by the equation $dx/dt = k(a - x) \pm k'(b - x)$, where k' and b may or may not be zero. This expresses the rate for a reversible reaction, a side reaction, a subsequent reaction and a reaction where the product combines with the reactant making it relatively inert, as well as for a simple unimolecular reaction. The reversibility can be determined from free energies and the other exceptions by chemical analyses and by trying the effect of adding some of the product to the reacting mixture. Thus one can obtain strong but not absolute evidence of unimolecularity when the original concentration cannot be measured.

In order to best show up a trend, the time intervals should be short, but

[4] **R. C. Smith,** ***Phil. Mag.,*** [7] 1,496 (1926).

to obtain the most probable value, the intervals should be longer. Since the value of $x_3 - x_2$ can never be greater than $x_2 - x_1$ and the probable error in x is a constant quantity independent of the time, the error in k will be due principally to the error in $x_3 - x_2$. Therefore, for the case when the error in determining the concentration has a greater effect on k than the error in measuring the time, the error may be considered as due to the error in $x_3 - x_2$ alone. In this case the accuracy will be greatest when $x_3 - x_2$ is greatest. If we let the concentration be a at t_1, then x_1 will be zero and Equation 3 becomes

$$k\tau = \ln \frac{x_2}{(x_3 - x_2)} \text{ or } x_3 - x_2 = x_2e^{-k\tau}$$

Setting the derivative with respect to τ of $x_3 - x_2$ equal to zero will make the latter a maximum and the error in k a minimum. Since $e^{-k\tau}$ does not equal zero, this gives

$$kx_2 - \mathrm{d}x_2/\mathrm{d}\tau = 0 \qquad (4)$$

By differentiating Equation 1 with respect to τ with $x_1 = 0$, one finds $\mathrm{d}x_2/\mathrm{d}\tau = k(a - x_2)$. Substituting this in Equation 4 gives $x_2 = a/2$, the condition for maximum accuracy in k. This means that if ln $(x_3 - x_2)$ is less accurately determined than τ, then the greatest accuracy is obtained when the concentration decreases 50% during the first interval and one-half that much during the second interval.

In order to best utilize data, when the error in measurement of time is negligible and one wishes to use this method as evidence for unimolecularity, it is best to take six measurements at equal time intervals near the beginning, six with the same time intervals when about 50% has reacted, and six more when about 75% has reacted, such that the time interval between the first and seventh equals that between the seventh and thirteenth, etc. Then one can calculate a rate constant from the first three, another from the second three, etc., giving two constants for the beginning, two for the middle and two nearer the end. This will show if there is a trend not represented by $\mathrm{d}x/\mathrm{d}t = k(a - x) \pm k'(b - x)$. To obtain the most probable value of the rate constant one should calculate it from the first, seventh and thirteenth; the second, eighth and fourteenth, etc. These constants will all have practically the same weight and will be independent and therefore may be averaged arithmetically.

When $(a - x)$ Is Measured Directly.—In this case one can calculate k from any two measurements of concentration and the time between them, but when there are more than two points, one is faced with the problem of deciding how to combine them. If the time is the least accurate measurement, then all points will have practically the same weight. On the other hand, if ln $(a - x)$ is least accurately determined, then each point will have a different weight since $a - x$ and not ln $(a - x)$ is directly measured. The probable error in $a - x$ in general is a constant quantity rather than a constant percentage error. In Fig. 1a the dotted lines show the limits of error due to a constant error in time and Fig. 1b shows the limits of error for a possible error in $(a - x)$ equal to one-tenth of the initial concentration. The weight changes in the same way regardless of the size of the error, the very large error being used merely to facilitate graphing. If r_c is the probable error in the concentration, then by expanding ln (C + r) in series and neglecting terms of second and higher powers, one has r_c/C as the probable error in ln C. Letting r_t be the probable error in measurement of the time, one can see from Fig. 2 that $r_t \tan \theta$ or kr_t is the probable error in ln C which would produce the same probable error in k as does r_t. Therefore, one may consider the time as entirely correct and that there are two probable errors in ln C, one due to error in measurement of C and the other due to error in measurement of t. The effective probable error of a point in terms of ln C will be $\sqrt{(kr_t)^2 + (r_c/C)^2}$. The weight p of any point will be inversely proportional to the square of its probable error, and therefore

$$p = \frac{1}{(kr_t)^2 + (r_c/C)^2} \qquad (5)$$

Thus one can calculate the weight of any point. It will be seen from formula (5) that if the error was due only to the error in measuring time, all points would have the same weight. On the other hand, if the error was due only to the error in determining concentration, the weight of each point would be proportional to C^2. The weight is important in the latter case, since if the weight at the start is taken as unity, the weight will be one-quarter when the reaction is 50% complete and one-hundredth when 90% complete,

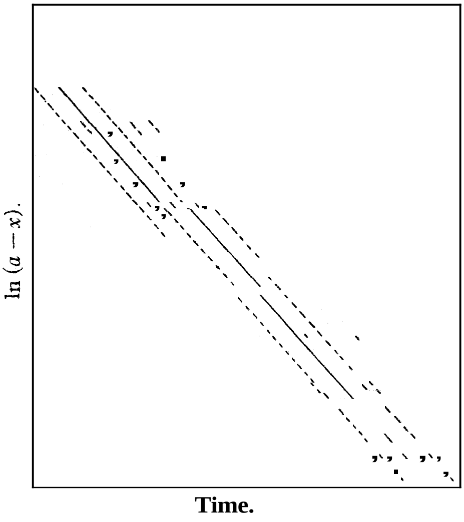

Fig. 1a.

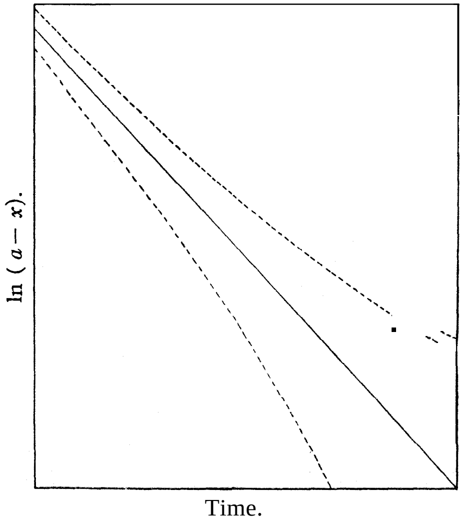

Fig. 1b.

1. Graphical Method.—This method of plotting ln $(a - x)$ against the time and drawing the best straight line through the points is well known. It has the advantage of showing trends and at present is certainly the best method for such cases. However, it has the disadvantage in that large graphs cannot be published and some data are more accurate than can be represented graphically.

2. Arithmetical Mean.—Where the weights of all points are nearly the same, a very convenient mean is obtained by dividing the points into two equal parts and taking a time weighted average of the slopes of pairs of points. If there are six points on the plot of ln C against t, one would take the slopes of the pairs of points 1-6, *2-5* and **3-4** and weight these according to the distance between the points. However, the distances between the points is very nearly proportional to their projection on either axis. Therefore, the weights may be taken as the difference in t for each pair of points. The slope from points 1 and 6 is $(\ln C_6 - \ln C_1)/(t_6 - t_1)$ and its weight will be $(t_6 - t_1)$. Then the weighted mean will be

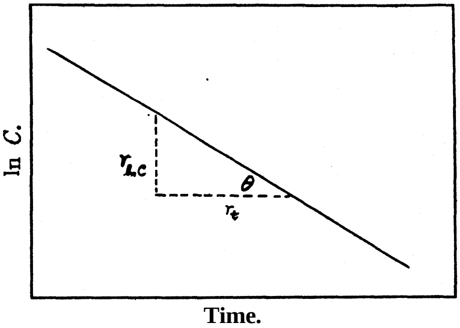

Fig. 2.

$$k_m = \frac{\frac{\ln C_6 - \ln C_1}{t_6 - t_1}(t_6 - t_1) + \frac{\ln C_5 - \ln C_2}{t_5 - t_2}(t_5 - t_2) + \frac{\ln C_4 - \ln C_3}{t_4 - t_3}(t_4 - t_1)}{(t_6 - t_1) + (t_5 - t_2) + (t_4 - t_5)}$$

Since the time differences in the numerator cancel out

$$k_m = \frac{(\ln C_6 + \ln C_5 + \ln C_4) - (\ln C_3 + \ln C_2 + \ln C_1)}{(t_6 + t_5 + t_4) - (t_3 + t_2 + t_1)}$$

and in general

$$k_m = 2.303\left[\frac{\sum\limits_{i=\frac{1}{2}n+1}^{i=..}\log C_i - \sum\limits_{i=1}^{i=\frac{1}{2}n}\log C_i}{\sum\limits_{i=\frac{1}{2}n+1}^{i=n} t_i - \sum\limits_{i=1}^{i=\frac{1}{2}n} t_i}\right]$$

A given error in time or log C produces the same magnitude of error in the above mean regardless of the time. Thus all points have equal weight. If there are an odd number of points, the middle one is not used, and therefore n is always even. This method should only be used for cases where the time is the least accurate measurement or for the rare case when the percentage error in analysis is a constant quantity.

3. Method of Least Squares.—This method of obtaining the slope of a straight line is well known, but it has rarely been used to calculate rate constants and when used **has** not been weighted. It has the disadvantage of requiring a great deal of arithmetical work, and weighting considerably increases the amount of work. The general formula for the slope of a straight line by the method of least squares is

$$s = \frac{\Sigma px\,\Sigma py - \Sigma p\,\Sigma pxy}{(\Sigma px)^2 - (\Sigma p)(\Sigma px^2)}$$

where p is the weight of a point whose coordinates are x and y. The rate constant of a unimolecular reaction will be

$$k = \frac{\Sigma pt\ 29\ \ln\,(a-x) - \Sigma p\,\Sigma pt\ln\,(a-x)}{(\Sigma pt)^2 - (\Sigma p)(\Sigma pt^2)}$$

The weight p of each point can be determined by the method previously given. This method has the advantage in that one can calculate the "probable error." The formula for calculating the probable error is given by Birge.[5] Professor Ingraham of the Mathematics Department of the University of Wisconsin pointed out to the author that the above method of least squares does not give the most probable value of the rate constant. Therefore the use of this method is questionable.

Concentration **Change** for Maximum Accuracy.—It is important to know how long to let a chemical reaction proceed in order to obtain the greatest probable accuracy in the rate constant, when the rate is calculated from the concentrations at two times. If r and r_0 are the probable errors in the concentrations C and C_0, then r/C and r_0/C_0 will be the corresponding errors in $\ln C$ and $\ln C_0$, providing the error is small. If one assumes that the error in k is due only to the error in concentration, then the probable error in k will be

$$r_k = \frac{1}{t}\sqrt{\left(\frac{r_0}{C_0}\right)^2 + \left(\frac{r}{C}\right)^2} \qquad (6)$$

If we let $y = C/C_0$, the fraction which has reacted at time t, then $kt = -\ln y$. Dividing Equation **6** by k, substituting $C = yC_0$, and $kt = -\ln y$, then the fractional error in k is

$$\frac{r_k}{k} = \frac{-1}{C_0 \ln y}\sqrt{(r_0)^2 + \left(\frac{r}{y}\right)^2} \qquad (7)$$

Taking the derivative of r_k/k with respect to y and setting it equal to zero, we have

$$(r_0/r)^2y^2 + 1 + \ln y = 0 \qquad (8)$$

which is the condition that the percentage error in k shall be a minimum. Since the probable error in the concentration, instead of being a constant percentage error, is almost always a constant quantity independent of the concentration, r_0 will be equal to r. Equation 8 then becomes: $-\ln y = y^2 + 1$ or $y =$ **0.33.** Thus, for the case when the error in time is negligible,

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[5] *R. T.* Birge, *Phys. Rev. Suppl.*, *1*, **5** **(1929).**

the greatest probable accuracy in k is obtained by calculating it for the interval during which 67% of the material reacts.

In the case of fast reactions, the error in measuring the time may have a greater effect on the rate constant than the errors in measuring the concentration. One may calculate r'_0, the probable error in the initial concentration which would produce the same error in k as does the error in $(t_n - to)$. From Fig. 2 one can see that $\tan \theta = k$ and therefore for small values of r_{t_0}, $r'_{\ln C_0} = kr_{t_0}$. $r'_{\ln C_0}$ is the probable error in $\ln C_0$ which would produce the same probable departure from the line as does the actual probable error in t_0. The probable error r_t in reading the time is independent of time, and therefore the probable error in $(t, - t_0)$ will be $\sqrt{2}$. One may consider that t_n is entirely accurate and that all the error is in t_0 and equal to $r_t\sqrt{2}$. Since $r'_{\ln C_0} = r'_0/C_0$, and r_{t_0} is set equal to $r_t\sqrt{2}$, we have

$$r'_0 = kr_tC_0\sqrt{2} \tag{9}$$

Therefore one may consider the time as always correct and that there is a probable error in the initial concentration r_0 due to error in measurement of the concentration, and another probable error in the initial concentration r'_0 or $kr_tC_0\sqrt{2}$ due to errors in measurement of the time. Since the probable error in concentration r is independent of time, then r_0 may be replaced by r and the effective probable error expressed in terms of the initial concentration will be $\sqrt{r^2 + (kr_tC_0\sqrt{2})^2}$. Substituting this for r_0 in Equation 8, the general equation for optimum time will be

$$\left(\frac{kr_tC_0}{r}\right)^2 2y^2 + y^2 + 1 + \ln y = 0 \tag{10}$$

Table I gives for different ratios of $(kr_tC_0)/r$, the values of $1 - y$, the fraction which has reacted. Thus one can determine how far to let a

TABLE I

Y	$1 - y$ (fraction changed)	Ratio (kr_tC_0)
0.33	0.67	0.0
.3	.70	0.8
.2	.8	2.7
.1	.9	8.0
.05	.95	20.0

unimolecular reaction proceed in order to obtain the greatest probable accuracy in the rate constant, regardless of the probable errors in time and concentration. The probable errors in time and concentration must be estimated by the experimenter. When applying this formula it is only necessary to know an approximate value of the rate constant k, but it must be in terms of natural logarithms and the unit of time in which r_t is expressed. It should be remembered that these probable errors are probable departures from the correct values and not percentage errors.

Methods Applicable to Bimolecular Reactions

When x Is Measured Directly.—When the concentrations of the reacting substances are the same, one can calculate the rate constant from the amount reacting during two equal consecutive time intervals. For these intervals

$$k(t_2 - t_1) = \frac{1}{a - x_2} - \frac{1}{a - x_1} \tag{11}$$

$$k(t_3 - t_2) = \frac{1}{a - x_3} - \frac{1}{a - x_2} \tag{12}$$

If $t_2 - t_1 = t_3 - t_2$ then

$$\frac{1}{a - x_2} - \frac{1}{a - x_1} = \frac{1}{a - x_3} - \frac{1}{a - x_2} \tag{13}$$

and

$$a = \frac{2x_1x_3 - x_1x_2 - x_2x_3}{x_1 - 2x_2 + x_3} \tag{14}$$

Substituting this value of a in either equation (11) or (12), one obtains

$$k = \frac{1}{2\tau}\,\frac{[(x_2 - x_1) - (x_3 - x_2)]^2}{(x_3 - x_1)(x_2 - x_1)(x_3 - x_2)} \tag{15}$$

where τ is the time interval between x_1 and x_2 as well as between x_2 and x_3. If ΔC_1 and ΔC_2 are the changes in concentration during two equal and consecutive time intervals, Equation 15 may be written

$$k = \frac{1(\Delta C_1 - \Delta C_2)^2}{2\tau(\Delta C_1 + \Delta C_2)\Delta C_1 \Delta C_2} \tag{16}$$

Equation 15 may also be written

$$k = \frac{1}{2\tau(x_3 - x_1)}\left[\frac{x_2 - x_1}{x_3 - x_2} - 1\right]\left[1 - \frac{x_3 - x_2}{x_2 - x_1}\right] \tag{17}$$

Since $(x_3 - x_2)$ is always smaller than $(x_2 - x_1)$, which is smaller than $(x_3 - x_1)$, one can see from equation (17) that when τ is more accurately known than $(x_3 - x_2)$, the error in k will always be largely due to the error in $(x_3 - x_2)$. The probable accuracy in k will be very nearly a maximum when $(x_3 - x_2)$ is a maximum. Letting $t_1 = 0$, then $x_1 = 0$ and equation (13) becomes

$$\frac{2}{a - x_2} = \frac{1}{a} - \frac{1}{a - x_3} \tag{18}$$

or

$$(x_3 - x_2) = \frac{x_2(a - x_2)}{(a + x_2)} \tag{19}$$

In order that $x_3 - x_2$ shall be a maximum, its derivative is set equal to zero.

$$\frac{d(x_3 - x_2)}{dx_2} = \frac{-x_2}{a + x_2} - \frac{x_2(a - x_2)}{(a + x_2)^2} + \frac{a - x_2}{a + x_2} = 0 \tag{20}$$

This reduces to $x_2 = 0.414a$. Thus, when the rate is calculated from Formula 15 and the time interval is more accurately known than $x_3 - x_2$, the probable error in k will be smallest when about 41% reacts during the first time interval.

When *(a − x)* is Measured Directly.—The integrated equation for a bimolecular reaction, when the concentrations of the reactants are the same, may be written

$$k = \frac{1}{t}\left[\frac{1}{C} - \frac{1}{C_0}\right]$$

The probable error in concentration r is small compared to the concentration, and therefore one may use the series expansion $1/(c - r) = 1/C - r/C^2 + r^2/C^3 - \ldots$ and neglect all terms except the first two. The error in $1/C$ will then be r/C^2 and the probable error in k due to errors in concentration will be

$$r_k = \frac{1}{t}\sqrt{\left(\frac{r_0}{C_0^2}\right)^2 + \left(\frac{r}{C^2}\right)^2} \tag{21}$$

Letting $y = C/C_0$, dividing by k and letting $kt = 1/C - 1/C_0$, one obtains

$$\frac{r_k}{k} = \frac{\sqrt{r_0^2 + \frac{r^2}{y^4}}}{C_0(1/y - 1)} \tag{22}$$

The probable error will be a minimum when the derivative of r_k/k with respect to y is zero.

$$\frac{d(r_k/k)}{dy} = \frac{1}{C_0}\left[\left(\frac{1}{y} - 1\right)\left(\frac{-2r^2}{y^5}\right)\left(r_0^2 + \frac{r^2}{y^4}\right)^{-1/2} + \frac{1}{y^2}\left(r_0^2 + \frac{r^2}{y^4}\right)^{1/2}\right]\left[\frac{1}{y} - 1\right]^{-2} \tag{23}$$

Setting this equal to zero, we have

$$\left(\frac{r_0}{r}\right)^2 y^4 + 2y = 1 \tag{24}$$

One may calculate the probable error in the initial concentration r_0' that would produce the same probable error in k, as does the actual probable error in time r_t. By the same procedure that was used for the unimolecular reaction, one obtains $r_0' = kr_tC_0^2\sqrt{2}$, the effective probable error in the initial concentration will be $\sqrt{(kr_tC_0^2\sqrt{2})^2 + r^2}$ and the general equation for optimum accuracy will be

$$\left(\frac{kr_tC_0^2}{r}\right)^2 2y^4 + y^4 + 2y = 1 \tag{25}$$

Table II gives the values of $(1 - y)$ for different values of the ratio $kr_tC_0^2/r$. Thus for the case when the concentrations of the reactants are the same,

TABLE II

OPTIMUM CONCENTRATION CHANGE FOR BIMOLECULAR REACTION

Fraction changed $(1-y)$	0.53	0.6	0.7	0.8	0 9	0.95
Ratio $kr_tC_0^2/r$	.0	1.8	5	14	63	268

one may determine how much should react in order to obtain the maximum accuracy in k. In order to do this, one needs to know an approximate value of k and one has to estimate the probable error in measuring the time and concentration.

Summary and Conclusions

The rate constants of both unimolecular and bimolecular reactions can be calculated analytically when the initial concentration or time cannot be determined. This method, however, is not to be recommended when it is possible to determine the initial concentration accurately by direct means, since it has greater probable error.

The commonly used simple arithmetical average of rate constants is entirely incorrect and should never be used except for averaging rate constants calculated from entirely independent data, and then only when the probable errors are nearly alike. The method of least squares should be used with caution. The graphical method may be used in all cases where each point on the graph represents entirely independent data.

The author recommends that one should first determine whether the rate law holds within experimental error. Then, in case it does. one should take more data in such a manner that a number of values of k can be calculated from entirely independent data for approximately the optimum concentration change. These values of *k* may be averaged graphically or by taking the simple arithmetical average.

MADISON, WISCONSIN

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

THE PHYSICAL IDENTITY OF ENANTIOMERS. THE CAMPHORIC ACIDS

BY ALAN NEWTON CAMPBELL

RECEIVED JANUARY 20, 1931 PUBLISHED MAY 6, 1931

In a recent paper[1] the author in collaboration with another was able to produce evidence that the d- and *l*-mandelic acids are not absolutely identical in their physical properties. Private criticism made at that time rested upon the contention that the d-form was not quite pure, despite the facts that the rotation of d-form was normal, and that the rotatory dispersions or rather differences in rotation for the two lines used, were the same, which would not be the case if one form were impure. Nevertheless, in view of this contention, it was thought advisable to prepare the next pair of enantiomers from independent optically active sources of opposite rotation. I am indebted to Dr. Kenyon for the suggestion that I should use the d- and I-camphors, or rather the camphoric acids obtainable from them. I have been exclusively occupied for the past fifteen months with this work, most of the time being spent on preparation and purification. As I surmise that criticism will, as usual, be directed rather to this question of purity than to ability to determine physical constants, I give a detailed statement of the methods of preparation and purification.

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[1] Campbell and Garrow, *Trans. Faraday Soc*, 26, 560 (1930).

Preparation and Purification

Pure d-camphor was purchased from British Drug Houses (m. p. **176.3°** (uncorr.)): three hundred grams of d-camphor was heated with *2400* cc. of nitric acid (d **1.42)** and *1600* cc. water for sixty-five hours on the water-bath. The product was cooled and the crude d-camphoric acid filtered off.

The crude product was purified as follows. It was dissolved in 10% caustic soda and extracted with ether to remove unchanged camphor. The acid was reprecipitated with hydrochloric acid, dried and converted into its anhydride by refluxing with acetyl chloride. Excess acetyl chloride was removed by shaking with cold water. The anhydride was then dissolved in boiling alcohol and the solution allowed to crystallize. The purified anhydride was then hydrolyzed by boiling with potassium carbonate solution. d-Camphoric acid was precipitated from the alkaline solution by addition of hydrochloric acid. The precipitate was filtered and washed, and then recrystallized ten times from boiling water, the first crop of crystals being always rejected; *50* g. of *d*-camphoric acid was eventually obtained.

In order to decide whether this repeated recrystallization would constitute a purification from the opposite enantiomer, supposing it to be present, the solubility diagram for d-, *l*- and r-camphoric acids was determined, for 16°. The results were

	Solid phase		
	Dextro	Inactive	Inactive and dextro
Solubilities, g. per *100* g of water	0.679	0.12 *d* **0.121**	0.63 *d* *0.041*

When these figures are plotted Fig. 1 is obtained.

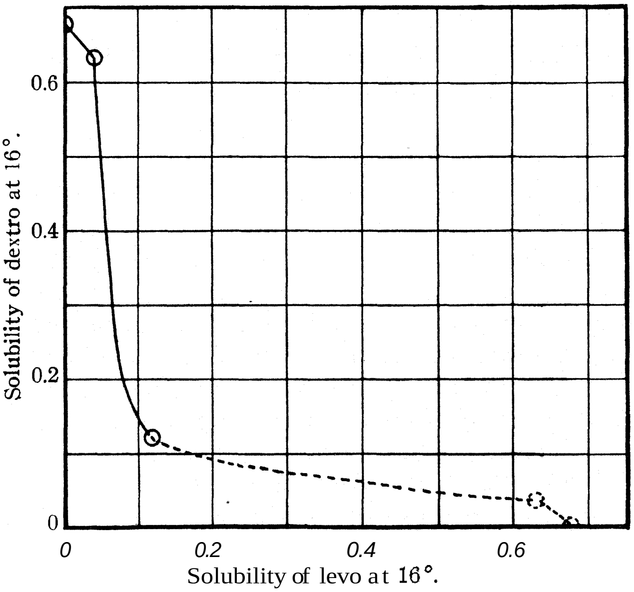

Fig. *1.*

The titration of the two acids eventually obtained, by standard baryta, gave equivalent weights of 99.90 (levo) and 100.00 (dextro); calcd., $^1/_2 \cdot 200.13$.

From the diagram it is apparent that the solid phase in contact with solution throughout the greater course of the curve is the racemic form. It therefore follows that if a solution of the d-form contains any appreciable quantity of the *l*-form, racemic form will separate from the solution (at room temperature) until the solution contains 0.63 g. of dextro and 0.04 g. of levo per 100 g. of water. Further evaporation will result in the deposition of *d*- and *l*- in the above proportions. Further than this, therefore, the purification of dextro cannot be carried. If, however, as has hitherto been stated, enantiomers are completely identical, then the complete solubility diagram will be perfectly symmetrical, and the recrystallization of the levo form will also result in a product which will be impure with opposite enantiomer, to precisely the same extent. Hence any objections urged against the differences in physical properties on the score of impurity fall to the ground.

Each recrystallization was allowed to stand overnight, in contact with the mother liquor, after separation and rejection of the crystals first appearing. Under these circumstances it is improbable that equilibrium was not attained, in view of the relatively large amount of active form separating from the solution.

The form of the solubility diagram bears out the contention of Ross and Summerville[2] that the racemate is a very stable one.

It was at first attempted to prepare *l*-camphoric acid from *l*-camphor, but it was found that commercial *l*-camphor was hopelessly impure. Recourse was therefore had to *l*-borneol as the starting material. *l*-Borneol was obtained from British Drug Houses, and it had the following physical constants: m. p. 203.5°; $[\alpha]_D^{16}$ −37.6 (in alcohol). The *l*-borneol was purified by the method of Haller.[3] The *l*-borneol acetate was distilled under reduced pressure, before freezing, to free it from non-volatile impurities. The purified *l*-borneol was then oxidized with nitric acid and purified in the above manner. The product eventually obtained had a chemical equivalent of 99.90, as against 100.00 for the d-form (calcd. 100.07).

In connection with the question of purity, the appearance of the preparations was well worth noting. They consisted entirely of large, clear, well-shaped crystals, of an average diameter of 5 mm. Apart from occasional twinning, they were well-shaped rhombohedra, having the hemihedral facets well developed. Admixture with the opposite enantiomer would have resulted in the formation of the racemic form, with a holohedral structure. After examining such a preparation carefully with a low-power lens, it is impossible to believe that it is not homogeneous.

Melting Points of the Camphoric Acids.—These were determined by the method described in the previous paper.[1] The precautions there described were repeated in the present instance. The following figures were obtained for the melting points of successive crops of crystals.

[2] Ross and Summerville, *J. Chem. Soc.*, 2778 (1926).

[3] Haller, Ann. *chim. phys.*, [6] 27,422 (1892).

TABLE I

MELTING POINTS

All these figures are uncorrected and therefore low, but the same thermometer was used for all determinations.

Dextro	187.5	188.0	186.0	186.0	186.0
Levo	183–189[a]	186.5[b]	186.5[b]	186.5[b]	186.5[b]

[a] Large but distorted crystals deposited slowly from aqueous solution of crude product [b] Successive recrystallizations of product.

Solubilities.—The solubilities were determined in water, since, though the solubility in acetone is conveniently large, camphoric acid forms a compound with acetone (private communication from Professor Smits). All solutions were filtered in the thermostat, by means of an apparatus previously described,[4] the saturated solution was weighed, and a weighed portion titrated with baryta. Solubilities are expressed, as usual, in grams per 100 g. of solvent.

TABLE II

SOLUBILITIES IN WATER

Temp., °C.	Dextro	Levo	Temp., °C.	Dextro	Levo
16.0	0.665		25.5		0.705
16.0	.657		29.9		.710
18.0	.715		30.0	0.802	
20.1		0.682	35.0	.92	
24.8	.74		35.5		.77
25.0	.765		40.0	1.00	.88

These results, when plotted, yield Fig. 2.

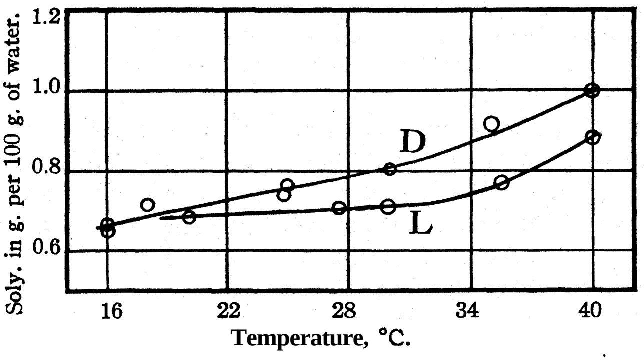

Fig. 2.—Solubilities of *d*- and *l*-camphoric acids in water: D, dextro; L, levo.

Specific Rotatory Power.—The instrument which I used in Aberdeen and the method of work are described in the previous paper.' Since coming to Winnipeg, I have used an identical instrument, except that it has no

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[4] Campbell, *J. Chem. Soc.*, 179 (1930).

spectrometric attachment. Determinations with this instrument were therefore made with sodium light. Solutions were made up by weighing in the first place, but in order to be entirely independent of graduated apparatus, the densities of the solutions were determined in a pycnometer holding 11.660 cc. of water at 4°. A weighed portion of the solution was then titrated with baryta and calculated by the formula

$$[\alpha]^t_\lambda = \frac{\alpha \times 100}{l \times d \times p}$$

Specific Rotatory Power in Water.—A single determination of this was made, with the result $[\alpha]^{16}_{\lambda = 5960} + 46.3°$.

Specific Rotatory Power in Alcohol.—The alcohol used was the ordinary rectified alcohol, having d^{18}_4 0.80275. It therefore contained 96.99% of alcohol by weight. An 8-liter glass jar was filled with this alcohol, in order that identical solvent might be used throughout. In a few experiments carried out in Winnipeg I was of course obliged to use a different sample of alcohol, but it had an almost identical density and was used for both forms. The specific rotatory powers, at 18°, were as given in Table III.

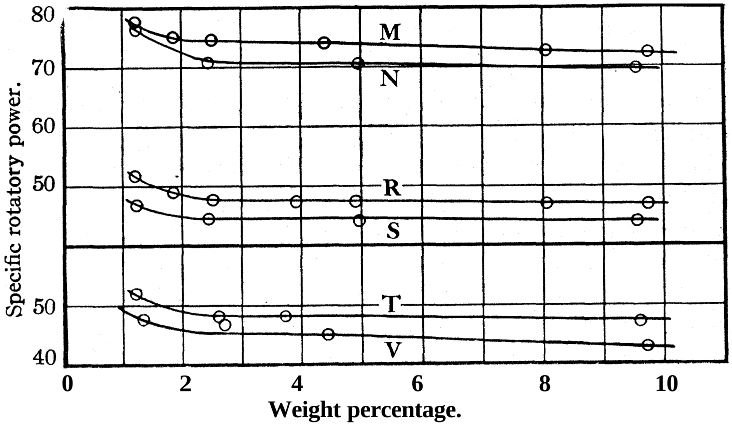
TABLE III

SPECIFIC ROTATORY POWERS IN ALCOHOL

	Dextro		Levo		Dispersion,
p	$\lambda = 5960$	$\lambda + 4610$	$\lambda = 5960$	$\lambda = 4610$	$[\alpha]_{\lambda = 6960} - [\alpha]_{\lambda = 4610}$
1.21	+51.8	+77.5			25.7
1.24			−47.0	−76.5	29.5
1.86	+49.0	+75.0			26.0
2.44			−44.7	−70.9	26.2
2.50	+47.7	+74.4			26.7
3.92	+47.5	+73.8			26.3
4.90	+47.3	+73.5			26.2
4.95			−44.4	−70.4	26.0
8.05	+46.9	+72.7			24.8
9.55			−44.05	−69.5	25.45
9.75	+46.7	+72.1			25.4

p $t = 25.2°$	Dextro $\lambda = 5896$	Levo A = 5896
1.22	+52.0	
1.33		−48.0
2.51	+48.3	
2.52		−47.0
3.73	+48.3	
4.43		−45.0
9.6	+47.3	
9.70		−43.0

When these figures are plotted the curves of Fig. 3 are obtained. The dispersions appear to be identical, while the rotations differ. Apart from the evidence of purity which this affords, it may have a theoretical significance. According to Hunter[5] dispersion is a more fundamentally constitutive property than rotation and, if this view is correct, it would seem to indicate that the difference between enantiomers is not constitutive, in the ordinary sense of that word, as indeed it could not be, but of a more superficial character.



M, Dextro, λ = 4610; N, levo, λ = 4610. R, Dextro, λ = 5960; S, levo, λ = 5960. T, Dextro, λ = 5986, 5890; V, levo, λ = 5896, 5890.

Fig. 3.

Conclusion.—The theoretical implications of these results have already been discussed in the previous paper.'

Summary of Results

1. Dextro and levo camphoric acids have been prepared in a state of purity.
2. The melting points, solubilities and specific rotatory powers of the two forms have been determined and compared.

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[5] Hunter, J. *Chem. Soc.*, 123,1671 (1923).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 249]

THE SOLUBILITY OF CHLORINE IN AQUEOUS SOLUTIONS OF CHLORIDES AND THE FREE ENERGY OF TRICHLORIDE ION

BY M. S. SHERRILL AND E. F. IZARD

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Introduction

Previous investigations[1] show that the solubility of chlorine in water is decreased by small additions of hydrogen chloride, but is increased by larger additions. The initial decrease in solubility is readily explained by the depression of the hydrolysis of the dissolved chlorine by the added acid. At the higher concentrations of added acid, however, where the percentage hydrolysis is reduced to an extremely small value, a further decrease in solubility might be expected to arise from the salting-out effect of the hydrogen chloride. Actually an increase in solubility has been observed which indicates the formation of a complex ion, probably the trichloride ion, in sufficient amount to more than compensate the salting-out effect.

In contrast to hydrogen chloride, additions of sodium chloride to water continue to decrease the solubility of chlorine, even at the higher concentrations. This indicates that the salting-out effect predominates over the complex ion formation in determining the total solubility. This view is confirmed by the fact that the salting-out effect of the metallic chlorides is in general considerably greater than that of hydrochloric acid.[2]

In order to test these views more quantitatively, a systematic study was made of the solubility of chlorine at a pressure of one atmosphere and 25° in solutions of sulfuric acid, hydrogen chloride and a series of other chlorides. The results were compared with existing values of the solubility of oxygen in the presence of the same series of electrolytes. The solubility data relating to oxygen were taken from the compilation of Randall and Failey[2] and from an investigation by McArthur.[3] The theoretical considerations involved in the interpretation of the results of the solubility determinations are briefly as follows.

The dissolved chlorine exists in the saturated solutions partly in the form of free chlorine (Cl_2), partly in its hydrolyzed form (HClO), and the remainder in the form of the complex ion (Cl_3^-). In the case of the sulfuric acid solutions saturated with chlorine the complex-ion formation is inappreciable, and the small hydrolysis can be computed, so that the salting-out effect of the electrolyte on the chlorine as such can be estimated and compared with the corresponding effect on the dissolved oxygen in its

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[1] Jakowkin, *Z. physik. Chem.*, 29, 613 (1899).

[2] Scatchard, *Chem. Reviews*, 3, 398 (1927); Randall and Failey, *ibid.*, 4, 271 (1927).

[3] McArthur, *J. Phys. Chem.*, 20, 495 (1916).

saturated solution. This is conveniently done by computing the ratio s_0/s of the saturation concentration of chlorine (Cl_2 as such) in pure water to its value in the presence of the electrolyte, and comparing it with the corresponding value for oxygen. This ratio represents the activity coefficient of the chlorine, or of the oxygen, in the presence of the different electrolytes.

Debye and McAuley[4] have shown, with the aid of the ion attraction theory, how the activity coefficient of a non-electrolyte in the presence of electrolyte varies, for a given solvent, with the nature and concentrations of the non-electrolyte and electrolyte. Though the derivation of this theoretical relation is complicated, the final result may be expressed for this special case of gas solubility by the relatively simple equation

$$\text{Log}\,\frac{s_0}{s} = \kappa\left(\frac{\partial D}{\partial s}\right)\frac{1}{r}\,\Sigma(C_i z_i)^2$$

In this equation κ is a constant characteristic of the solvent at a temperature T, the ratio $\partial D/\partial s$ is the rate of change of the dielectric constant of the solution (containing only non-electrolyte) with the concentration s of the non-electrolyte, r is a mean of the radii of the ions present, and c_i is the concentration and z_i the charge of any ion of kind i (hence $^1/_2\Sigma(c_i z_i)^2$ is the ionic strength). The ratio $\partial D/\partial s$ may be assumed to be independent of the concentration s, and therefore regarded as a constant characteristic of the non-electrolyte.

It follows from this theory that the saturation concentrations of chlorine and oxygen in different electrolytes of the same ionic strength must bear the definite relation to each other expressed by the equation

$$\frac{\text{Log}\,(s_0/s)_{Cl_2}}{\text{Log}\,(s_0/s)_{O_2}} = \text{Const.}$$

That is, the theory requires that at small concentrations this logarithmic ratio be independent of the particular ionic strength at which the solubilities of the two gases are compared, and also of the nature of the ions which make up that ionic strength.

Direct comparison of the solubility of chlorine with that of oxygen in solutions of sulfuric acid up to a concentration 1 formal (the concentration range covered by the compilation of Randall and Failey[2]) showed the activity coefficients of these two gases to be nearly the same, and correspondingly the logarithmic ratio to be approximately equal to unity. Thus, in 1.036 formal sulfuric acid the activity coefficients of the chlorine and oxygen in their saturated solutions were 1.170 and 1.185, respectively, and the corresponding logarithmic ratio was **0.925.**

In the interpretation of results this value for the logarithmic ratio was assumed to hold at all ionic strengths, and accordingly the concentration of free chlorine (Cl_2) in the various chlorine saturated solutions of chlorides

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[4] Debye and McAuley, *Physik. Z.*, **26,** 22 (1925).

was computed from the known values of the solubility of oxygen in the same solutions with the aid of the equation

$$\text{Log } (s_0/s)_{Cl_2} = 0.925 \log (s_0/s)_{O_2} \qquad (1)$$

The hydrolyzed portion (HClO) of the dissolved chlorine was calculated, as indicated below, with the aid of the mass action law, and the remainder of the dissolved chlorine was assumed to be trichloride ion (Cl_3^-).

The equilibrium conditions of the reaction $Cl_2 + H_2O = H^+ + Cl^- +$ HClO, are represented by the equation

$$\frac{[H^+][Cl^-][HClO]}{[Cl_2][H_2O]} = \frac{\alpha^2(H^+)(Cl^-)(HClO)}{(Cl_2)(p/p_0)} = K \qquad (2)$$

in which the activities of the substances are indicated by brackets and the concentrations (expressed in moles per 1000 g. of water) by parentheses. The symbol a is the mean activity coefficient of the H^+ and Cl^- ions; and p/p_0 is the ratio of the vapor pressure of water in the solution to that of pure water. The value for the equilibrium constant K of the hydrolysis reaction was taken from Lewis and Randall[6] to be 4.84 X 10^{-4}. The mass action expression for the hydrolyzed part of the dissolved chlorine varies with the type of added electrolyte. The equations employed in computing the concentration of the hypochlorous acid (HClO) in c formal solution of the various substances were as follows

$$(HClO)^2 = K\,\frac{(p/p_0)[\Sigma(Cl_2) - (HClO)]}{2c\alpha^2} \quad \text{for } H_2SO_4 \qquad (3)$$

$$(HClO) = K\,\frac{(p/p_0)\,s}{c^2\alpha^2} \quad \text{for HCl} \qquad (4)$$

$$(HClO)^2 = K\,\frac{(p/p_0)\,s}{c\alpha^2} \quad \text{for NaCl or KCl} \qquad (5)$$

$$(HClO)^2 = K\,\frac{(p/p_0)\,s}{2c\alpha^2} \quad \text{for } BaCl_2 \qquad (6)$$

In applying Equation 3, the mean activity coefficient of the H^+ and Cl^- ions was placed equal to that found by Livingston[6] at the same ionic strength for H^+ and Br^- in mixtures of sulfuric acid and potassium bromide. The equation was derived under the assumption that H_2SO_4 is completely ionized into $2H^+$ and SO_4^-, since Livingston had made this assumption in evaluating the mean activity coefficients of hydrogen and bromide ions.

The values for the activity coefficient a substituted in Equation 4 were taken from Lewis and Randall;? in Equation 5 from Harned;[8] and in Equation 16 from Harned and Brumbaugh.[9]

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[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 508.

[6] Livingston, THIS JOURNAL, 48, 45 (1926).

[7] Ref. 5, p. 336.

[8] Harned, THIS JOURNAL, 48,326 (1926).

[9] Harned and Brumbaugh, *ibid.*, 44,2729 (1922).

Experimental Procedure

The solutions of the various electrolytes which were to be saturated with chlorine were prepared of known strength, and the conditions of saturation, described below, were so regulated that no change in concentration could result from the absorption of the chlorine. In consequence it was only necessary to analyze the saturated solutions for the total amount of dissolved chlorine. The solutions of sulfuric and hydrochloric acid were prepared by adding a weighed amount of distilled water to a weighed amount of a stock solution whose composition by weight had been carefully determined. The sodium, potassium and barium chloride solutions were prepared by adding weighed amounts of distilled water to weighed amounts of the carefully purified and dried salts.

The chlorine was prepared by the action of hydrochloric acid on chromic acid. and bubbled through the solution under investigation in an absorption train. As a precaution the absorption train was painted black to prevent the decomposition of chlorine by light. A brief description of the apparatus and method of saturating the solution with chlorine follows.

Two hundred cubic centimeters of 6.0 normal hydrochloric acid (the constant boiling mixture of hydrochloric acid and water) was added to a one-liter round-bottomed flask provided with a water-cooled return condenser. Into this flask were sealed two side tubes connecting with large funnels, and so arranged that concentrated hydrochloric acid could be delivered through one of these tubes beneath the surface of the liquid in the flask, and a saturated solution of chromic acid introduced through the other. The flask was heated by means of a ring burner, and the rate of influx of the two acids was regulated so as to keep the concentration of the hydrochloric acid in the flask nearly equal to that of the constant boiling mixture. The moist chlorine on leaving the condenser was bubbled through the solution under investigation in two washing bottles placed in series, and finally through a third portion of the solution in a bubble-tube, shown in the figure, which was especially designed to insure complete saturation and easy removal of a sample for analysis without loss of chlorine. The preliminary washing of the chlorine served to prevent loss by evaporation in this final absorption tube. When all air had been displaced from this train of apparatus and the solution approximately saturated at atmospheric pressure and room temperature with chlorine, the stopcock J was closed to supersaturate the solution by building up a somewhat larger pressure. After a few minutes stopcock H was closed, and the tube disconnected at the ground glass joint G. The tube was then placed in a rocking device in a thermostat at 25 ± 0.01°, and slowly rocked under these conditions for a short time. Finally stopcock J was opened and the agitation continued for three or four hours to ensure the solution being saturated with chlorine at the barometric pressure. In removing a sample for analysis the tube was placed in a vertical position in a rack in the thermostat. By applying pressure at J with both stopcocks open, the sample of solution was forced out through H directly into a weighiig bottle containing a solution of potassium iodide. The iodine liberated in this weighed sample was determined by titration with sodium thiosulfate using starch as an indicator.

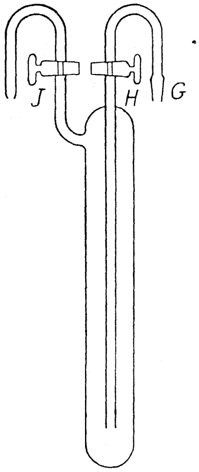

Fig. 1.

Tabulation and Discussion of Results

The results of the determination of the solubility of chlorine at 25° and one atmosphere in pure water, and in the presence of the various electrolytes are recorded in the following tables. In computing the solubilities from the experimental data the partial pressure of chlorine above the solution was found by deducting from the observed barometric pressure the vapor pressure of water in the respective solutions. Then the solubility corresponding to a saturation pressure of chlorine equal to one atmosphere was calculated by applying Henry's law, which is valid over the small range of pressure involved. The values for the vapor pressure of water, shown in the third column, were obtained for the solutions of sulfuric acid from Brönsted[10] and from Grollman and Frazer,[11] of hydrochloric acid from Dobson and Masson,[12] of sodium chloride from Negus,[13] of potassium chloride from Lovelace, Frazer and Sease[14] (calculated over from 20° to 25°), and of barium chloride, where no data were available, under the assumption that the vapor pressures of these solutions were equal to those of potassium chloride of the same formality.

The equilibrium concentrations recorded in the tables were calculated from the total solubility by the equations considered in the introduction. The value (0.0592 molal) given in Table I for the molality s_0 of Cl_2 in pure water saturated with chlorine at 25° and 1 atmosphere was obtained by extrapolation of the values for s, the molality of Cl_2 in the different sulfuric acid solutions saturated with chlorine, to zero concentration of sulfuric acid. This value for the solubility constant of chlorine in water was confirmed by making a similar extrapolation of the concentrations of the unhydrolyzed portion of the dissolved chlorine in solutions of hydrochloric acid saturated with chlorine. Since hydrochloric acid has a much larger effect in depressing the hydrolysis of chlorine than does sulfuric acid, and since the trichloride formation in the diluter solutions of hydrochloric acid is inappreciable, this latter method of extrapolation is attended with much less error.

A comparison of the values (in Table I) for the activity coefficient (s_0/s) of chlorine in the sulfuric acid solutions with the corresponding values for oxygen given by Randall and Failey[2] led to the adoption of equation (1) for the converse calculation of the values (in Table II) for the activity coefficient of chlorine in the chloride solutions. For these calculations reference was made to the solubility data for oxygen given by Randall and Failey,[2] and by McArthur.[3]

The equilibrium constant of the reaction $Cl_2(g) + Cl^- = Cl_3^-$ may be expressed in either of the following forms

$$K = \frac{\alpha_{Cl_3^-}\ (Cl_3^-)}{\alpha_{Cl^-}(Cl^-)\, p_{Cl_2}} \text{ or } K = \frac{\alpha_{Cl_3^-}\ (Cl_3^-)}{\alpha_{Cl^-}\, \alpha_{Cl_2}\, (Cl^-)(Cl_2)} \cdot s_0$$

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[10] Brönsted, *Z. physik. Chem.*, 68, 693 (1910).

[11] Grollman and Frazer, THIS JOURNAL, 47,712 (1925).

[12] Dobson and Masson, *J. Chem. Soc.*, 125, 668 (1924).

[13] Negus, "Dissertation," Johns Hopkins University.

[14] Lovelace, Frazer and Sease, THIS JOURNAL, 43, 102 (1921).

The values for this complex constant recorded in the tenth column of Table II were calculated by the first of these expressions under the assumption that the activity coefficients ($\alpha_{Cl_3^-}$ and α_{Cl^-}) of the ions were equal; and those in the eleventh column by the second under the assumption that the activity coefficient ($\alpha_{Cl_3^-}$) of the complex ion is equal to the product ($\alpha_{Cl^-}\alpha_{Cl_2}$) of the activity coefficients of the chloride ion and of the

TABLE I

SOLUTIONS OF SULFURIC ACID SATURATED WITH CHLORINE AT 1 ATM.

Formality of H_2SO_4, C	Total solubility, $\Sigma(Cl_2)$	Vap. press. water, p_{H_2O}	Act. coeff. of HCl α	Equilibrium concentrations (HClO)	$(Cl_2) = s$	Act. coeff. of Cl_2 $\alpha_{Cl_2} = s_0/s$
4.9901	0.04066	16.7 mm.	..	0	0.04066	1.45
3.9934	.04278	18.3	..	0	.04278	1.39
3.0090	.04550	19.9	1.186	0.0014	.04410	1.34
1.9686	.04977	21.7	0.719	.00318	.04659	1.270
1.0240	.05617	22.8	.634	.00535	.05082	1.165
0.4995	.06272	23.3	.579	.00874	.05398	1.097
0.0000	.0923	23.8	..	(.0331)	(.0592)	1.000

TABLE II

SOLUTIONS OF VARIOUS CHLORIDES SATURATED WITH CHLORINE AT 1 ATM.

Formality of electrolyte, C	Total solubility, $\Sigma(Cl_2)$	Vap. press. of water, p_{H_2O}	Act. coeff. of HCl α	Act. coeff. of Cl_2 s_0/s	Equilibrium Concentrations $s = (Cl_2)$	(HClO)	(Cl_3^-)	(Cl^-)	Complex constant $K = [Cl_3^-]/[Cl^-]p_{Cl_2}$ $(Cl_3^-)/3$	$\frac{(Cl_3^-)(0.0592)}{(Cl_2)(Cl^-)}$
Hydrochloric Acid										
5.180	0.1004	17.2	...	1.228	0.04821	0.000	0.0522	5.128	0.0100	0.0123
3.987	.0914	19.0	...	1.180	.05017	.000	.0412	3.946	.0104	.0123
2.990	.0824	20.4	...	1.138	.05200	.000	.0304	2.960	.0103	.0117
1.991	.0737	21.7	...	1.095	.05404	.000	.0197	1.971	.0100	.0110
1.019	.0665	22.8	...	1.052	.05630	.000	.0102	1.009	.0101	.0106
0.496	.0630	23.3	0.762	1.027	.05766	.0001	.0052	0.4908	.0106	.0109
.200	.0619	..	...	...	....	....	....	....	....	...
.100	.06394	..	...	...	....	....	....	....	....	...
.010	.08264	..	...	...	....	....	....	....	....	...
Sodium Chloride										
4.989	0.03087	19.2	1.995	4.076	0.01452	0.00017	0.01618	4.973	0.00325	0.0132
3.989	.03601	20.2	1.336	3.075	.01925	.001054	.01571	3.974	.00395	.0121
2.991	.04161	21.2	1.083	2.318	.02554	.001772	.01430	2.978	.00480	.0112
0.998	.05795	23.0	0.766	1.319	.04488	.005987	.00708	0.997	.00710	.0094
0.501	.06575	23.3	0.731	1.151	.05144	.00954	.00477	0.5058	.00943	.0108
Potassium Chloride										
3.913	0.04724	20.7	1.028	2.36	0.02509	0.00160	0.02055	3.984	0.00528	0.0128
3.014	.04865	21.4	0.866	1.96	.03014	.00241	.01610	3.003	.00536	.0105
2.013	.05388	22.3	.783	1.58	.03737	.00370	.01281	2.004	.00639	.0101
1.000	.06109	23.0	.711	1.26	.04694	.00659	.00756	0.9990	.00757	.0097
0.500	.06610	23.4	.706	1.12	.05266	.01003	.00341	0.5066	.00673	.0075
Barium Chloride										
1.333	0.04468	22.5	1.011	2.046	0.02894	0.00220	0.01354	2.655	0.00508	0.0106
1.000	.04924	23.0	0.884	1.696	.03491	.00323	.01110	1.992	.00557	.0095
0.667	.05494	23.3	.784	1.406	.04210	.00493	.00791	1.331	.00593	.0085
0.330	.06216	23.5	.731	1.173	.05046	.00822	.00348	0.6713	.00521	.0061

dissolved chlorine. Each series of values thus computed should, on extrapolation to zero concentration of the added chloride, give the true value for the complex constant.

The best agreement of the complex constants among themselves was obtained in the case of the hydrogen chloride solutions. Furthermore, both expressions for computing the complex constant lead to substantially the same value, namely, nearly equal to 0.01.

This good agreement is accounted for by the fact that in the hydrogen chloride solutions an increase in solubility of chlorine due directly to the formation of the complex ion is the predominating effect, and hence the calculation of the concentration of the trichloride ion from the total solubility is attended with slight error. On the contrary, in the case of the other chloride solutions the increase in solubility due to complex ion formation becomes of minor influence, and is more than compensated by the very large decrease in solubility due to salting-out effect. The effect of hydrolysis also enters as a small but appreciable factor.

For example, in the 3.987 formal solution of hydrochloric acid the increase in solubility of chlorine (referred to 0.0592 m) due to hydrolysis is negligible, the decrease due to the salting-out effect is 15.3% whereas the increase due to complex-ion formation is 69.6%. In contrast, in the 3.989 formal solution of sodium chloride, the increase in solubility due to hydrolysis is 1.8%, the decrease due to the salting-out effect is 67.5%, and the increase due to complex-ion formation is 26.5%.

In the case of the solutions of sodium, potassium and barium chlorides the agreement of the values computed for the complex constants with each other, and with those obtained from the investigation of the hydrogen chloride, is very satisfactory when there is taken into consideration the fact that the large salting-out effect of these chlorides on chlorine was indirectly estimated by comparison with their salting-out effects on oxygen. Thus, for the sodium chloride and potassium chloride solutions, the complex constants recorded in the last column agree well among themselves, and yield an average value approximately equal to 0.01, the value found for solutions of hydrogen chloride. The values in the tenth column show greater variation among themselves and are all less than 0.01, but there appears to be a trend toward this value as the concentration of the added electrolyte approaches zero. The least satisfactory agreement was found in the case of the barium chloride solutions, due probably to the additional approximate assumptions involved in the calculations.

If 0.01 be adopted as the value for the complex constant of the trichloride ion, the free-energy decrease attending its formation out of chlorine gas and chloride ion may be computed by the familiar expression $-\Delta F = RT \ln K$. The result is shown by the free-energy equation

$$Cl_2(g) + Cl^- = Cl_3^- - 2730 \text{ calories}$$

According to Lewis and Randall at 25°

$$^1/_2H_2(g) + {}^1/_2Cl_2(g) = H^+ + Cl^- + 31{,}367 \text{ calories}$$

By addition of these two free-energy equations there results

$$^1/_2H_2(g) + {}^3/_2Cl_2(g) = H^+ + Cl_3^- + 28{,}637 \text{ calories}$$

That is, $\Delta F_{298} = -28{,}637$ calories for Cl_3^- (or for one formula weight of aqueous HCl_3).

Summary

The solubility of chlorine was determined at 25° and 1 atmosphere in solutions of sulfuric acid, of hydrogen chloride, of sodium chloride, of potassium chloride and of barium chloride, and compared with the corresponding solubilities of oxygen. By means of such a comparison the salting-out effect of these electrolytes on the dissolved chlorine was estimated, This made it possible to compute from the total solubility of chlorine the extent of trichloride formation in the chloride solutions, and the corresponding value for the equilibrium constant of the reaction $Cl_2(g) + Cl^- = Cl_3^-$. The value for this constant was found to be 0.01, the corresponding free energy of formation of trichloride ion, in the system of Lewis and Randall being $-28{,}637$ calories.

CAMBRIDGE, MASSACHUSETTS

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

THE COMPARISON OF CERTAIN COMMERCIAL GETTERS

BY MARY R. ANDREWS AND JOHN S. BACON

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For many years certain materials have been used in lamps and vacuum tubes for the removal of traces of gases so as to improve the vacuum. These materials may be divided into two classes: (1) those acting as adsorbents by virtue of their finely divided condition or activation, that is, those having tremendous surfaces upon which gases can be strongly held by adsorption, and (2) those which possess high chemical activity. To the first class belong active charcoal, copper oxide powder, powdered thoria, etc. The second class includes the alkali metals, alkaline earth metals, and probably phosphorus—the material so much used in incandescent lamps. All of these materials are called "getters" in the technical slang of the day.

The work reported here is confined to a comparison of the efficacy of the common getters of class two. We have tested calcium, barium, magnesium, sodium and phosphorus for the degree of vacuum produced under given conditions and the speed with which this vacuum is reached. These getters are all used as thin coatings on the walls of bulbs or tubes. They are produced by evaporation and deposition of the element at much reduced pressures. This gives a film of large surface and presumably of material which has been freed of gas.

Kaye, in his book on high vacua (page 31), says that a pressure of 10^{-8} mm., or approximately 10^{-5} baryes, is probably the lowest *measured* pressure reached as yet. Working with Dr. Dushman, Mr. Bacon, in the Research Laboratory, recently attained a pressure of less than 5×10^{-9} mm. in a gage connected to a large tube of well degassed charcoal immersed in liquid air. This, then, is a degree of vacuum which it would be desirable to reach in production of vacua with getters. The best pressure we have attained in the experiments reported below is about 10^{-7} mm., but it is hoped that further work will so improve getter technique that this pressure may be materially reduced.

Method.—A 40-watt lamp-bulb containing the getter (see Fig. 1) was connected to an ionization gage of the type developed by Dushman and Found.[1] There was a short side arm at C by which the set was sealed to the exhaust system. The anode and leads of the gage were of molybdenum and the filaments of tungsten so that the whole could be thoroughly degassed by current, electron bombardment and high frequency induction heating. The bulb and gage were usually of soft glass.

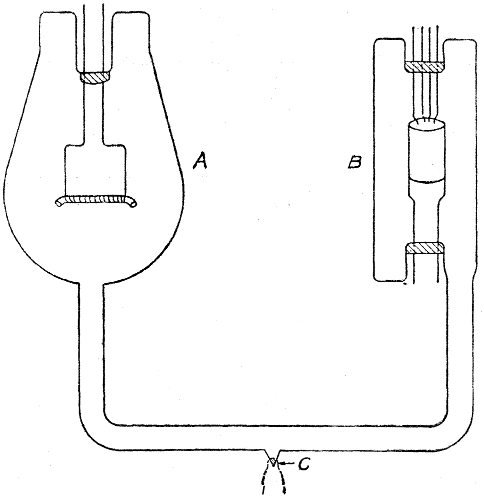

Fig. 1.—A, Bulb containing getter; B, ionization gage; *C*, point of exhaust and seal-off.

After exhaust and "bake-out" for an hour at 360°, the gage was thoroughly degassed and then enough getter vaporized and condensed on the walls of the lamp bulb to form a mirror over most of the inside surface. During the vaporization of the getter a considerable amount of gas which had been contained in it was evolved. This was reabsorbed in large part by the getter during its deposition, but an appreciable amount remained free. Therefore liquid air was applied to a trap below the set to catch any mercury vapor diffusing from the McLeod gage and traps and, after a short interval of pumping to remove gases that had not been absorbed by the getter during deposition, the set was sealed off. Pressures were usually read immediately after seal-off and at suitable intervals thereafter.

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[1] Dushman and Found. *Phys. Rev.*, 17, 7 (1921); 23, 734 (1924).

The ideal method of laying down a getter of this type would be to vaporize and deposit it in a perfect vacuum so that immediately after deposition it is completely gas free. Gases appearing later in the bulb would then find a clean reagent in the best condition for reacting with or absorbing them. In practice there are several different methods of obtaining deposited getters. First is the chemical pellet, that is, a mixture of dry reagents which when heated to a high temperature will react to produce the desired metal, which is volatile at the temperature of the reaction. Thus sodium is produced from a mixture of NaCl + Ca. While this method has been much used, it has the objection that it is difficult, always, to remove the gas completely from any finely powdered material. It is bound to act like a getter of the first class mentioned at the beginning of the paper, retaining in considerable quantities adsorbed gas which will be freed when the mixture is heated. Moreover, if the reaction is exothermic, the temperature of the powdered mix rises suddenly once the reaction is started, and the metal is thrown out almost explosively. It would appear inevitable that in such a case a considerable quantity of dust from the mixture should be carried out with the metal vapor and be deposited on the walls of the bulb, where it might easily adsorb gas and later free it. The gas thrown out at the moment of reaction often gives a pressure of 25–50 baryes or more. It follows that the metal would deposit in the bulb in the presence of gas and possibly be contaminated with a considerable amount

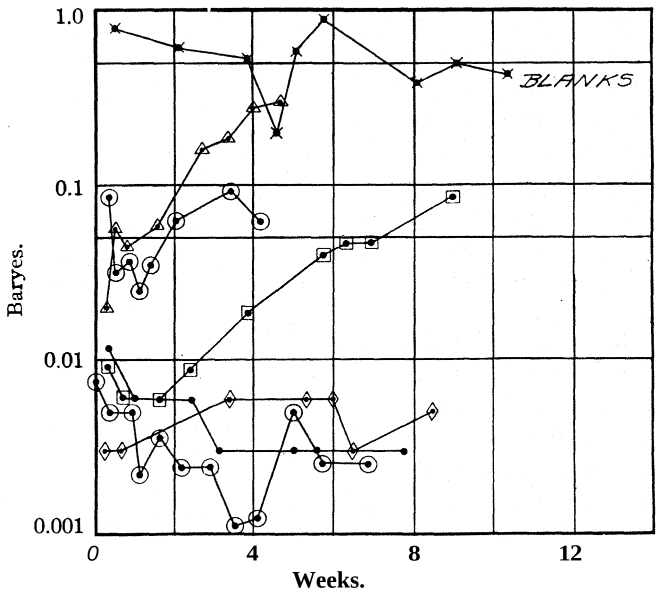

Fig. 2.—Magnesium: effect of increasingly thorough degassing.

of powdery solids. The reason for the widespread use of such pellets is, of course, the convenience of handling the mixture.; as compared with that of introducing the inflammable, low-melting metal as such.

A second method, used in depositing such metals as calcium and magnesium which can be produced in the form of large diameter wire, or rods, is to mount a short piece inside a spiral filament. When a current is passed through the filament, the metal inside is vaporized. The objection to this method is that the wire as manufactured at present always contains a large amount of gas and it appears to be impossible to preheat it evenly with the spiral so as to degas completely before vaporizing.

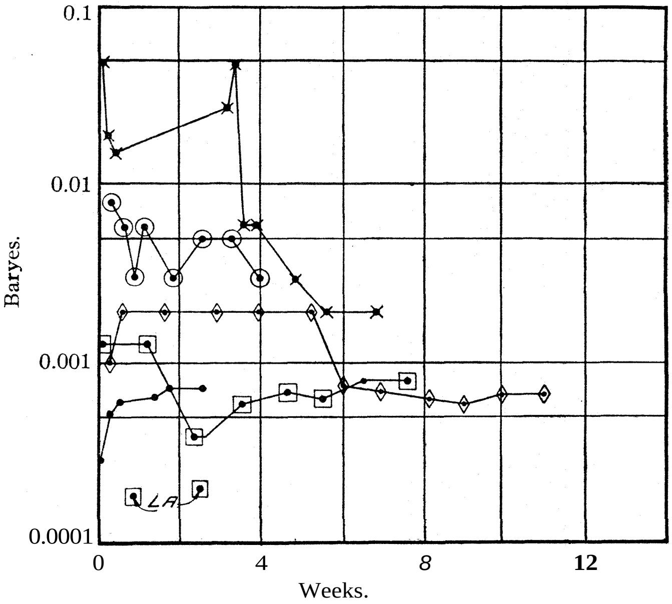

Fig. 3.— Calcium: effect of degassing.

A third method is to enclose the getter either pure or as an alloy in an envelope of a highly refractory metal such as molybdenum which will not give off any appreciable amount of gas and which can be heated by high frequency induction to a low temperature at first for degassing and later to a higher temperature for vaporizing the getter. This gives better results than the other two methods, as is shown in the curves.

Figure 2 shows the very marked effect of degassing magnesium in a spiral and in an envelope. The upper curve gives the average of two tubes run without getter, the two next lower curves are of magnesium flashed from spirals without a previous degassing, the next is of magnesium degassed by running the spiral at a bright red temperature for about fifteen minutes before the temperature was raised to vaporize the metal. The fifth and sixth curves are of magnesium degassed in molybdenum envelopes at a dull red for about fifteen minutes. The seventh curve is of magnesium in a molybdenum envelope, very well degassed and slowly vaporized in a system which pumped off the gas very rapidly.

Figure 3 shows the action of calcium. The two upper curves are of metal degassed for fifteen minutes in spirals, the three lower of metal much more carefully degassed. Two of these were calcium heated in spirals just to the evaporation point so that deposits were formed in two hours. The third was calcium which had been distilled twice in vacuum in a side tube before being distilled into the bulb. Barium gave very similar curves. It was used in the form of the barium–aluminum alloy (50–50) from which the barium metal was vaporized by high frequency induction heating.

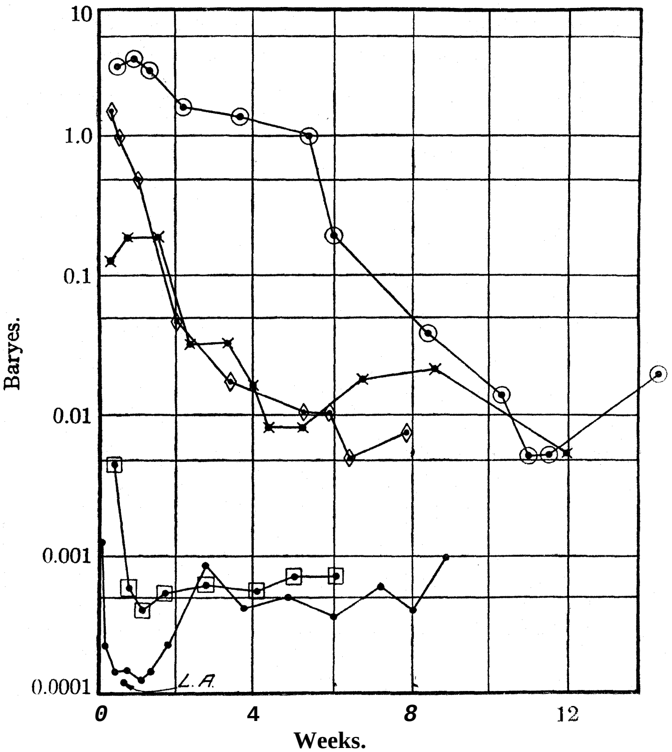

Fig. 4.—Sodium: effect of degassing. **Note slow rate of clean-up by gassy material.**

Sodium (Fig. 4) shows some interesting characteristics. For the three upper curves, chemical pellets were used. The clean-up was very slow and not very complete, though the pellets were always preheated to degas them as well as possible. But when sodium was deposited in the bulb by submerging the latter in a bath of molten sodium nitrate and passing sodium into the bulb by electrolysis, clean-up occured quickly and very much more completely, as is shown in the two lower curves.

Phosphorus (Fig. 5) was deposited by coating tungsten filaments with a suspension of red phosphorus and flashing them to a high temperature. This vaporizes the phosphorus very quickly, which seems to be essential to its effectiveness as a getter. There has been considerable work[2] done on the action of phosphorus as a getter, but our curves show this material to be only fair. Possibly larger amounts would yield better results. Our bulbs were tinged yellow by the deposit but were completely transparent.

We are unable to account with certainty for the irregularity of the curves shown. During our earlier tests we had some difficulty with readings obtained with the ionization gages when the pressures were low, in that they occasionally became negative. We found that when this occurred, the gage was generating oscillations of audible frequency so that a telephone inserted in the plate circuit emitted noises. We eliminated this by lowering the potential of the plate, but it appears possible that there might be higher frequency oscillations present at times, which would affect, somewhat, the pressure readings. We have not verified this. We thought temperature might have some influence, but tests on all the getters made after they had cleaned up most of the gas in the tube showed that the pressure was not affected by change of temperature from 0 to 90°. We are now testing other forms of ionization gages designed to operate without oscillating.

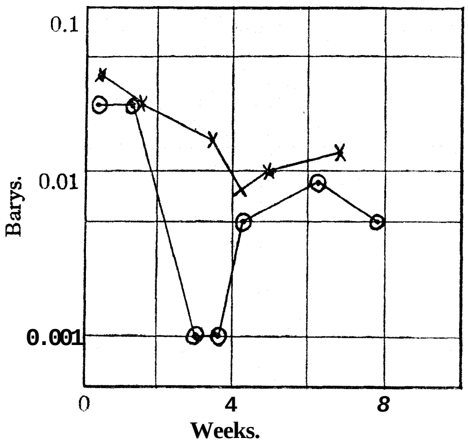

Fig. 5.—Phosphorus.

The above results point so conclusively to the fact that getters are good getters only when they are deposited quite gas-free that we are making experiments on vacuum fusion of them before they are used in vacuum tubes. The results will be reported later. That it is impossible to degas getters properly in a spiral and probably impossible without fusion, but that an effective getter can absorb considerable quantities of gas and eventually produce a fair vacuum, is shown by Fig. 6. This is the record of calcium held in a tungsten spiral which had been degassed for three

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[2] N. R. Campbell, *Phil. Mag.*, 41, 685 (1921); 43, 914 (1922).

hours by running the spiral at red heat. Before the getter was deposited, the tube was sealed off. The bulb containing the getter was then immersed in liquid air (point L.A. Fig. 6) and the getter deposited by heating the spiral. It had been thought that by this procedure the depositing metal might carry down and hold all gases evolved from the hot calcium rod, but the gas pressure rose to some tenths of a barye during deposition (see point B). After complete deposition, the bulb was removed from the liquid air.

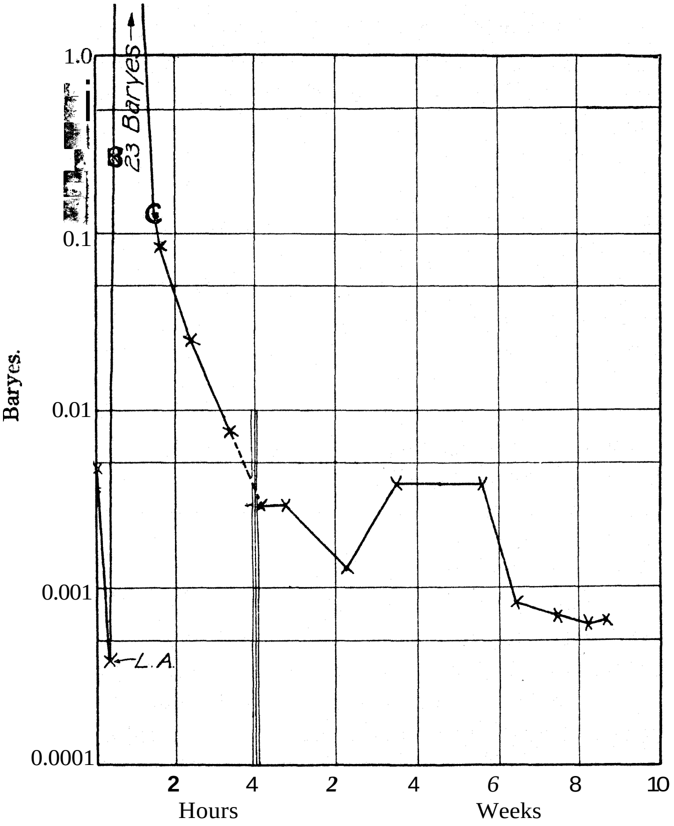

Fig. 6.—Calcium vaporized and deposited after seal-off.

The pressure promptly rose to twenty-three baryes. But the getter was active and absorbed this gas rapidly so that in half an hour the pressure had fallen to a small fraction of a barye (point C) and in the course of some weeks had gone below a thousandth of a bar, *i.* e., less than 10^{-6} mm.

It seems probable that some of these getters may have specific reactions with certain gases. The above experiments were all made with residual gas, that is, chiefly gas freed from the getter itself plus the possible traces escaping from the walls and metals of the getter bulb and gage. We have under way, however, a series of experiments in which getters are dosed with pure gases such as hydrogen, water vapor, etc. These will be reported later also.

The curves obtained from getters in vacuum suggest that the final clean-up of traces of gas in vacuum tubes is due to voltage discharge, *i. e.*, voltage clean-up. We are undertaking some experiments of this effect both without getters and in their presence.

Summary

Measurements made on a series of chemically active getters show that differences in the previous treatment of the getters to remove gas are of far greater importance than differences between the getters themselves in production of high vacuum. Poorly degassed getters absorb residual gas slowly and reach equilibrium at higher pressures than those attained by more gas-free material. These pressures do not depend on temperatures between 0 and 90°.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF UNION COLLEGE]

THE THERMAL DISSOCIATION OF CALCIUM HYDRIDE

BY CHARLES B. HURD AND KENNETH E. WALKER

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Introduction

The thermal dissociation of the hydrides of the alkali metals and of the alkaline earth metals has been the subject of considerable study. Various methods have been used, the general procedure being to heat the solid hydride to a definite temperature and measure the equilibrium pressure of the gaseous hydrogen.

In the earlier studies little or no attempt was made to shield the glass or quartz system from possible chemical action with the metal hydrides or their dissociation products. This action is serious at the high temperature at which calcium hydride undergoes appreciable dissociation. Recent investigators have attempted to shield the quartz tubing from chemical action. In the present paper, the writers describe an apparatus which is the result of experiments over a period of about four years. The apparatus is the only one which has been found to work satisfactorily with calcium hydride. It will, we believe, give satisfactory results in any of the higher temperature hydride investigations. Results are given here for the dissociation of calcium hydride. The dissociation of barium hydride is being studied and it is hoped that work on strontium hydride may be started soon

Historical

Calcium hydride is easily prepared by heating metallic calcium or certain alloys of calcium in hydrogen gas. The work of Guntz and Bassett,[1] of Moissan,[2] and of Brönsted,[3] is typical. Recently, Proskurnin and Kasarnowsky[4] have used the utmost care in preparing and handling the product. It is interesting to note, however, that the observations of the different investigators on the rate at which hydrogen is absorbed by the heated metallic calcium do not agree.

The results of the several studies on the thermal dissociation of calcium hydride appear to fall into two classes. The results of some investigators show a series of equilibrium pressures and temperatures which are reproducible and which fall upon a single curve. This curve is typical of a monovariant equilibrium consisting of a gas phase with one or more condensed phases. The results of Brönsted,[3] of Kraus and Hurd,[5] and of Remy-Cennetê,[6] show only one equilibrium curve.

Other investigators have found evidence that more than one equilibrium is possible, depending upon the relative proportions of calcium and hydrogen present. Moldenhauer and Roll-Hausen[7] believe that the dissociation takes place in two stages according to the equations

$$CaH_2 = CaH + {}^1/_2H_2$$
$$CaH = Ca + {}^1/_2H_2$$

Kassner and Stempel[8] have also found two equilibrium curves. The results of Ephraim and Michel,[9] and those of Hiittig and Brodkorb,[10] also show the apparent existence of more than one type of equilibrium, depending upon the relative amount of hydrogen which has been withdrawn from the original calcium hydride.

A source of error, common to the work which has been mentioned, is the possibility that calcium hydride or some solid product of the dissociation, may come into contact with the quartz container. Calcium hydride and quartz react at the elevated temperatures employed, setting free gaseous hydrogen. Hiittig and Brodkorb[10] found a steady increase in the pressure of hydrogen when the system was held at constant temperature. On the other hand, Kassner and Stempel[8] have shown by experiment that only a negligible loss of solid out of the equilibrium mixture occurred in their

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[1] Guntz and Bassett, *Compt. rend.*, 140, 863 (1905).

[2] Moissan, *Ann. chim. phys.*, 7, 18, 289 (1899).

[3] Bronsted, *Z. Elektrochem.*, 20, 81 (1914).

[4] Proskurnin and Kasarnowsky, *Z. anorg. allgem. Chem.*, 170, 301 (1928).

[5] Kraus and Hurd, THIS JOURNAL, 45, 2559 (1923).

[6] Remy-Cennetê, *Compt. rend.*, 189, 579 (1929).

[7] Moldenhauer and Roll-Hausen, *Z. anorg. Chem.*, 82, 130 (1913).

[8] Kassner and Stempel, *Z. anorg. allgem. Chem.*, 181, 83 (1929).

[9] Ephraim and Michel, *Helv Chim. Acta*, 4, 907 (1921)

[10] Huttig and Brodkorb, *Z. anorg. allgem. Chem.*, 153, 309 (1926)

experiments. In the work of Kraus and Hurd,[5] the calcium hydride was held in a vertical iron cylinder, with the lower end closed and the upper end open. The purpose of the iron cylinder was to protect the quartz tube. Some blackening of the quartz tube occurred, however, near the mouth of the iron cylinder.

Another possible source of error in these experiments is, obviously, that some of the solid products of decomposition may sublime to a cooler part of the quartz tube. Here they may reabsorb hydrogen, reducing the measured pressure and giving a false value for the equilibrium pressure at the temperature measured. The present study was made to eliminate these possible sources of error.

Apparatus

The logical improvement in the apparatus used for the determination of the dissociation pressure of calcium hydride would be to hold the calcium hydride inside the quartz tube in a closed container which would be permeable to hydrogen but not to calcium or calcium hydride. There are few such materials.

It was found that platinum or palladium could not be used, since small pieces of these metals alloyed with calcium. A long series of experiments was made, using closed cylinders of pure iron.[11]

This material was abandoned during 1929 when we found that consistent results could not be obtained. We note that Remy-Cennetté[6] has recently used the same method with one difference. He used an iron cylinder with a thin sheet of iron welded over one end.

We have found that nickel is the best material which we have tried. It is possible that cobalt might work successfully. The results with nickel over a period of a year have been so successful that we are prepared to recommend nickel.

The apparatus used is shown in Fig. 1 A clear quartz tube, A, 16-mm. in diameter and 102 cm. long was supported horizontally, in the electric furnace D. A chromel–alumel thermocouple B was so placed that its end touched the quartz tube even with the nickel cylinder C.

The nickel cylinder C was made of a 10 2 cm. length of pure nickel tubing. The wall thickness was 1.27 mm. and the outside diameter 9.6 mm. Two short tapered plugs of pure nickel were turned in a lathe. The short cylindrical tube and the plugs were carefully cleaned A plug was driven in one end of the short tube. Several pieces of freshly cleaned calcium were inserted in the cylinder and the other nickel plug inserted. These operations were carried out in a standard hydrogen bottle, the calcium having been cleaned in the bottle before being inserted in the cylinder. The calcium was a special pure calcium secured from the Research Laboratory of the General Electric Company. The plugs were pounded into the cylinder. Of six cylinders, made and filled in this way, two have leaked and four have been satisfactory at high temperatures.

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[11] Unpublished thesis. Douglas Small, Union College, 1927; unpublished thesis, Dudley C. Smith, Union College, 1928

The outside of the nickel cylinder was cleaned and the cylinder was pushed to the end of the quartz tube A connection was made by means of a glass tube F to the glass measuring system The tube F must be slid over the quartz tube A and the de Khotinsky joint E must be built up outside the glass tube F. If a glass tube should be inserted into the end of the quartz tube and a de Khotinsky joint built over the end of the quartz tube, it will always soften and suck in when the inner end of the quartz tube is at temperatures of 800° or over, since the clear quartz transmits radiation very well from its hot end to the cement at the cool end. An ordinary vacuum manometer G and a connection H to a vacuum pump complete the apparatus. The mercury manometer ***G*** was read by a high grade cathetometer, reading to 0.01 cm.

The chromel–alumel thermocouple B was calibrated at several points. The cold end was kept in a mixture of cracked ice and distilled water in a vacuum bottle.

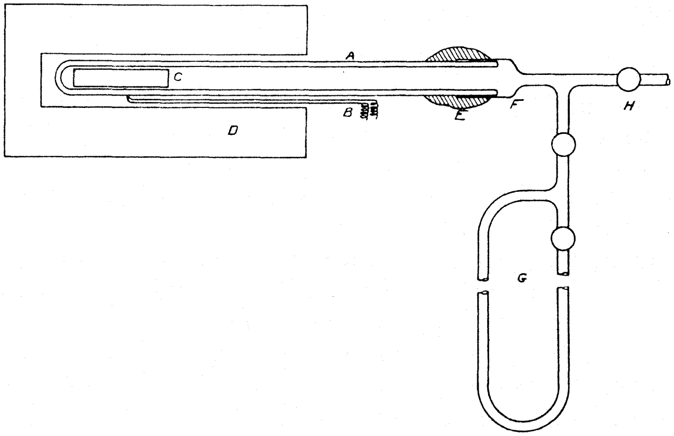


Fig. 1.—Apparatus employed in determining the dissociation pressures of calcium hydride.

Current through the electric furnace D was controlled, in spite of line voltage variations of as much as 10 volts by the use of UV-876 ballast tubes. One tube or two or three in parallel were used in series with the furnace on a 220 volt a. c. line. The single tube or the parallel two or three tube combinations gave constant currents of 1.7, **3.4** or 5.1 amps. A variable resistance shunted across the furnace allowed any fraction of the current to pass through the furnace. The necessary ammeters and voltmeters were included in the circuit.

A run was made as follows. **A** cylinder with a fresh charge of calcium, 1.0 to 1.4 g., was placed in tube A. The glass system was attached. The system was pumped out and the furnace raised to a temperature of 300°. The gases evolved were pumped out and the system tested for several days for leaks. The temperature was then slowly raised to 700° any gases evolved being pumped out. Enough specially purified hydrogen was then admitted to convert not over 90% of the calcium to hydride. After the calcium had had time enough to absorb 90 to 95% of the hydrogen (several days at this temperature), the gas remaining unabsorbed was quickly pumped out. All impurities which would not pass through the nickel were thus removed. The system was then held at a series of constant temperatures until a constant reading was obtained for the pressure of the hydrogen. Equilibrium pressures were approached from above and from below. To secure constancy of such pressures requires about a week at 800°. The securing of accurate results is, therefore, a very slow process.

A word of warning might not be out of place. The nickel cylinder works very well if not heated too high. At temperatures of 950–1000° the process of dissociation and diffusion takes place much more rapidly than at 800°, but the nickel cylinder undergoes a change, possibly forming an alloy with the calcium which then becomes nearly impermeable to hydrogen. No method was found of preventing this, and such cylinders were rendered useless.

Data

The results of three independent series of determinations are given in Table I. To obtain such data with the apparatus employed requires considerable time, several days being necessary to obtain a satisfactory equilibrium reading at the lower temperatures.

TABLE I

DISSOCIATION PRESSURES OF CALCIUM HYDRIDE AT DIFFERENT TEMPERATURES

T, °K	P, cm	$1/T \times 10^3$	$\log_{10} P$
Series 1 (Fig 2 circle)			
1090	3 93	0 917	0 594
1126	7.75	888	.889
1155	13 65	866	1.135
1177	20 25	850	1.306
1210	37 22	.826	1 571
Series 2 (Fig. 2 cross)			
1044	1.33	0.958	0.124
1065	2.04	.939	.310
991	0.42	1.009	−.377
1088	3.26	0.919	+.513
1109	5.21	.902	.717
1131	8.01	.884	.904
1082	2.84	,924	.453
Series 3 (Fig. 2 X)			
1011	0.45	0.989	−0.347
1041	1.13	.960	+ .053
1061	1.80	.942	.255
1091	3.53	.916	.548
1116	6.28	.896	.799

The results of these three runs are plotted on Fig. 2. The three sets of data agree reasonably well, giving a single curve. The greatest discrepancy occurs at the lowest temperature, where the pressures are lowest and are subject to the greatest error. In Fig. 3 we plot the results of several investigators in the field for comparison.

Discussion of Results

We are able to calculate the heat of reaction, ΔH, for the dissociation of calcium hydride from the relation

$$\frac{d \ln K_p}{d\ 1/T} = -\frac{\Delta H}{R}$$

where the symbols have their ordinary meaning and where $K_p = P_H$. We find from the slope of the curve, Fig. 2

$$\Delta H_{1100^\circ} = 51{,}100 \text{ calories}$$

If we use the equation

$$\Delta H = \Delta H_0 + 1.0\,T$$

we are able to estimate $\Delta H_0 = 50{,}000$ calories.

Values for the heat of reaction have been given by several investigators. Guntz and Bassett give 46,200 calories as the heat of formation of solid calcium hydride from its elements, calorimetrically determined, at ordinary temperatures. Bronsted gives a value of 45,100 while Kraus and Hurd with open cylinders found 48,400. Kassner and Stempel give 43,300 as the sum of the heats of reaction for their two stages. The data of Remy-Cenneté as shown by Fig. 3 would give about 50,000.

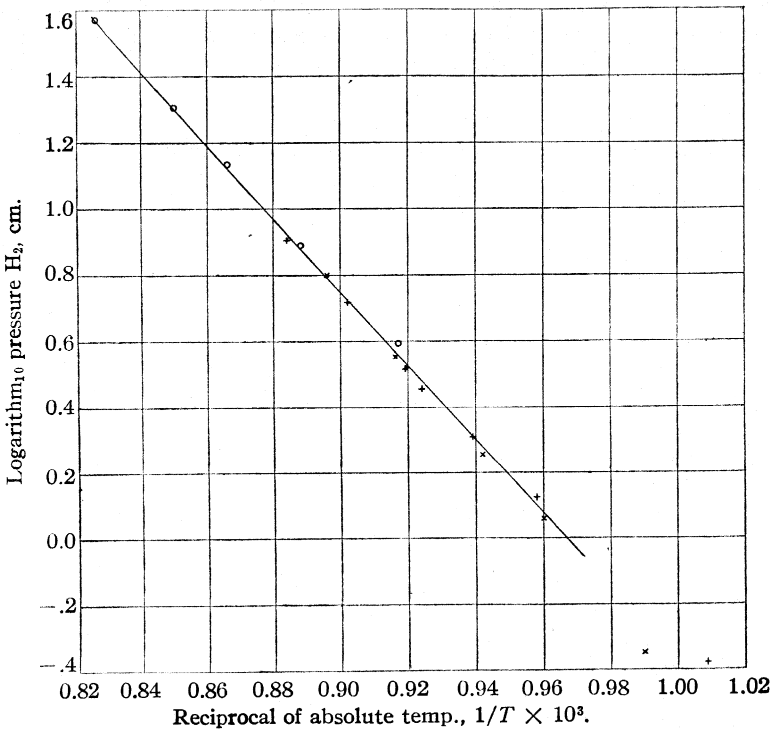
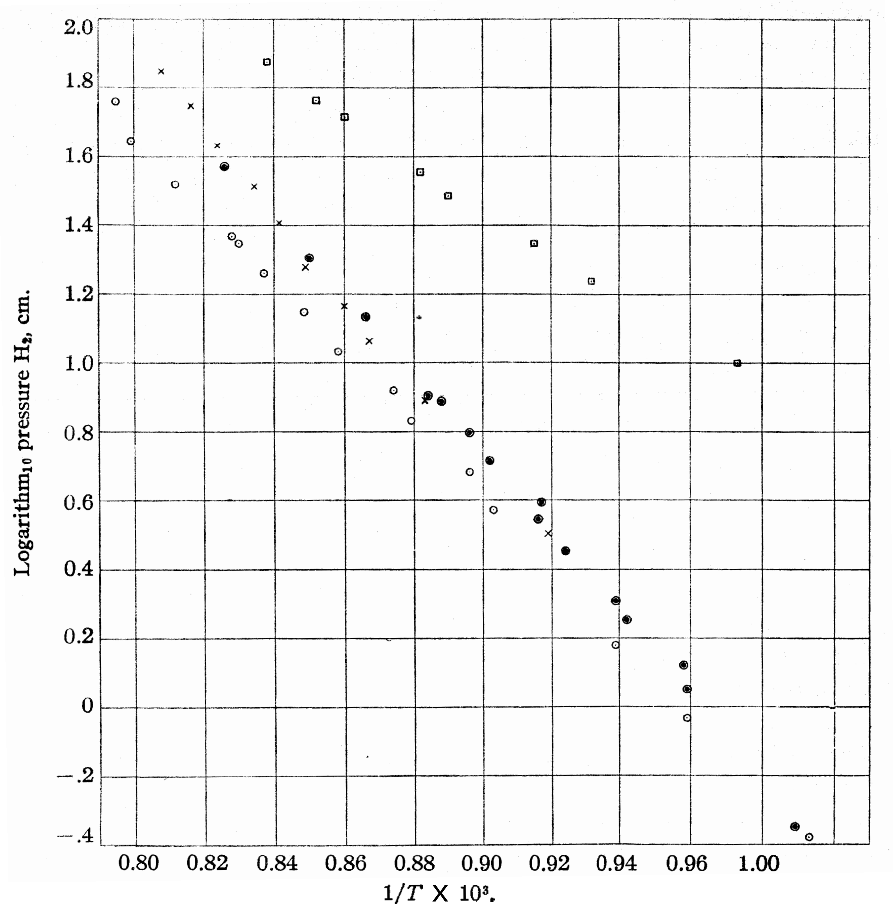


Fig. 2.

The value which we find for the heat of reaction, 51,100 calories, is seen to be considerably higher than former results, with the exception of the work of Remy-Cenneté. The agreement between our value and that of Remy-Cenneté is the more interesting, inasmuch as these two investigations utilize similar methods of confining the materials other than hydrogen which are present in the equilibrium mixtures.

The Mechanism of the Reaction

The opinions of various investigators in this field upon the course of the reaction for the dissociation of calcium hydride differ. All agree, apparently, that molecular hydrogen constitutes the gaseous product. The composition of the solid product or products is not definitely determined, as we have already mentioned in this paper. The results of Kassner and Stempel for what they believe to be the equilibrium



⊙, Kraus and Hurd; ◉, **Hurd and Walker**; ⊡, **Kassner and** Stempel; ×, Remy-Cenneté.

Fig, 3.—Comparison of results of several investigators on dissociation of calcium hydride.

$$CaH_2 \rightleftharpoons CaH + {}^1/_2H_2$$

are plotted in Fig. **3.**

We have been unable to detect any such equilibrium in our investigation.

We have admitted 90% of the hydrogen necessary to react with a weighed quantity of calcium to form CaH_2, and measured the equilibrium pressure at about 850°. Then at constant temperature we have withdrawn hydrogen by means of the pump in several steps until only about 20% of the hydrogen necessary to form CaH_2 was present. The equilibrium was allowed to establish itself after each withdrawal of hydrogen. The pressures measured agreed within the experimental error.

Experiments were also made where the equilibrium was approached by lowering the temperature from a higher temperature equilibrium. This, of course, caused an absorption of hydrogen and an increase of the combined hydrogen to calcium ratio. The same equilibrium pressure was found to establish itself as was found when the equilibrium was approached from a lower temperature, hydrogen having been removed.

We have not, in any case, added to the calcium more than 90% of the hydrogen, calculated as necessary to form CaH_2 with the weighed sample of calcium present in the nickel tube. Experiments are planned in which the calcium hydride will be formed by enclosing the calcium in the same type of closed nickel cylinder, placing this in a quartz tube, heating to 800° and passing a stream of pure hydrogen over it until the material has absorbed all the hydrogen possible. The tube will then be cooled to room temperature, still in hydrogen, removed, and placed in equilibrium apparatus shown in Fig. 1.

There is no apparent change in curvature of the log p against $1/T$ curve of Fig. 2 at the melting point of calcium, 810°, where $1/T \times 10^3 = 0.923$ Either these data are not sufficiently accurate to show this change of curvature or there is no calcium present.

Investigators who have worked with open containers have shown that calcium, if present, would have escaped from the containers at the higher temperatures, because of its appreciable vapor pressure. In the present investigation, only hydrogen could escape through the nickel cylinder, and we can, therefore, conclude nothing concerning the presence or absence of calcium.

Summary

An improved method for studying the thermal dissociation of calcium hydride has been described. The calcium hydride is contained in a closed nickel cylinder. This prevents action of the calcium or calcium hydride, on the quartz tube and removes a previous source of error in the determinations.

The method is recommended for any study where hydrogen is the only volatile constituent and where alloying does not occur with the nickel.

Three sets of data giving the equilibrium pressure of hydrogen as a function of temperature are given.

A graph, showing a comparison of results with those of other investigators, is given.

The value of the heat of reaction for the dissociation of calcium hydride is found to be 51,100 calories at 1100°K.

A brief discussion is given of the mechanism of the reaction.

SCHENBCTADY, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE OXIDATION OF FREE ALKYL GROUPS. PHOTO-OXIDATION OF GASEOUS METHYL IODIDE

BY JOHN REGINALD BATES AND ROBERT SPENCE

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One of the greatest difficulties facing most investigations connected with the oxidation of gaseous organic compounds such *as* the hydrocarbons, is the occurrence, at the relatively high temperatures which have previously been necessary, of numerous incomplete side reactions. These side reactions mask the fundamental processes, making complete elucidation of reaction mechanisms from kinetic studies almost impossible. However, it can be shown that the photochemical oxidation of alkyl halides, occurring at 0°, is essentially the oxidation of free alkyl groups and an investigation of the photo-oxidation of methyl iodide, the simplest member of the series, seemed to promise some information regarding the fundamental processes of hydrocarbon oxidation.

Previous workers studying the action of light on alkyl halides dealt with the liquids, and have, for the most part, come to conflicting conclusions. Donnan and Burke[1] and Stobbe and Schmidt[2] found that oxygen was necessary for decomposition of ethyl iodide as determined by the production of iodine. Job and Empschwiller[3] found that oxygen was not necessary for the decomposition of either ethyl or methyl iodides. In the former case they were able to obtain what was believed to be a photochemical "threshold" of reaction at 4100 Å., which was ascribed to the fact that the energy of this wave length coincided with the then accepted value for the C–I linkage. More recently, Iredale[4] has determined the quantum yield of ethyl iodide decomposition in the absence of oxygen. This he finds to be unity, as measured by the iodine liberated, and therefore concludes that the primary process is the separation of an ethyl group and an iodine atom. Work on gaseous methyl iodide has been confined to its absorption spectrum, first studied by Herzberg and Scheibe.[5] The absorption is con-

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[1] *Donnan and* **Burke,** *J. Chem. Soc., 85, 574* **(1904).**

[2] **Stobbe** *and* **Schmidt,** *Z. Wiss. Phot.,* 20, *57* **(1920).**

[3] **Job** *and* **Empschwiller,** *Compt. rend.,* **179, 52 (1924).**

[4] Iredale, **J.** *Phys. Chem.,* **33, 290 (1929).**

[5] **Herzberg** *and* **Scheibe,** *Trans. Faraday Soc.,* 25, **716 (1928);** Z. *physik. Chem.,* **[B] 7, 390 (1930)**

tinuous above 2000 Å., terminating in a short wave limit at 3000 Å. According to the band spectra theories of Franck and his co-workers[6] this indicates decomposition as the primary act of light absorption. Since the band in question is characteristic of the C–I linkage it may be safely assumed that the electronic excitation concerns **an** electron which goes to make this bond, and therefore that the decomposition is into a methyl group and an iodine atom. Mills and Iredale[7] have also studied the band and show that its long wave limit corresponds to the latest value for the C–I linkage, and come to the same conclusion. Absorption spectra taken by us before the publications of Herzberg and Scheibe are in agreement with these statements and indeed led to the present investigation.

Experimental

The reaction was followed by observing changes in pressure at constant volume as recorded on a mercury manometer. The cylindrical reaction vessel was of clear fused quartz, 50 mm. in diameter, 130 mm. long and having a volume of 240 cc., with two plane, circular, polished windows fused onto either end. This was fitted into a metal tank in such a way that one window was flush with the outer side of the tank, the latter being filled with ice and water to maintain a temperature of 0°. In this way the window was free from any condensation of iodine on the inside and the disturbing effects on the light intensity of ice or other foreign matter was eliminated. This would not have been possible had the vessel been totally immersed in ice water. Oxygen was taken directly from a tank, dried over calcium chloride and stored in a large bulb, from which samples could be admitted to the reaction vessel. Methyl iodide (Merck and Company) was distilled once, in *vacuo,* and kept under its own pressure, as a perfectly colorless liquid. The source of illumination was a mercury vapor lamp of the Kromayer type, so arranged that it could always be returned to exactly the same position after tilting to start the arc.

Experimental Results

The Action of Light on Methyl Iodide in the Absence of Oxygen.—Pure methyl iodide vapor undergoes a very slow decrease in pressure when illuminated for long periods and only small amounts of iodine are freed. For example, in Expt. 8, Table II, 80 mm. of methyl iodide was illuminated for six hours with a light intensity which, in the subsequent experiments with oxygen, gave a pressure decrease of 6 mm. per minute. The decrease in pressure after six hours was only 5.5 mm., iodine liberated being equivalent to 1.4 mm., and residual gas pressure when frozen out by carbon dioxide snow only about 10 mm. A series of experiments in which the change in pressure and the amount of permanent gas formed were

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[6] Franck and co-workers, *Trans. Faraday Soc.,* 21, 536 (1925).

[7] Mills and Iredale, *Nature,* Oct. 1930, p. 604.

measured simultaneously showed an approximate parallelism between the decrease in total pressure and the increase in residual gas (Table I).

Table I

Decomposition of Methyl Iodide

Time of illumination, minutes	$-\Delta p$, mm.	P residual gas. mm.
50	0.7	0.6[a]
50	.6	.6
70	.7	.7

[a] 20 mm. of hydrogen present

Budde Effect.—Immediately upon illumination, the pressure of the methyl iodide increased in a manner similar to the Budde effect in chlorine.[8] The increase is proportional to the total pressure up to about 100 mm., but appears to fall off somewhat above this pressure. Thus, we were able to obtain increases up to 2 mm. at 80–100 mm. of methyl iodide, while only 1.2 mm. was observed at 110–120 mm. This effect was also obtained in the presence of oxygen, especially when the latter was in high concentration, as can be seen from the curve in Fig. 1.

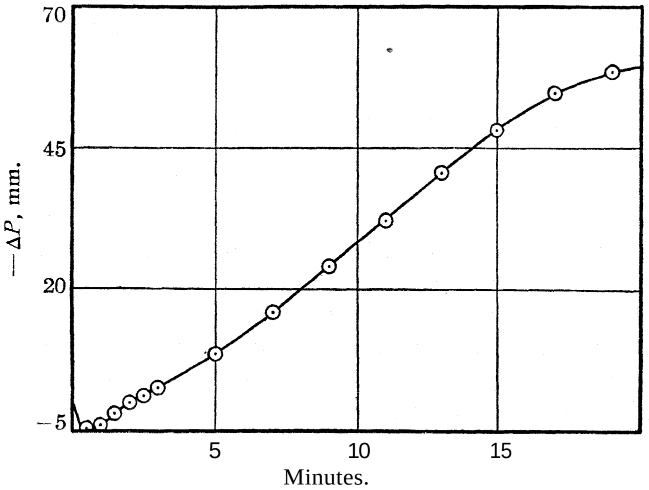

Fig. 1.—Typical experimental curve, ΔP plotted against time.

The Action of Light on Methyl Iodide in the Presence of Oxygen.—With oxygen present, the reaction velocity increases over a hundred-fold, thus becoming sufficiently rapid to permit of kinetic measurements. Iodine is liberated and upon reaching its vapor pressure of 0.03 mm. at 0°, condenses on the walls. This pressure of iodine does not absorb sufficient light to have any further photochemical influence upon the reaction. There is a variation in the total pressure decrease accompanying the re-

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[8] Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., 1928, p. 138.

action from a value slightly lower than the initial pressure, at low methyl iodide pressures, to about 20% greater at high methyl iodide pressures.[9] That iodine does not enter into the constitution of the final oxidation products was demonstrated by carrying a number of runs to completion and titrating the free iodine with $N/10$ thiosulfate. These values, together with the initial pressures of methyl iodide and oxygen, the total pressure decrease, and the value of the iodine titrations expressed in mm. of methyl iodide in the reaction vessel (1 mm. = 1.41×10^{-5} mole), are given in the first five columns of Table II. The values in the last column were calculated from the equation on page 1694.

TABLE II

IODINE TITRATIONS

P_{CH_3I}	P_{O_2}	$N/10$ thiosulfate, cc.	$-\Delta P$, obs.	$-\Delta CH_3I$	$-\Delta P$, calcd.
37.2	263.0	5 24	39.6	37.2	41.9
59.8	308.2	7.85	66 5	55.6	65.2
98.2	110.8	14.05	123.2	102.8	118.1
14.7	111.6	2.07	13.2	14.7	14.7
108.5	17.7	5 15	38.0	36.5	39.6
101.7	106.1	13 70	125.6	98 5	122.7
101.0	100.0	13.95	126.7	99.0	121.1
80.1	0.0	0.18	5.5	1 4	...
104.0	98.0	4.25	34.2	30.2	33.1[a]
102.3	20.0	2.45	16.4	17.4	16.6[a]
51.0	52.6	0.69	4.8	4.9	4.9[a]

[a] *AP* calcd. obtained from $-\Delta CH_3I$, since these runs were not carried to completion

The general course of the reaction is shown by the $-\Delta P/T$ curve (Fig. 1). After a small immediate expansion, the reaction proceeds rapidly for a few seconds, then slows up for several minutes before proceeding at an almost uniform rate, finally slowing down to zero when the reaction is complete. For high initial pressures of methyl iodide and oxygen, the period of uniform pressure decrease is of long duration but at low initial concentrations it practically disappears.

Identification and Analysis of Reaction Products. (a) **Noncondensable Gaseous Products.**—105.0 mm. of methyl iodide and **38** mm. of oxygen were illuminated until reaction was complete and the gaseous products slowly pumped off through a liquid air trap. No difference in pressure was observed when the liquid air was replaced by carbon dioxide–ether mixture and, when the trap was allowed to return to room temperature, the condensate exerted a pressure less by only 4 mm. than its pressure before evacuating. Hence, the hydrogen, carbon monoxide, ethane or methane formed in the reaction amounted to less than 4 mm.

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[9] The highest pressure of methyl iodide studied was 110 mm., since its vapor pressure is 141 mm. at 0° and condensation of liquid in the capillary leads to the reaction vessel introduced errors between these pressures.

(b) Condensable Gaseous Products.—About 1 cc. of product condensable in liquid air was collected from about fifteen experiments in which 100 mm. of methyl iodide and 60 mm. of oxygen were allowed to react to completion. This liquid was carefully distilled, giving first a fraction boiling at 38–40°, slightly colored by iodine, then a colorless mobile liquid came over between 40 and 43°, identical in appearance, solubility and smell with a sample of pure methylal.[10] The vapor density, as measured by the Victor Meyer method, using 0.0185 g. of liquid, gave a value 52.5 for the molecular weight. Although the correct molecular weight of methylal is 76, pure methylal is partially hydrolyzed at 100° and 0.060 g. has an apparent molecular weight of 61.1. The condensate was soluble in water and did not smell of formaldehyde but gave the characteristic p-nitrophenylhydrazone of formaldehyde upon warming with an acid solution of p-nitrophenylhydrazine. The aqueous extract of the liquid from a flowing system, when treated with dilute resorcinol solution and poured over concentrated sulfuric acid, gave the reddish layer, tinged with purple and covered with a white, cloudy layer, characteristic of formaldehyde and methylal. Water was shown to be a constituent of the condensate by the fact that it turned anhydrous copper sulfate blue. Therefore, it was concluded that the condensable gaseous products of the reaction consist of methylal and water.

(c) Solid Products.—After having removed the gaseous and liquid products, the reaction vessel was washed out with ether to remove iodine. A white solid remained on the walls which was insoluble in water, alcohol or ether, but which reacted vigorously with concentrated nitric acid. Upon warming, the deposit evaporated, producing a powerful odor of formaldehyde.

(d) Determination of **Methylal,** Iodine **and Paraformaldehyde.**—Methylal was determined by collecting in a liquid air trap and titrating with thiosulfate after treating with a known excess of iodine. The iodine and paraformaldehyde formed were weighed in the vessel, the iodine determined by titration and paraformaldehyde obtained by difference.

TABLE III

ANALYSIS OF THE REACTION PRODUCTS

P_{CH_3I}, 101.0 mm.; P_{O_2}, 100.0 mm.; vol., 240 cc.; temp., 0°; time, 200-minutes

	Gram molecules 10^4	
Product	At beginning	At end
CH_3I	14.24	..
I_2	...	14.02
$(CH_3O)_2CH_2$	...	3.29
$(HCHO)_n$	...	3.47

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[10] Boiling point of pure methylal 42–43°, Timmermans and Martin, *J. chim. phys.*, 25, 411 (1928).

Therefore, the total process may be represented as

$$4CH_3I + 2O_2 \longrightarrow (HCHO)_n + (CH_3O)_2CH_2 + H_2O + 2I_2$$

Polymerization of Formaldehyde and Synthesis of Methylal.—Formaldehyde was observed to polymerize both thermally and photochemically when introduced into the reaction vessel at 0°. The gas was produced by warming paraformaldehyde contained in a side tube. Figure 2 shows the general course of the reaction with formaldehyde alone, in the dark and in the light, and in the presence of methyl iodide or oxygen. A quantitative study of the polymerization was precluded owing to the varying rates at which the window became covered with polymer and to other undetermined factors such as the presence of small amounts of water vapor.[11] Thus, when the reaction vessel had been heated and evacuated for a long time, the velocity of polymerization of formaldehyde was lower, but when a small amount of methyl alcohol was introduced and allowed to react with formation of methylal and water, both the light and the dark polymerizations were greatly accelerated. According to the work of Bowen and Tietz,[12] acetaldehyde, in the presence of oxygen, partly reacts and partly polymerizes when illuminated with ultraviolet light, Formaldehyde should show similar properties, for Henri and Schou[13] find that below 2700 Å., predissociation bands and continuous absorption occur, while

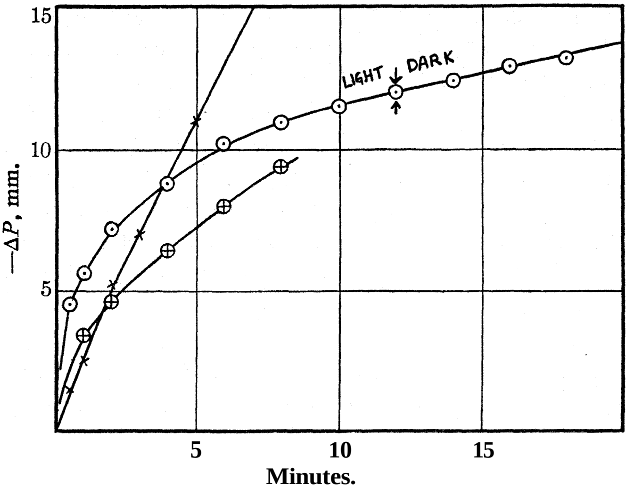

Fig. 2.—$\Delta P/T$ curves for polymerization of formaldehyde alone (dotted circles), for formaldehyde and oxygen (crosses) and for formaldehyde and methyl iodide (crossed circles).

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[11] *Cf.* Trautz and Ufer, *J. prakt. Chem.*, *113*, 105 (1926); Tropsch and Roelen, *Abhandl. Kennt. Kohle*, *7*, *175* (1925).

[12] Bowen and Tietz, *J. Chem. Soc.*, 234 (1930).

[13] Henri and Schou, *Z. Physik*, 49, *778* (1928).

above 2700, the bands show discontinuous, fine structure. Actually, the rate of polymerization is so great compared with the rate of oxidation that only polymerization is observed. However, Bredig and Goldberger[14] observed photochemical decomposition at 80°. Thus, 32.0 mm. (0.0135 g.) of formaldehyde and 104.0 mm. of oxygen gave 104.9 mm. of residual gas and 0.0150 g. of paraformaldehyde. The residual gas was slowly pumped off through a liquid-air trap but no condensate formed.

Formaldehyde and methyl alcohol condense together in the dark at 0°, giving methylal and water as the principal products. The reaction is so extremely rapid that only an approximate idea of the amounts of gas introduced could be obtained. The form of the $-\Delta p/T$ reaction curve appears in Fig. 3.

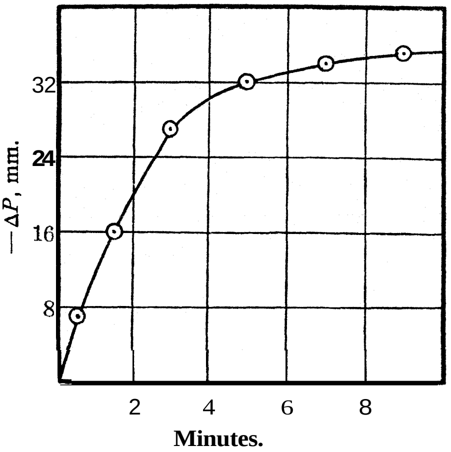

Fig. 3.—$\Delta P/T$ curve for condensation of formaldehyde and methyl alcohol.

Kinetic Studies

Variation of Rate of Oxidation of Methyl Iodide with Light Intensity.—The influence of varying light intensities was studied by measuring the rate after the induction period was over and a steady speed obtained. By interposing blackened copper gauze screens which had previously been calibrated on a visual photometer, it was possible to reduce the light intensity to known fractions. Table IV contains the results obtained in this manner and which point to a linear proportionality of reaction rate and light intensity to within 10%.

Table IV

Dependence on Light Intensity

% light intensity	$-\Delta P$ in mm. 2 min	5 min	7 min.	10 min.	$-dx/dt$	$-dx/dt/$ % intensity
100	0.6	2.1	3.3	5.1	5.60	5.60
50	0.7	1.4	1.9	2.6	2.50	5.00
35	0.5	0.9	1.4	2.2	1.83	6.23
29	0.3	0.8	1.2	2.1	1.70	5.86
100	1.0	2.9	4.1	5.3	5.60	5.60

Quantum Yield.—An attempt was made to determine an approximate quantum yield of the oxidation process. A normal solution of monochloroacetic acid, which Rudberg[15] has shown to have a quantum yield of unity in the region around 2500 Å., was placed in a cell of 1 cm. thickness,

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[14] Bredig and Goldberger, *Z. physik. Chem.*, **110**, 521 (1924).

[15] Rudberg, *Z. Physik*, **24**, 247 (1924).

in front of the reaction vessel. The relative rates of reaction were obtained for the cell filled with this solution and with distilled water. After having done this, the reaction vessel itself was filled with chloroacetic acid of such a concentration as to absorb the same fraction of light as the 1 cm. cell, illuminated for a given time with the arc running as before, and the resulting hydrochloric acid titrated with standardized silver nitrate and ammonium thiocyanate. Using these observations, the quantum yield was calculated as follows

$$\frac{\text{Molecules}}{h\nu} = \frac{-\frac{\mathrm{d}p}{\mathrm{d}t} \times 1.41 \times 10^{-5} \times 6}{\frac{\text{Moles HCl}}{\text{hr.}} \times \frac{V_{\mathrm{H_2O}}}{V_{\mathrm{ClCH_2COOH}}}} - \frac{4.72 \times 1.41 \times 6 \times 10^{-5}}{1.0 \times 10^{-4} \times \frac{4.65}{2.70}} \equiv 2.3$$

where $-\mathrm{d}p/\mathrm{d}t$ is the maximum rate of methyl iodide consumption in mm./10 minutes obtained from Tables V and VI, 1.41×10^{-5} is the number of moles/mm. in the reaction vessel, $V_{\mathrm{H_2O}}$ and $V_{\mathrm{ClCH_2COOH}}$ rates with the small cell in front of the reaction vessel, filled with water and chloroacetic acid, respectively.

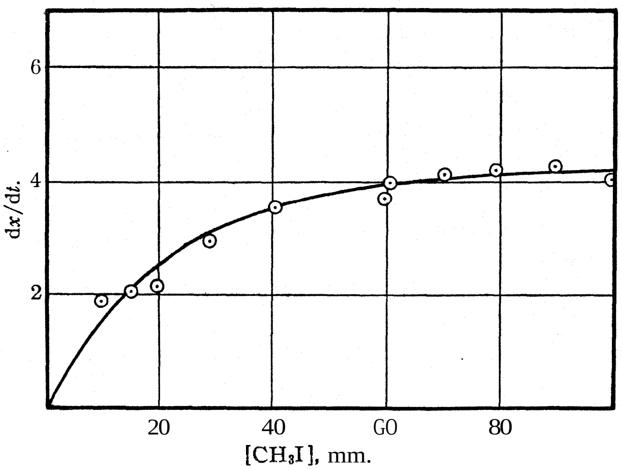

Fig. 4.—Variation of reaction rate with methyl iodide concentration, at constant oxygen concentration (100 mm.).

A value of 2 molecules/$h\nu$ for the oxidation process would give, according to the relative rates of the oxidation and decomposition of methyl iodide, a value of 0.02 for the quantum yield of the latter.

Variation with Methyl Iodide and Oxygen Concentrations.—In all the kinetic measurements, every effort was made to maintain uniform light intensity for each series of experiments, and constant conditions throughout the whole series. The uniformity of the light intensity during a series of experiments was checked by repeating one of the earlier experiments at the end, and if no change in rate occurred, then the light intensity was assumed to have remained constant. When an appreciable fall in intensity was detected, that series was discarded. Manometer readings were taken every minute for the first five minutes, then every five minutes and the results of each experiment plotted as $-\Delta P$ against time. The slope of the portion of these curves after the induction period was measured and expressed as mm. change/ten minutes. Table V contains the results obtained for varying concentrations of methyl iodide and constant oxygen concentration, while the relation between rate and methyl iodide concentration is illustrated graphically in Fig. 4. Taking the light intensity of this series as standard, the intensity of each subsequent series was compared with the standard intensity at 100 mm. of oxygen. Results for varying oxygen concentrations and constant methyl iodide concentrations appear in Table VI and Fig. 5.

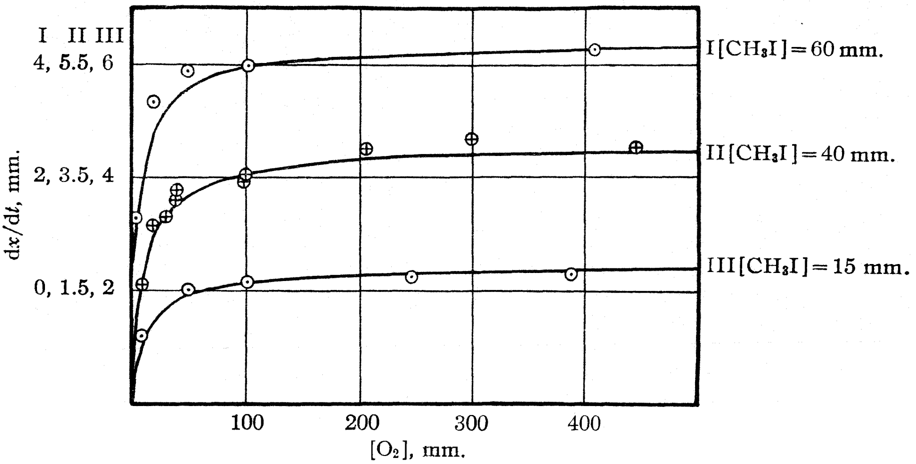

Fig. 5.—Variation of reaction rate with oxygen concentration at constant methyl iodide concentration.

TABLE V

DEPENDENCE OF RATE ON METHYL IODIDE CONCENTRATION

No.	CH_3I, mm.	O_2, mm.	$-\Delta P$ 6 min.	10 min.	20 min.	30 min.	dp/dt	I/I_0	dx/dt	K
D1	9.9	100.7	0.9	1.8	3.6	5.0	1.88	1.00	1.88	5.68
D4	19.8	102.7	.7	1.9	3.9	6.1	2.15	1.00	2.15	3.98
D5	29.1	100.2	.9	2.1	4.8	7.3	2.95	1.00	2.95	4.44
D2	59.7	100.2	1.0	2.8	6.1	9.9	3.70	1.00	3.70	4.42
D6	70.1	101.0	1.0	2.7	7.1	11.0	4.13	1.00	4.13	4.81
D3	79.2	101.6	1.0	2.5	6.3	10.9	4.20	1.00	4.20	4.82
D7	89.6	100.4	1.0	2.5	6.8	11.1	4.25	1.00	4.25	4.83
D8	99.5	107.4	1.5	3.8	7.6	11.6	4.03	1.00	4.03	4.53

The figures under dx/dt are obtained by dividing the values under dp/dt by the ratio of the light intensities which appear under I/I_0.

TABLE VI

DEPENDENCE OF RATE ON OXYGEN CONCENTRATION

No.	CH_3I, mm.	O_2, mm.	$-\Delta P$				dp/dt	I/I_0	dx/dt	K
			5 min.	10 min.	20 min.	30 min.				
J4	15.0	10.1	0.6	1.4	3.2	5.1	1.90	1.52	1.25	5.46
J6	15.6	11.2	0.6	1.4	3.2	5.0	1.82	1.52	1.20	4.85
J1	15.5	50.7	1.4	2.6	4.6	6.4	2.30	1.52	1.51	3.63
J8	15.2	101.2	0.5	2.7	5.3	8.6	3.25	1.52	2.14	4.73
J5	15.1	245.9	− .8	0.8	4.3	7.5	3.40	1.52	2.24	4.62
J3	15.7	388.1	− .4	1.3	4.1	8.2	3.48	1.52	2.30	4.56
C6	40.1	10.4	.0	0.5	1.5	2.6	1.60	1.00	1.60	4.11
C4	40.0	19.6	.5	1.6	4.4	6.8	2.65	1.00	2.65	5.07
C5	41.8	31.3	.1	1.3	4.0	6.8	2.80	1.00	2.80	4.53
C9	39.2	39.3	.9	2.3	4.9	8.1	3.27	1.00	3.27	5.05
C2	40.1	39.4	.4	1.7	4.7	7.8	3.10	1.00	3.10	4.79
C1	39.5	41.3	.3	1.5	4.8	7.7	3.27	1.00	3.27	4.99
C3	38.8	98.7	.0	1.0	4.0	7.5	3.42	1.00	3.42	4.58
C11	40.7	100.2	.7	2.4	5.6	9.1	3.54	1.00	3.54	4.68
C10	40.0	204.9	1.2	2.6	5.9	10.7	4.00	1.00	4.00	4.99
C7	39.4	299.3	0.8	2.3	5.8	9.9	4.18	1.00	4.18	5.02
C12	40.8	446.8	.9	2.7	6.6	10.7	4.05	1.00	4.05	4.89
C8	39.3	614.2	.1	2.0	5.9	10.0	4.00	1.00	4.00	4.80
13	61.6	5.3	0.5	1.8	4.0	6.0	2.30	1.78	1.29	4.53
12	61.6	21.0	1.7	3.8	10.5	16.2	5.95	1.78	3.33	5.59
14	60.5	50.3	1.6	4.2	10.5	17.3	6.95	1.78	3.89	5.14
I1	60.6	102.5	2.2	5.6	12.7	20.5	7.10	1.78	3.98	4.73
I6	60.5	103.0	1.3	3.8	10.1	17.5	7.00	1.78	3.92	4.66
I5	59.7	409.1	−0.7	2.9	10.8	18.1	7.60	1.78	4.26	4.67

Theoretical Discussion

Decomposition of Methyl Iodide.--Since the absorption spectrum of methyl iodide is continuous, we may assume that the primary process of light absorption is

$$CH_3I + h\nu \longrightarrow CH_3 + I' \qquad \text{(a)}$$

The rate of this reaction will be proportional to the number of quanta absorbed in unit time. From the absorption laws, then

$$-\frac{d[CH_3I]}{dt} = I_1(1 - e^{-[CH_3I]\alpha_1 d}) + I_2(1 - e^{-[CH_3I]\alpha_2 d}) + \dots$$

where I_1, I_2, etc., are the intensities of the various lines of the mercury arc, α_1, α_2, etc., are the absorption coefficients of methyl iodide for these lines, both expressed in appropriate units, and d is a constant, being the length of the vessel. Within the accuracy of our experiments, we are justified in taking as an approximation

$$-\frac{d[CH_3I]}{dt} = I(1 - e^{-[CH_3I]\alpha})$$

where I and a are over-all wave lengths, d being included in a, and $[CH_3I]$ is expressed in mm. of mercury.

In the absence of oxygen, the following reactions may take place

$$CH_3 + CH_3 + M \longrightarrow C_2H_6 + M' \qquad (b)$$
$$CH_3 + I + M \longrightarrow CH_3I + M' \qquad (c)$$
$$I + I + M \longrightarrow I_2 + M' \qquad (d)$$

The above processes involve collision either with a third molecule or with the wall (M). It must, however, be noted that any iodine atom colliding with the wall will probably be adsorbed or "cleaned up" as, for instance, is the case with hydrogen atoms, there to combine with other iodine atoms already absorbed. Bonhoeffer and Farkas[16] have found this to be the case in the photochemical decomposition of hydrogen iodide at low pressures. As soon as iodine molecules have been formed, the following two body process may occur

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (e)$$

and the bimolecular reactions

$$CH_3 + I \longrightarrow CH_2 + HI^{17} \qquad (f)$$
$$CH_3 + CH_3I \longrightarrow C_2H_6 + I \qquad (g)$$
$$CH_3 + CH_3 \longrightarrow CH_4 + CH_2 \qquad (h)$$

are also possible. In addition, the presence of iodine on the walls will effectively reduce the probability of occurrence of the wall reaction (b) which can then only take place as a three-body process in the gas phase, for the probability of two methyl groups recombining on a surface of iodine will be much less than the probability of their combination with iodine itself. On the other hand, the reactions

$$I + CH_3I \longrightarrow CH_3 + I_2$$
$$I + CH_3I \longrightarrow CH_2I + HI$$
$$I + CH_3I \longrightarrow CH_2I_2 + H$$

are thermally impossible (H–I = 69 Cal.; C–H = 120 Cal.; I–I = 35 Cal.; C–I = 68 cal.).[17] The very low rate of formation of permanent gas and of free iodine when pure methyl iodide is illuminated indicates that the processes (b) and (g) must be of relatively infrequent occurrence. Therefore, methyl groups will, for the most part, reform methyl iodide by reason of reactions (c) and (e) and the remainder will form ethane according to (b) and (g) with (f) and (h) occurring as a subsidiary reaction. Also, the probability of (g) occurring must be extremely small; otherwise, owing to the relatively high concentration of methyl iodide as compared with iodine, there would be a rapid formation of ethane and consequently a high rate of pressure decrease.

From one point of view, methyl may be regarded as a pseudo halogen and reaction (g) could, therefore, be considered as an elementary replacement of I by CH_3. However, the fact that every "Elementar prozess" does not

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[16] Bonhoeffer and Farkas, *Z. physik. Chem.*, 132, 235 (1928)

[17] The second hydrogen atom stripped from a carbon atom has a heat of linkage of only 30 k. cal., Mecke, *Z. Elektrochem.*, 36, 595 (1930).

occur on every collision, even when energetically possible, has become recognized during the past year. Kistiakowsky[18] has shown, for example, that oxygen atoms do not react with hydrogen molecules. The subject has been summarized by Franck and Rabinowitsch.[19]

In a paper which has just appeared, Hartel and Polanyi[20] have described a series of reactions of this type which, although exothermic, have an activation energy, and, therefore, do not go on every collision. Among those considered by them are the reaction of sodium atoms with alkyl halides, and methyl groups with hydrogen molecules. They find that the activation necessary for the exothermic reactions of sodium with methyl halides varies from 0 with methyl iodide to >25 Cal. with methyl fluoride, showing that it is a specific property of each reaction. In the case of methyl plus a hydrogen molecule, they give an activation energy of 8 Cal. In some experiments with methyl iodide and hydrogen in light, we found no effect on the rate of decomposition as measured by permanent gas formed, which would have been the case had the reaction

$$CH_3 + H_2 \longrightarrow CH_4 + H$$

been a probable one. An activation energy of 8 Cal. is equivalent to 10^6 collisions per reaction at 0°.

Methyl Iodide and Oxygen.—The photochemical oxidation of methyl iodide proceeds sufficiently rapidly to allow determinations of the rate of removal of methyl iodide to be made, and of the influence of such factors as light intensity, concentration of reactants, etc., upon this rate. Results obtained from a series of such measurements are set forth in the experimental part above. It is evident from Figs. 4 and 5, that the variation in the reaction rate follows fixed rules, which must have their origin in those fundamental chemical processes whose aggregate effect makes up the measured reaction. If, then, we can construct a mechanism of fundamental reactions, based on sound theoretical considerations, which will take account of all the observed phenomena and whose kinetic equation affords a complete description of the dependence of the reaction rate upon its physical parameters, then we can assume that mechanism to represent the true state of affairs, at least to the extent of our present knowledge.

For all practical purposes, the mechanism need only be concerned with reactions which make an appreciable contribution to the total rate of reaction. Now, all those reactions which we considered in the photochemical decomposition of methyl iodide, may be taken as occurring in the oxidation process also, but fortunately the greater part of them can be omitted from our kinetic considerations. Thus all reactions involving the formation of methane or other permanent gases (reactions b, f, g and h)

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[18] Kistiakowsky, THIS JOURNAL, 52, 1868 (1930)

[19] Franck and Rabinowitsch, *Z. Elektrochem.*, 36, 794 (1930).

[20] Hartel and Polanyi, *Z. physik. Chem*, [B] **11**, 97 (1930).

can be neglected because experiment shows them to be over a hundred times slower than the oxidation process. Reaction (c) has been shown to be extremely improbable as a wall reaction and its extremely infrequent occurrence in the gas phase does not warrant its inclusion in our kinetic treatment, leaving only three of these processes which can materially affect the rate of oxidation.

$$\begin{aligned} CH_3I + h\nu &\longrightarrow CH_3 + I \\ CH_3 + I_2 &\longrightarrow CH_3I + I \\ I + M(I) &\longrightarrow I_2 \end{aligned}$$

In the presence of oxygen, methyl may react in the following way

$$CH_3 + O_2 \longrightarrow CH_2O + OH$$

Now, the possible three-body reaction of O_2 with CH_3 or I, can be neglected as being extremely infrequent, while reactions between OH and I_2 or O_2 are thermally improbable, leaving

$$OH + CH_3I \longrightarrow CH_3OH + I$$

to account for the removal of hydroxyl groups.

Since the rate of formation of iodine molecules from the atoms does not affect the rate of removal of methyl iodide, and, assuming that the formaldehyde and methyl alcohol formed will not play any part in these reactions, we have only to consider the following reactions to determine the rate of removal of methyl iodide

$$\begin{aligned} CH_3I + h\nu &\longrightarrow CH_3 + I & k_1 \\ CH_3 + I_2 &\longrightarrow CH_3I + I & k_2 \\ CH_3 + O_2 &\longrightarrow CH_2O + OH & k_3 \\ CH_3I + OH &\longrightarrow CH_3OH + I & k_4 \end{aligned}$$

Therefore

$$-\frac{d[CH_3I]}{dt} = k_1I_0\,(1 - e^{-\alpha[CH_3I]}) - [CH_3][I_2]k_2 + [CH_3I][OH]k_4$$

Assuming stationary concentrations of OH and CH_3, we can equate their respective rates of formation and removal as follows

$$\begin{aligned} OH\colon\quad [CH_3][O_2]k_3 &= [CH_3I][OH]k_4 & (1) \\ CH_3\colon\quad k_1A &= [CH_3][I_2]k_2 + [CH_3][O_2]k_3 & (2) \\ \text{where } A &= I_0\,(1 - e^{-\alpha[CH_3I]}) \end{aligned}$$

Therefore

$$[CH_3] = \frac{[CH_3I][OH]k_4}{[O_2]k_3}$$

whence

$$\frac{[CH_3I][OH]k_4}{[O_2]k_3} = \frac{A\,k_1}{[I_2]k_2 + [O_2]k_3}$$

But, from Equations 1 and 2

$$k_1A - [CH_3][I_2]k_2 = [CH_3I][OH]k_4$$

and consequently

$$\begin{aligned} -\frac{d[CH_3I]}{dt} &= 2[CH_3I][OH]k_4 \\ &= \frac{2\,A\,k_1[O_2]k_3}{[I_2]k_2 + [O_2]k_3} \end{aligned}$$

Now, it is evident from Table II that for the initial part of the reaction, that is, the portion considered in the kinetic measurements, $-\mathrm{d}[CH_3I]/\mathrm{d}t$ is approximately equal to $-\mathrm{d}P/\mathrm{d}t$ and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{2I_0\,(1 - e^{-\alpha[CH_3I]})\,[O_2]}{\frac{k_2}{k_3}\,[I_2] + [O_2]}$$

assuming k_1 to be equal to unity.

It is to be noted that at high oxygen concentrations this mechanism gives a quantum yield of **2,** in terms of methyl iodide oxidation per quantum, which is the experimentally determined value.

Furthermore, even if we consider the total reaction, which will yield a slightly larger pressure decrease than corresponds to methyl iodide removed, as can be seen from the higher values in Table II, we can show that the kinetic equation remains essentially the same.

The formaldehyde and methyl alcohol react in the following ways

$$2CH_3OH + CH_2O \longrightarrow (CH_3O)_2CH_2 + H_2O \qquad k_5$$
$$nCH_2O \longrightarrow (CH_2O)n \qquad k_6$$
$$nCH_2O + h\nu \longrightarrow (CH_2O)n \qquad k_7$$

Assuming stationary concentrations of formaldehyde and methyl alcohol, we arrive at the equations

$$CH_3OH\text{:}\quad [CH_3I][OH]k_4 = [CH_3OH]^2[CH_2O]k_5 \tag{3}$$

$$CH_2O\text{:}\quad [CH_3][O_2]k_3 = \frac{[CH_3OH]^2[CH_2O]k_5}{2} + k_7A' + [CH_2O]^n\,k_6 \tag{4}$$

Equation 4 assumes the form it does if the rate of removal of formaldehyde by the methylal reaction is only half that of an equal volume of methyl alcohol, as we have shown to be true.

By a reasoning similar to that used above it may be shown from (1), (2), **(3)** and (4) that

$$\frac{\mathrm{d}(CH_2O)}{\mathrm{d}t} = \frac{\mathrm{d}(CH_3OH)}{\mathrm{d}t} = \frac{\mathrm{d}[(CH_3O)_2CH_2]}{\mathrm{d}t} = \frac{2\mathrm{d}(CH_2O)_n}{\mathrm{d}t} = \frac{k_1A\,[O_2]k_3}{[I_2]k_2 + [O_2]k_3} \tag{5}$$

Since the total pressure decrease must be proportional to the sum of these rates, we have again

$$-\frac{\mathrm{d}P}{\mathrm{d}t} = K\,\frac{k_1A\,[O_2]k_3}{[I_2]k_2 + [O_2]k_3}$$

and, therefore, the rate of pressure decrease is proportional to the rate of decrease of methyl iodide concentration. Approximate values for the constants α and k_2/k_3 were derived from the experimental results and, using these figures, the value of K was calculated and appears in the last column of Tables V and **VI.**

$$-\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{K\,(1 - e^{-0.047[CH_3I]})\,[O_2]}{12.3 + [O_2]} \tag{6}$$

Curves appearing in Figs. 4 and 5 were obtained theoretically from this equation and the experimental points plotted for purposes of comparison.

The constant **12.3** is equal to $k_2/k_3[I_2]$ and since $[I_2] = 0.03$ mm., $k_2/k_3 = 410$. Therefore, if methyl reacts with iodine on every collision, only one collision in about every four hundred between methyl and oxygen can be fruitful. Since this reaction is strongly exothermic, this is another elementary reaction which does not go on every collision, such as we have already discussed on page 1700. A more general discussion of the relative collision efficiencies of these reactions will be included in a forthcoming paper.

Besides the mechanism involving intermediate production of free hydroxyl groups, which is given above, another alternative mechanism is possible. The comparative inefficiency of the collisions between methyl and oxygen suggests the possible intervention of a third body and, indeed, the number of collisions of this type would be roughly of the same order as the number of efficient collisions between methyl and oxygen. The theory of intermediate peroxide formation, which has received considerable support in the case of hydrocarbon oxidation,[21] at once suggests itself and requires the following scheme of reaction: methyl iodide would be dissociated according to reaction (1) above and would be formed by reactions (2) above. Since the formation of a peroxide would necessitate a three-body process, we have

$$P + CH_3 + O_2 \longrightarrow CH_3O_2 + P' \qquad k_3'$$

where P represents the total pressure

$$CH_3I + CH_3O_2 \longrightarrow CH_2O + CH_3OH + I \qquad k_4'$$

while formaldehyde and methyl alcohol would be removed by reactions (5), (6) and (7) of the previous scheme, and by precisely the same reasoning that was used to derive Equation 6, we can obtain the equation

$$-\frac{dP}{dt} = \frac{K\,(1 - e^{-\alpha[CH_3I]})\,[O_2]}{\dfrac{k_2'[I_2]}{k_3'[P]} + [O_2]} \qquad (7)$$

According to this, increase in total pressure at low oxygen concentrations should increase the reaction velocity. Thus, comparing 50 mm. of methyl iodide and 10 mm. of oxygen, with 50 mm. of methyl iodide, 10 mm. of oxygen and 40 mm. of nitrogen, as predicted from Equation 7, the respective rates ought to be in the ratio of 1:2.35. Actually, we find by experiment that they are as 1:0.9. It would seem then, that the photochemical oxidation of methyl iodide is to be represented by the hydroxyl scheme and kinetic Equation 6, rather than by the peroxide scheme and Equation 7.

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[21] **Lewis,** *J. Chem. Soc.,* 58 (1930); **Brunner and Rideal,** *ibid.,* 1162 (1928); **Thompson and Hinshelwood,** ***Proc. Roy. Soc.*** **(London), A125,** 277 (1929); **Callendar.** ***Engineering,*** 123, 147, 182, 210 (1927); **Fort and Hinshelwood,** ***Proc. Roy. Soc.*** **(London) A125,** 218 (1930).

Without wishing to lay too much stress upon this conclusion, the writers would point out that such a "hydroxyl" scheme is at least as probable a mechanism of hydrocarbon oxidation as a peroxide scheme, especially when it is considered that hydrocarbons generally do not react appreciably with oxygen until they reach temperatures at which dissociation begins to occur.

One of the authors (R. S.) wishes to express his indebtedness to the Commonwealth Fund for a Fellowship which enabled him to take part in the research.

Summary

1. Gaseous methyl iodide decomposes extremely slowly when illuminated with ultraviolet light, and exhibits a Budde effect similar to that obtained with chlorine.

2. The photo-oxidation of gaseous methyl iodide has been shown to be essentially an oxidation of free methyl groups.

3. Iodine, paraformaldehyde, methylal and water are practically the sole products of reaction.

4. The kinetics of the process have been investigated and found to agree with the theoretically derived mechanism.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

THE OXIDATION OF IODIDE ION BY PERSULFATE ION. IV. KINETICS OF THE REACTION IN HIGHLY DILUTE AQUEOUS SOLUTION

BY CECIL V. KING AND MORRIS B. JACOBS

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Introduction

A combination of Bronsted's equation for the velocity of a bimolecular ionic reaction and the Debye–Hiickel limiting expression for the activity coefficient of an ion (in water at 25°) leads to the expression

$$\log k = \log k_0 + z_A z_B \sqrt{\mu} \qquad (1)$$

where k is the velocity constant observed and k_0 that at zero ionic strength. Introduction of the Debye–Hiickel expression necessitates velocity measurements at very low salt concentrations to test this expression; previously only three ionic reactions have been measured at concentrations below $\sqrt{\mu} = 0.14$ and two others below $\sqrt{\mu} = 0.25$. An excellent summary of this work has been given by Livingston[1] and we have reproduced his plot of ($\log k - \log k_0$) against $\sqrt{\mu}$ for the various reactions, including for comparison (in black circles, Fig. *1)* some of our measurements on the persulfate–iodide reaction.

[1] Livingston, *J. Chem. Ed.*, 7, 2887 (1930).

This reaction has been the subject of several previous investigations at higher ionic strengths than reported here. Price[2] found the reaction to be kinetically bimolecular, and noted the positive salt effect. He also observed the disturbing influence of the iodine formed in the course of the reaction on the velocity, a factor which has been clarified in this Laboratory (papers I and II of this series) and elsewhere.[3] Brönsted used the earlier measurements in verifying his theory of primary salt effect.[4]

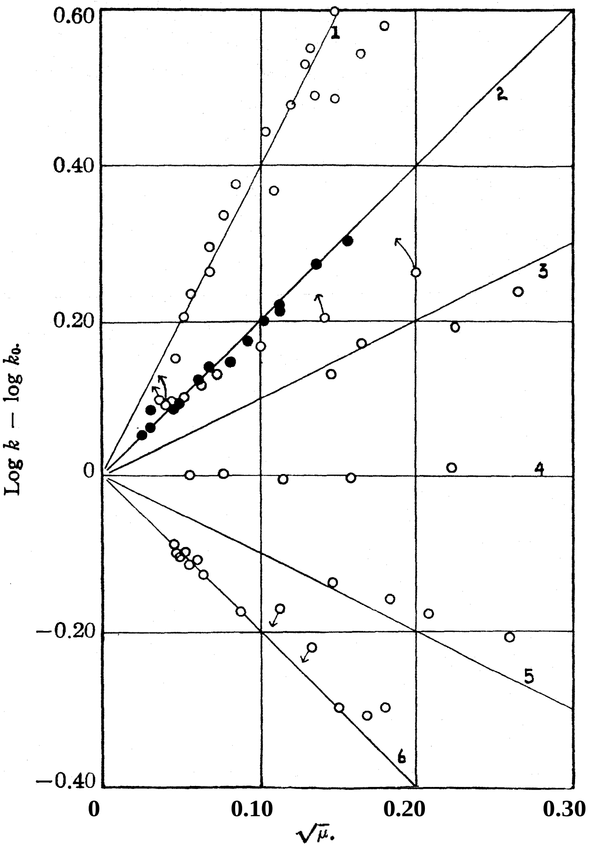

Fig. 1.—The effect of ionic strength on the velocity of ionic reactions.

The Experimental Method

The reaction has been followed in the past by titrating the iodine produced with standard thiosulfate. Such titrations become difficult in the

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[2] Price, *Z. physik. Chem.*, *27*, 474 (1898).

[3] Jette and King, This Journal, 51, 1034, 1048 (1929); Oostveen, *Rec. trav. chim.*, 48, 697 (1929).

[4] Brönsted, *Z. physik. Chem.*, *102*, 169 (1922).

dilute solutions we wished to use, although the similar titration of thiosulfate with standard iodine has been carried out successfully in equally dilute solutions.[5] However, in addition to this difficulty we wished to avoid also the complicating factor of tri-iodide formation mentioned above, and therefore resorted to a scheme similar to that used in studying the Landolt reaction $(HIO_3 + H_2SO_3 \longrightarrow)$. To the solution of potassium persulfate and potassium iodide was added a small amount of sodium thiosulfate, which by its very rapid reaction with the iodine as it was liberated, kept the solution clear until it was all used up. The time of first appearance of iodine was determined with the aid of a balanced photo-cell circuit and sensitive galvanometer, with a long absorption cell; for accuracy the amount of thiosulfate was adjusted so that the iodine never appeared in less than approximately ten minutes. From this time and the known concentrations the velocity constant was calculated.

The velocity of other reactions has been measured in a similar manner, without using a photo-cell method and at much higher concentrations. The Landolt reaction has been mentioned above. Abel measured the velocity of the potassium iodide–hydrogen peroxide reaction by adding thiosulfate (which also reacts with the hydrogen peroxide, at a known, slow rate).[6] Abel and Fürth studied the oxidation of iodide by periodate by using arsenite to react with the liberated iodine and so prevent its appearance.[7]

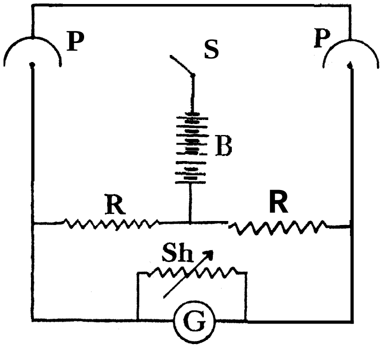

Fig. 2.—The photo-cell circuit: P, P, General Electric PJ14 photocells; S, switch; B, 90-volt battery; R, R, 100-000-ohm resistances: G, Leeds and Northrup wall galvanometer, resistance 1090 ohms, sensitivity 1133 megohms, period 13.1 seconds; Sh, shunt box.

Thiosulfate is oxidized very slowly by persulfate,[8] especially in dilute solutions of persulfate and at low ionic strength, so that this factor was negligible except when the persulfate concentration was much higher than the iodide concentration, as will be noted later.

The photo-cell circuit used is shown diagrammatically in Fig. 2. Vacuum type cells were used, since the circuit was too unstable with gas-filled cells. The source of light was a 400-watt projection bulb operated on 110 volts d. c. The lamp was inclosed in a metal housing, cooled by a small fan. Two beams of light were first passed through glass filters—a combina-

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[5] La Mer, This Journal, 51,3341 (1929).

[6] Abel, *Z. Elektrochem.*, 14, 698 (1908).

[7] Abel and Fürth, Z. *physik. Chem.*, 107,313 (1923).

[8] King and Steinbach, This Journal, 52, 4779 (1930).

tion of Corning "Didymium" and "Theater Blue^{M}—to filter out most of the light not absorbed by iodine solutions. The light then passed, on one side through the reaction cell—a 5 × 20 cm. glass tube with plane glass ends and side tube for filling—thermostaled at 25 ± 0.02°, and on the other side through a similar cell containing distilled water. The beams then passed through iris diaphragms to the two photo-cells. Sufficient light was obtained without the use of a lens system.

This balanced circuit automatically compensates for most of the fluctuations in the source of light, in battery voltage, etc. Since it is difficult to find two photo-cells with exactly similar characteristics, two 100,000 ohm resistances exactly alike, etc., this compensation is not perfect. Sometimes the galvanometer reading was quite constant over a long period of time: sometimes there were small variations or a slow drift. To fix the time of appearance of iodine more exactly, galvanometer readings were plotted against time and by extrapolating as shown in Fig. 3, the time was determined to ±0.1 minute in most cases.

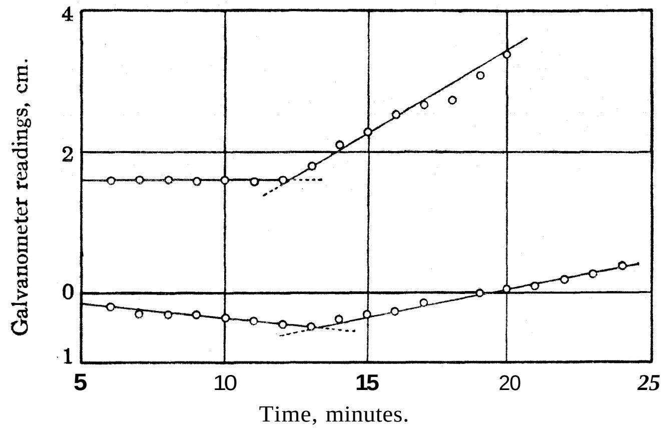

Fig. 3.—The method of obtaining the time of appearance of iodine.

The galvanometer shunt was used only while balancing the circuit and not when measurements were being made. It was found that the appearance of $3 \times 10^{-}$[illegible] moles per liter of iodine gave a galvanometer deflection of approximately 2 cm. The absorption of light increases somewhat more than linearly with the concentration of iodine, but the iodine appears more slowly as the time progresses, hence the approximate linearity of the curves in Fig. 3 over the first few minutes of iodine liberation.

This method gave a much more sensitive test for iodine than the visual test with starch. The latter is, according to Kolthoff,[9] sensitive to about

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[9] Kolthoff, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929, Vol. 11. p. 350.

1×10^{-5} mole of iodine per liter (if 4×10^{-5} M I^- is present). This may under certain conditions be increased to 5×10^{-6} mole of iodine per liter.

Partington[10] states that one part per million of iodine (approximately 2.5×10^{-5} mole per liter) can be detected with starch. He also states that basic lanthanum and praseodymium acetates can be used to detect traces of iodine. Experiments in this Laboratory showed the first of these to be slightly more sensitive than starch. However, the photo-cell method was far better for our purpose.

Materials and Method

All the water used was redistilled from dilute alkaline permanganate and condensed in a block tin condenser. All salts were recrystallized at least twice from this water. Especial pains were taken to free the potassium iodide from traces of iodine since this would react immediately with some of the thiosulfate added. Measurements made with different lots of several of the salts agreed well. Measurements at the highest ionic strengths used checked previous measurements within 2%. King and Steinbach[8] found the velocity of this reaction to be some 25% less in the presence of 0.02 M thiosulfate than in the presence of 0.02 M potassium sulfate. However, in the presence of $10^{-7} - 10^{-5}$ M thiosulfate, as used in this investigation, the agreement with previous measurements indicates that the reaction is perfectly normal.

Standard solutions of all the salts except the thiosulfate were made by weighing the salt and dissolving in the required volume of water. Sodium thiosulfate was standardized by titrating the iodine liberated from potassium iodide by a known amount of persulfate.[11] Aliquot parts of the standard solution were diluted to the required concentrations.

All solutions were brought to 25° before mixing, the time of mixing noted, and galvanometer readings started as soon as the absorption cell was filled and in the bath.

The velocity constants were calculated from the differential equation

$$\frac{-\mathrm{d}C_{S_2O_8^-}}{dt} = kC_{S_2O_8^-}\, C_{I^-}$$

The interval from the time of mixing until the first appearance of iodine was used as dt, $-\mathrm{d}C_{S_2O_3^-}$ was calculated from the known concentration of thiosulfate, and $C_{S_2O_8^-}$, C_{I^-} were the initial concentrations. Since the concentration of thiosulfate was seldom more than 2% of that of the persulfate or iodide, this procedure gives sufficiently accurate values of k.

Experimental

In the first series of experiments the potassium persulfate concentration

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[10] Partington, "Textbook of Inorganic Chemistry," The Macmillan Co., New York, 1929, p. 407.

[11] Paper III of this series, THIS JOURNAL, 52, 608 (1930).

was varied from 0.000125 to 0.0048 *M*, and the potassium iodide from one to three times the persulfate concentration. The values of $\sqrt{\mu}$ and log *k* are given in Table I; to save space, the concentrations are omitted. In Fig. 4, log k is plotted against $\sqrt{\mu}$. The straight line is drawn with the slope +2 in such a way that it best fits the points at the lowest values of $\sqrt{\mu}$; it is evident that the experimental values agree with the theoretical up to $\sqrt{\mu}$ = 0.06, but that above this value there is an increasing negative

TABLE I

THE EFFECT OF THE TOTAL IONIC STRENGTH ON THE VELOCITY OF THE PERSULFATE–IODIDE ION REACTION AT 25°

$C_{K_2S_2O_8}$ 0.000125 to 0.0048 *M*; C_{KI} one to three times $C_{K_2S_2O_8}$; $C_{Na_2S_2O_3}$ 7 X 10^{-7} to 3 X 10^{-4} M

$\sqrt{\mu}$	Log *k*	$\sqrt{\mu}$	Log *k*	$\sqrt{\mu}$	Log *k*
0.0250	$\bar{2}$.978	0.0571	$\bar{1}$.049	0.0841	$\bar{1}$.068
.0308	0.987	.0571	0.053	.1002	0.100
.0308	$\bar{1}$.013	.0592	.045	.1272	.100
.0308	0.009	.0592	.057	.1426	.121
.0354	.009	.0592	.061	.1426	.111
.0354	.021	.0654	.065	.1429	.114
.0354	.021	.0654	.072	.1490	.121
.0419	.017	.0654	.057	.1500	.124
.0419	.033	.0709	.090	.1574	.114
.0419	.037	.0709	.086	.1574	.111
.0500	.037	.0808	.072	.1574	.117
.0500	.045	.0808	.079	.1590	.124
.0571	.072	.0840	.068		

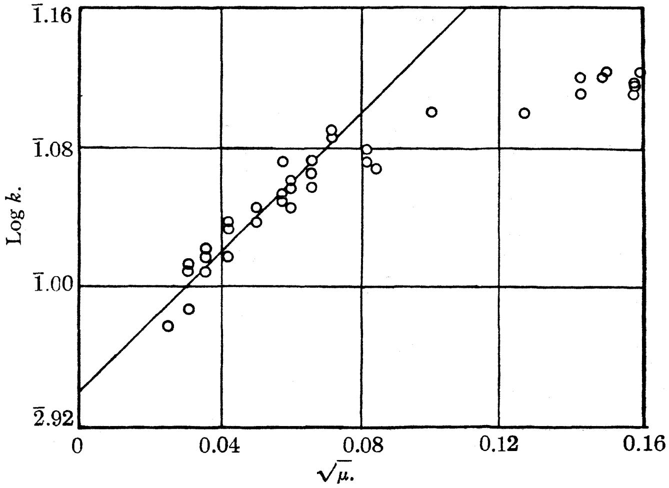

Fig. 4.—Experiments with persulfate and iodide in approximately equivalent concentrations.

deviation. Since the best straight line extrapolates to log $k_0 = \bar{2}.94$ or -1.06, Equation 6 becomes

$$\log k = -1.06 + 2\sqrt{\mu}$$

The figure -1.06 is not, however, the value we shall accept as best for log k_0 (see discussion at end of paper).

Since we should expect to find a reaction in solutions containing only univalent ions to follow the theoretical expressions to much higher ionic strengths than if bivalent ions are present, it appears that the above method of using mixtures containing uni- and bivalent ions is a poor choice. It would be preferable to keep the concentration of persulfate as low as possible and increase the iodide concentration, or keep both low and add an inert salt to raise the ionic strength. This was accordingly done in the succeeding experiments.

In the second series the potassium persulfate concentration was kept at 0.00015 M and the potassium iodide concentration at 0.0005 *M* (except for the four lowest points), while potassium chloride was added to raise the ionic strength. In a parallel series the persulfate concentration was kept at the same value while increasing concentrations of iodide were used to raise the ionic strength. The results are given in Tables II and III and plotted in Fig. 5, the experiments with added potassium chloride as open circles, those with potassium iodide as black circles. Here the best straight line with the slope +2 through the lowest points extrapolates to the value log $k_0 = \bar{2}.925$ or -1.075, which is only 1.6% different from the value found

TABLES II AND III

THE EFFECT OF UNI-UNIVALENT SALTS ON THE VELOCITY

0.00015 M $K_2S_2O_8$, 0.0005 M KI, 1.7 × 10^{-7} to 4 × 10^{-7} M $Na_2S_2O_3$

C_{KCl}	$\sqrt{\mu}$	Log k
0.00015	0.0336	$\bar{1}$.004
.0003	.0354	0.017
.0006	.0393	.000
.0012	.0464	.009
.0018	.0524	.017
.0036	.0675	.057
.0054	.0797	.083
.0060	.0834	.079
0060	.0834	.076
.0072	.0903	.107
.0090	.0998	.111
0096	.1028	.117
.012	.1138	.140
.012	.1138	.134
.0144	.1239	.164
.018	.1376	,199
.024	.1580	.230

0.00015 M $K_2S_2O_8$, 6 X 10^{-7} to 2 × 10^{-5} M $Na_2S_2O_3$

C_{KI}	$\sqrt{\mu}$	Log k
0.0016	0.0452	$\bar{1}$.013
.0020	0495	0.021
.0032	.0604	.049
.0040	.0667	.065
.0060	.0803	.072
.0080	.0919	.100
.010	.1022	.124
.012	.1116	.146
.012	.1116	140
.018	.1358	.199
.024	.1564	.228

before and probably within the experimental error of such velocity measurements. It will be seen that these experiments follow the theoretical slope quite well to $\sqrt{\mu} = 0.16$, the highest value used. The theoretical equation becomes

$$\log k = -1.076 + 2\sqrt{\mu}$$

In the fourth series an attempt was made to keep the potassium iodide concentration low (0.0005 M) and raise the ionic strength by adding larger amounts of potassium persulfate. These results are plotted in Fig. 6 (open circles). It will be seen that the results are not in accord with the theory in that the value of k rises far above the theoretical and at higher ionic strengths actually decreases again. The explanation lies in the fact that in most of these experiments the ratio of persulfate to thiosulfate concentrations was such that an appreciable percentage of the thiosulfate is oxidized directly instead of through the intermediate iodine. It was found before[8] that the rate of the persulfate–thiosulfate reaction is much more dependent on the persulfate concentration than on the thiosulfate concentration. In these experiments, with **0.00015** M persulfate **and 5** $\times 10^{-7}$ M thiosulfate, not over 1% of the thiosulfate is oxidized directly; while with 0.004 M persulfate and $1 \times 10^{-5} M$ thiosulfate the percentage is much larger. The iodide concentration was low; if this were raised to twice the

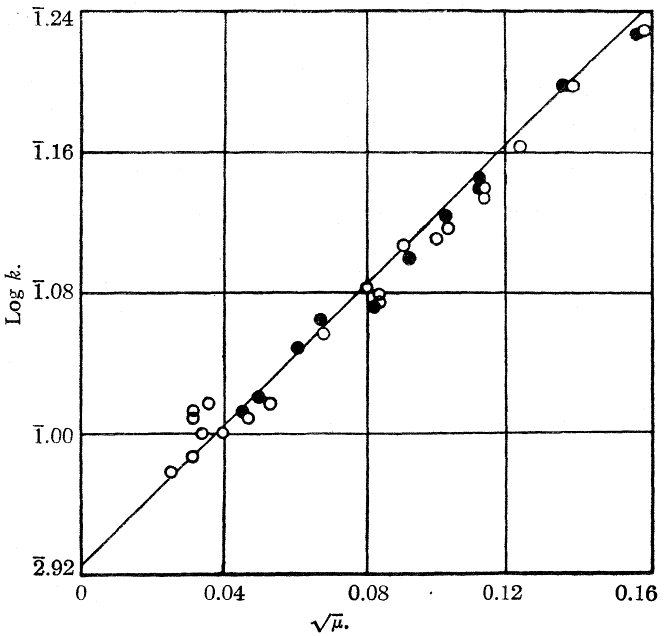

Fig. 5.—Persulfate concentration low; ionic strength raised by adding KCl (O)and KI (O).

persulfate concentration, as in the first series, the velocity of the main reaction would be increased 10–20 times and again not over 1% of the thiosulfate would be oxidized directly.

When the persulfate concentration was increased to the highest value used, 0.012 M, the thiosulfate concentration had to be increased to 4 X 10^{-5} *M*, almost 10% of the iodide concentration; the velocity of the main reaction was such that the percentage of thiosulfate oxidized directly was again low; while the fact that the differential equation was used to calculate k introduces an error of a few per cent.

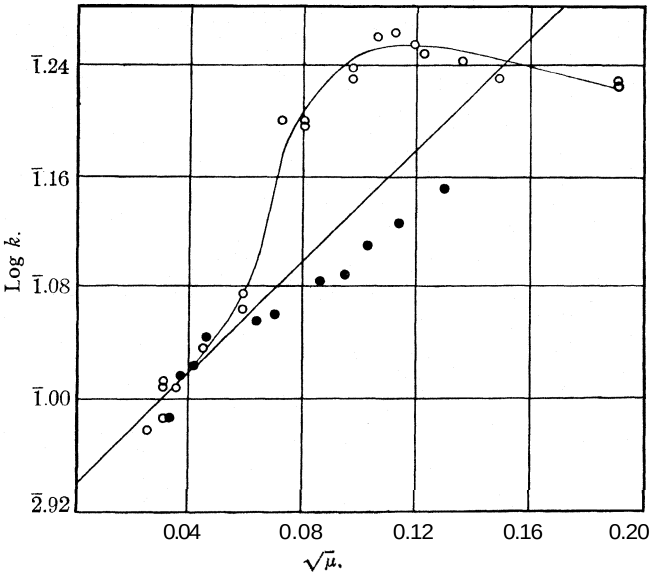

Fig. 6.—Iodide concentration low; ionic strength raised by adding $K_2S_2O_8$ (O) and $MgSO_4$ (@).

Calculation shows that if we assume a value of 2.5 × 10^{-5} as an average for the unimolecular constant of the persulfate–thiosulfate reaction over this range of ionic strengths, and correct the curve shown in Fig. 6 accordingly, reasonable values are obtained for the persulfate–iodide velocity. Unfortunately, no direct measurements of the persulfate–thiosulfate reaction at such low ionic strengths are available, but this value is not improbable.

To obtain better values for the effect of bivalent ions on this reaction, in the last series both the persulfate and iodide concentrations were kept low (0.00015 and 0,0005 *M*, respectively) and magnesium sulfate was used to raise the ionic strength. The results are given in Table IV and plotted in Fig. 6 (black circles). Here we see that the results are normal, the theorectical slope is followed to $\sqrt{\mu} = 0.05$ or 0.06, and the deviations at higher ionic strengths are in the expected direction, For the two sets of experi-

TABLE IV

THE EFFECT OF MAGNESIUM SULFATE ON THE VELOCITY

0.0015 *M* $K_2S_2O_8$, 0.005 M KI, 2.5 X 10^{-7} to 5 X 10^{-7} *M* $Na_2S_2O_3$

C_{MgSO_4}	$\sqrt{\mu}$	Log k	C_{MgSO_4}	$\sqrt{\mu}$	Log k
0.00004	0.0333	$\bar{2}.987$	0.0016	0.0857	$\bar{1}.083$
.0001	.0367	$\bar{1}.017$	.0020	.0946	0.090
.0002	.0418	0.025	.0024	.1027	.111
.0003	.0464	.045	.003	.1138	.127
.0008	.0644	.057	.004	.1302	.152
.0010	.0704	.061			

ments plotted in Fig, 6, the straight line which fits best extrapolates again to log $k_0 = -1.06$.

Discussion

It seems rather surprising that when the ionic strength is made up largely of univalent ions, the best straight line should extrapolate to log $k_0 = -1.075$, while with a large proportion of bivalent ions present the best straight line should extrapolate to log $k_0 = -1.06$. The difference is just at the limit of experimental error, but seems too consistent to be of no significance. The explanation may lie in the inaccuracy of the Debye–Hückel equation for bivalent and trivalent ions, even in very dilute solutions. This inaccuracy was noticed by Bronsted, La Mer[12] and their collaborators and finally explained by Gronwall, La Mer and Sandved,[13] who showed that an extension of the mathematical treatment of Debye and Hückel leads to a modified equation for the activity coefficient of ions of higher valence more in accord with experiment than the limiting expression. We cannot apply the Gronwall–La Mer–Sandved extension quantitatively for lack of sufficiently accurate data, but its qualitative significance can be shown. In the region $\sqrt{\mu} = 0.04$ to 0.08 (approximately) the activity coefficient of the bivalent persulfate ion (f_A) will be somewhat smaller than $\log^{-1}(-0.5\, z_2 \sqrt{\mu})$, and that of the iodide ion (f_B) will be practically equal to $\log^{-1}(-0.5\, z^2 \sqrt{\mu})$. But the activity coefficient of AB, a trivalent ion, will have a negative deviation from $\log^{-1}(-0.5\, z^2\sqrt{\mu})$ still greater than that of the persulfate ion, and the value of $\log f_A f_B/f_{AB}$ will therefore be greater than calculated and used in deriving equation (1). At higher concentrations the logarithmic value will again be equal to and finally less than $z_A z_B \sqrt{\mu}$.

For this reason we prefer to take the limiting equation found with added uni-univalent salts, namely

$$\log k = -1075 + 2\sqrt{\mu}$$

as extrapolating to the best value of k_0, the velocity constant at zero ionic strength. This gives the value

$$k_0 = 0.0841$$

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[12] Bronsted, La Mer and others, THIS JOURNAL, 43, 2265 (1921); 46, 555 (1924); 49, 363, 410 (1927).

[13] Gronwall, La Mer and Sandved, *Physik. Z.*, 29,358 (1928).

In view of the uncertainty regarding the quantitative application of the Gronwall–La Mer–Sandved equation, it is useless to attempt to apply a more or less empirically extended activity coefficient equation in explanation of the curves in Figs. 4 and 6.

Summary

The velocity of the persulfate–iodide ion reaction has been measured, in aqueous solution at 25°, between values of $\mu = 0.000625$ and $\mu = 0.025$, with an accuracy of about ±1.5%.

The velocity was measured by adding small known amounts of thiosulfate to the reacting solution and noting the time of first appearance of iodine with the aid of a photo-cell circuit far more sensitive to traces of iodine than the visual starch test. The velocity constants, in solutions containing as few ions of valence higher than unity as possible, follow accurately the linear equation

$$\log k = -1.075 + 2\sqrt{\mu}$$

to at least as high a concentration as $\mu = 0.025$.

The small difference in the extrapolation of the plot of log k against $\sqrt{\mu}$ for univalent and bivalent ions may be qualitatively explained by the difference between the original Debye–Hückel limiting equation for the activity coefficient of an ion and the Gronwall–La Mer–Sandved extension for ions of higher valence than unity.

NEW YORK, N. Y.

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

THE SOLUBILITY OF GOLD IN MERCURY. III

BY ARTHUR A. SUNIER AND LAW G. WEINER

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In earlier papers[1] the results of a study of the solubility of gold in mercury in the temperature interval 0 to 200° were presented. The present paper will deal with a similar study in the range 200 to 300°. The need of such a study will be apparent to all who critically examine the published data[2] in this range of temperature. Although the precision of measurement is not as great as that obtained in earlier papers, it is felt that the method and results are of sufficient interest to warrant publication at this time.

Materials

The mercury was carefully purified and tested as described in earlier papers. In one run (B) mercury was used which was obtained by evapora-

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[1] Sunier and Gramkee, THIS JOURNAL, 51, 1703 (1929); Sunier and White, *ibid.*, 52, 1842 (1930).

[2] Parravano, *Gazz. chim. ital.*, 48, II, 123 (1918); Braley and Schneider, THIS JOURNAL, 43, 740 (1921); Britton and McBain, *ibid.*, 48, 593 (1926); Plaskin, J. *Russ. Phys.-Chem. Soc.*, 61, 621 (1929).

tion from some earlier runs. Gold in the form of foil, said to contain less than 0.01% impurity, was used in about half of the determinations; in the other half (F to J) gold residues from earlier runs were used. No difference in solubility could be traced to this procedure.

Apparatus

Two types of solubility tubes were used. The first type will not be pictured as it differed only slightly from tubes used earlier The second type is pictured in Figs. 1 and 2 in the tube holders which will be described later. Instead of having a vacuum in these tubes, they were filled with hydrogen at a pressure a little below that of the atmosphere. At elevated temperatures a pressure greater than atmospheric was produced; consequently when the capillary A was broken, hydrogen issued from the capillary and the amalgam filtered through the fine capillary connecting the tubes R and H. It will be noted that the size of these tubes is somewhat smaller than those used earlier; this was necessary because of the increased solubility of gold at these higher temperatures.

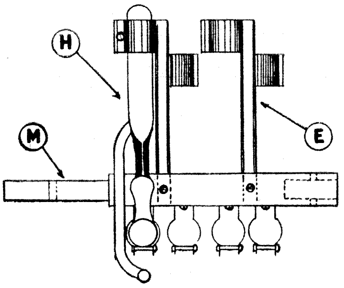
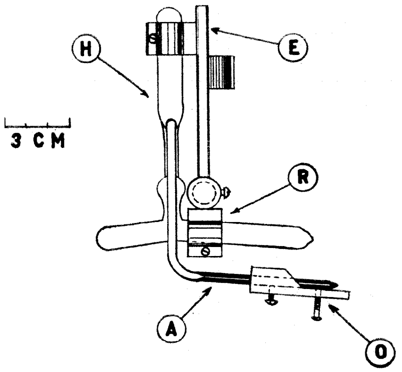


Fig. 1.



.Fig. 2.

The tubes were shaken in an air-bath, shown diagrammatically in its final form in Pig. 3, of about one cubic foot capacity. One five-hundred watt heater made of nichrome ribbon was placed in each corner (H) of the bath as indicated. Suitable combinations of heaters could be made, to enable a more even distribution of heat, and one heater was placed in circuit with a suitable rheostat to give the fine adjustments of heat required. A four bladed fan (F) rotated for the most part at 600 r. p. m. was placed at one end of the bath. Through the other end of the bath was placed the brass shafting, having a diameter of 16 mm., holding the eight solubility tubes. This shaft was made in three parts, A, B, C The first part was the longest and was held in place by suitable self-aligning bearings (not shown) and was connected with a double eccentric mechanism (which need not be described in detail) in such a way that the shaft oscillated back and forth through an angle of about ninety degrees about eleven times per minute. Parts B and C were of about equal length and were so constructed that they could be removed from or fastened to part A with little difficulty. Figures 1 and 2 give front and side views of part B, to scale. Four pairs of clamps were provided on each of these sections. In Figs. 1 and 2 only one solubility tube is shown in place so as not to complicate the figures.

The thermometer was placed in a small metal cup (N) containing about 50 g. of bismuth solder. As some of the thermometer emerged from the bath, a glass chimney was provided in later runs. This chimney could be electrically heated to very nearly the temperature of the bath, thus eliminating large stem corrections. Temperature measurements were made with a nitrogen-filled mercury thermometer standardized against a similar thermometer recently standardized by the Physical Laboratory of the Taylor Instrument Company. It is believed that most of the recorded temperatures are accurate to ±0.2°. In the runs up to 275° a Beckmann thermometer was inserted in another metal cup (not shown) in the opposite end of the bath; this thermometer rarely showed changes of 0.1° when the apparatus was working smoothly.

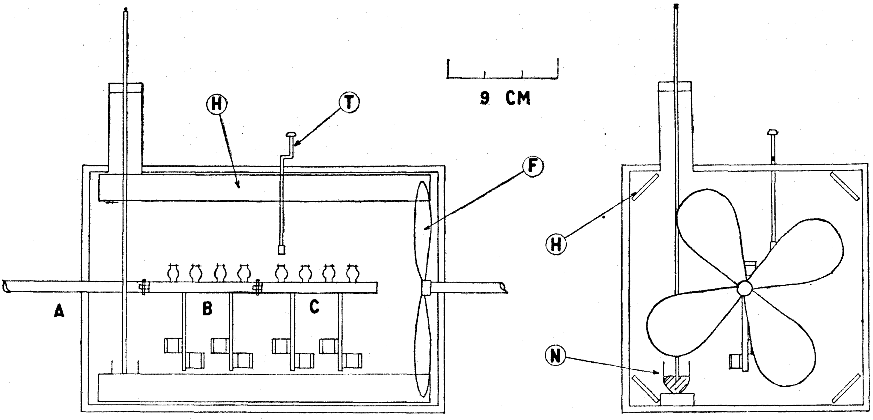


Fig. 3.

The air-bath was very heavily lagged with transite and magnesia board. It was provided with a mica window, kept covered except when it was desired to inspect the tubes. The top of the bath was provided with removable sections to allow inserting the brackets with care and also breaking the capillaries.

Experimental Procedure

The tubes of the first type were filled in the same way as described in earlier papers Tubes of the second type were supplied with mercury and for the most part about 100% excess gold, using Britton and McBain's data as a guide. These elements were placed in part R of the tube (Fig. *2)* and the tube R was sealed as indicated. The capillary was connected to a Hy-vac pump and the tube was thoroughly evacuated, then it was filled with hydrogen and re-evacuated, this flushing process being repeated three or four times. Then, when the pressure of hydrogen was a little less than that of the atmosphere, the capillary was sealed off as indicated. A slight indentation was made on the capillary A, to keep the breaker block in position; the capillary was also file marked a little below the point where the screw O touches the capillary. The tube was next placed in the clamps and the breaker block fastened on in the proper place by means of the screw (not lettered), and also by means of some small asbestos blocks (not shown).

In every run but one, equilibrium was attained from both the high and low sides Eight tubes were made up, four being placed in bracket B and four in bracket C. When bracket B was fastened to the shaft A (by means of a screw) the oscillating mechanism was set in motion and the temperature of the bath was raised to five or ten degrees above the solubility temperature and held there for three or four hours. Then the temperature was lowered to about one degree above the solubility temperature, when a section of the top of the bath was removed and bracket C was quickly inserted and fastened to the end of bracket B. The temperature was then quickly brought to the desired point and held there manually for another three-hour period.

When it was time to sample, the shaking mechanism was stopped and the shaft **ABC** was rotated **180** degrees; the tubes thus were brought to the sampling position (in Fig. **2** the tubes are shown in the shaking position). **A** very narrow **(1** X **7** cm.) section of the top was next removed and the special breaking tool (T Fig. **3)** placed over the head of the breaking screw O, Fig. **2.** **A** slight turn of the tool sufficed to break the capillary in the proper place, thus allowing the amalgam to filter properly. The capillaries of the eight tubes were broken one by one, this operation taking about five minutes. After filtration the bath was allowed to cool somewhat, then the tubes were removed from the bath. The sampling tubes H were cut off when cool; their contents were **then** carefully transferred to weighed crucibles.

The amalgams were analyzed by the method described in the first paper of this series. For the purpose of developing technique and checking the method of analysis, the various preliminary experiments described in the first paper were repeated; the results were essentially the same as those presented earlier and need not be repeated. It may be said that when the weight of the gold residue approximated **1 g.,** the last traces of mercury were removed with difficulty; in fact on the average the analysis yielded results about 0.5% high.

Experimental Results

In Table I will be found data for the second run made at 239.2°. In Table II will be found a summary of the results obtained in all of the runs. It will be noted that some of the numbers in column two are placed in

TABLE I

SOLUBILITY OF GOLD IN MERCURY. COMPLETE DATA FOR ONE TEMPERATURE

No.	Temp., °C.	Gold at start, g.	Amalgam, g.	Gold, g.	Atomic % sol.
B1	High side	4 0	23 040	1.139	5.02
B2		4.0	22.849	1.176	5.23
B3	239.2	4.0	24.809	1.210	4.96
B4		4.0	24.876	1.249	5.10
B5	Low side	4.0	16.658	0.839	5.12
B6		4.0	22.580	1.151	5.18
B7	239.2	4.0	32.486	1.594	4.99
B8		4.0	14 222	0.695	4.97
				Average	5.07

TABLE II

SOLUBILITY OF GOLD IN MERCURY. SUMMARY OF EXPERIMENTAL DATA

Series no.	No. of detns.	Temp., °C.	Atomic % soly.	Av. dev. (from the mean) p. p. h.
C	5(3)	200.0	2.99	1.8
A	5(2)	219.6	3.67	2.9
B	8	239.2	5.07	1.7
G	8	260.2	6.50	2.4
D	7	269.6	7.81	3.6
F	7(1)	279 6	9.07	3.0
E	7	292 6	12.58	4.5
J	5(2)	299.5	13.95	1.5

parentheses; these indicate those tubes omitted from the computation of the average because the results were more than four times the deviation from the mean. The letters in column 1 indicate the order in which the runs were made. It will be noted that determinations H and I are missing. Eight tubes were made up for each of these determinations and the run conducted in the usual way, but at the end of the experiment it was evident that all of the gold had gone into solution, since no residue remained. This absence of excess gold was the first indication that the data of Britton and McBain were in error at the higher temperatures. Determination J was then made, four of the tubes containing a little less than 14 atomic % of gold, which is **50%** more than the value of the solubility at **300** recorded by Britton and McBain; the other four tubes contained **100%** excess of gold. These eight tubes were run for six hours, attaining equilibrium only from the low side. At the conclusion of the run the tubes containing the lesser quantity of gold had no residue, but the analyses showed that these tubes were apparently only slightly below the saturation point, hence the results are averaged in with those containing the larger amounts of gold.

All of the solubilities are expressed in atomic per cent. of gold. **A** table giving the solubility at rounded temperatures will, it is hoped, be presented in another paper.

Discussion of Results

In Fig. 4 the results are plotted as atomic per cent. of gold *versus* temperature. **A** log N *vs.* $1/T$ plot was constructed but there was a marked departure from a straight line, pointing most certainly to the fact that pure gold is not the solid phase but rather some compound of gold and mercury whose formula is not known at present.

The researches of both Parravano and Plaskin were carried out employing cooling curves. Britton and McBain analyzed the liquid phase in equilibrium with the solid phase, but no blank runs were recorded so it is difficult to estimate the probable accuracy of their results. It is hardly possible that the maximum reported by them is due to analytical errors; it would seem rather to be due to an error in sampling, but even this is not wholly satisfactory since below 225° their results are essentially in agreement with the present results. This marked discrepancy in the results at 300° led to the execution of some supplementary experiments which will be discussed under "Supplementary Experiments."

It may be well to discuss briefly, at this point, several possible sources of error in the present experiments. On the analytical side it is believed that 1% would be a very liberal estimate of the maximum error, and this error was occasioned by the large residues of gold obtained in several of the experiments—residues of **2** to 4 g. being obtained in runs D and E. In later runs a definite effort was made to keep the residues below one **gram.**

Occasionally it would be found that in several tubes of a given run the gold strips were not transferred from one end of the tube R to the other end, hence the attainment of equilibrium was hindered to some extent. Then, further, spattering tended to result especially with the larger weights of gold. If the tiny droplets of mercury or amalgam produced on the walls of the tube were not gotten into the main body of the amalgam in subsequent oscillations of the tube, a slight dilution effect (in the low side tubes) would be produced at the time of sampling when these droplets coalesced with the main portion of the amalgam. This is believed to be one of the greatest sources of error in the present experiments where such small amounts of amalgam are involved. It may be that this source of error can be eliminated by making the tube R straight and of smaller bore, and making a little larger the bulb and tube connecting the tubes H and R.

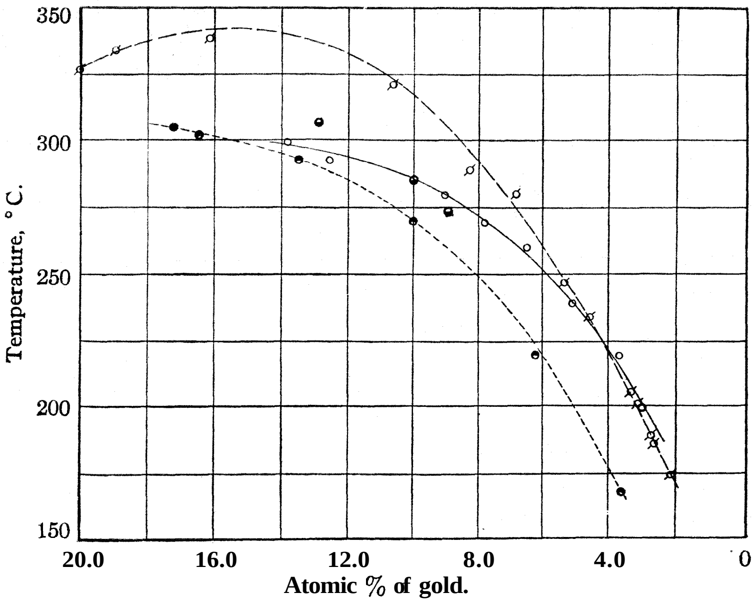


Fig. 4.—Solubility of gold in mercury: - -●- -, Parravano; —ø—, Britton and McBain; 8, Plaskin; —O—, Authors.

In the two earlier papers mention was made of a slight error which may have arisen from the capillary used in admitting air when filtering the amalgams. Such an error was eliminated in the present experiments by the new design of the solubility tube.

Temperature constancy and uniformity in an air-bath is rather difficult to obtain and this is believed to be largely responsible for the rather poorer precision of measurement in the present experiments.

Supplementary Experiments

Britton and McBain performed two supplementary experiments concerning which the following is said: "A satisfactory indication of the correctness of the above data has been obtained in the following manner. Two tubes having a narrow constriction in the middle, like an hour glass, and containing known mixtures of gold and mercury were sealed, and then heated in a small electric furnace provided with windows, and observations were made on the disappearance and reformation of the solid phase by complete inversion of the tube and furnace. Tube I contained a mixture of **30%** gold and **70%** of mercury; some solid was still present at 348° but none at 355°; the temperature of complete liquefaction determined from the curve was **352'.** Tube II contained 50% of gold and 50% of mercury; some solid was still present at 398° but none at **406';** the temperature of complete liquefaction was 392°."

Unfortunately no mention is made of further runs in the concentration range **8** to **18%** To supply this needed information several runs were made by the present authors with the special object of determining whether or not a maximum in the solubility curve was to be found at about 14.3%, this being the value given by Britton and McBain.

The tubes used in the present supplementary experiments were similar to those used in runs **A** to J; the capillary connecting the tubes H and R (Fig. 2) had a larger bore and the capillary A was affixed to the bottom of the sampling tube H. Weighed quantities of gold and mercury, as indicated in Table III, were introduced into the tubes, which were then evacuated to **0.3** mm. The tubes were now placed in the brackets, rocked back and forth and observations of the disappearance and reappearance of the solid phase on complete inversion of the tubes were made through the mica window. Considerable care was exercised in determining the solubility temperature. In another research involving non-metallic solutions it has been shown[3] that a rate of heating of **0.1'** per minute gave a result accurate

TABLE III

RESULTS OF SUPPLEMENTARY RUNS

				Temperature, °C		
Tube no.	Gold, g.	Mercury, g.	Atomic % gold	Disappearance of gold	Reapp of gold	From curve
K1	4.906	40.80	10.90	290.9	288	
K2	4.905	40.80	10.90	289.6	288	
K3	4.896	40.80	10.88	291.4	288	
		Average	10.89	290.6		290
L1	6.695	40.80	14.30	300.6	294	
L2	6.608	40.80	14.15	298.0	294	
L3	6.704	40.80	14.35	300.6	294	
		Average	14.27	299.7		299

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[3] **Sunier,** *J.* **Phys. Chem., 34, 2582 (1930).**

to about one-half of one degree. It is difficult to estimate what the corresponding error would be in metallic systems such as the one under consideration, but from preliminary observations in this Laboratory it would appear that the error would be no greater than that just mentioned. The solubility temperature was determined at a number of different rates of heating, 1, 0.25, 0.1° per minute. In Table III the results are for a rate of 0.1" per minute.

From an inspection of Table III it is apparent that these supplementary runs corroborate the data presented in Table II, and thus no maximum in the curve is found for a temperature of 300°. Considerable confidence is placed in these runs using the synthetic method; indeed it appears such a promising method that it is being used in another research in this system in the temperature range 300 to 400°.

Summary

About fifty determinations of the solubility of gold in mercury have been made, in the temperature interval 200 to 300°, with a modified solubility tube and an air-bath. No maximum in the solubility curve is found, the results being confirmed by six supplementary runs using the synthetic method.

ROCHESTER, NEW YORK

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

THE COMPRESSIBILITY ISOTHERMS OF HELIUM AT TEMPERATURES FROM –70 TO 200° AND AT PRESSURES TO 1000 ATMOSPHERES

BY R. WIEBE, V. L. GADDY AND CONRAD HEINS, JR.

RECEIVED FEBRUARY 12, 1931 PUBLISHED MAY 6, 1931

This is the eighth report of a series from this Laboratory concerning the physical properties at high pressures of gases and their mixtures that are of interest in the commercial synthesis of ammonia.[1] It was thought desirable to include helium in this program since its properties would assist in the solution of several problems of importance. The knowledge of the compressibility of a gas which is chemically inactive and only slightly adsorbed by most catalysts will aid greatly in the determination of the adsorption of various gases on catalysts at high pressures. It will also be of value in the theoretical study of gases under high pressures.

The gas was obtained from the Amarillo Helium Plant of the U. S.

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[1] (a) Bartlett, THIS JOURNAL, 49, 65 (1927); (b) 49, 687 (1927); (c) 49, 1955 (1927); (d) Bartlett, Cupples and Tremearne, *ibid.*, 50, 1275 (1928); (e) Bartlett, Hetherington. Kvalnes and Tremearne, *ibid.*, 52, 1363 (1930); (f) 52, 1374 (1930); (g) Kvalnes and Gaddy, *ibid.*, 53, 394 (1931).

Bureau of Mines and was 97.8% pure when delivered, the impurities being nitrogen and traces of methane. The crude helium was expanded into a gas-holder through a copper trap filled with charcoal cooled by liquid air. After this operation the analysis indicated an average purity of about 99.5%. The partly purified gas was compressed to about 125 atmospheres, passed under pressure through copper alloy traps containing charcoal kept at liquid air temperature, and finally stored in "200-foot" cylinders until ready for use. The compressibility of the final product did not change when a charcoal trap was put in the line at a point just before the gas entered the high pressure pipet. Kefractometric analysis by the Bureau of Standards[2] indicated a purity of 100% with an experimental accuracy of 0.05%. Altogether, nine cubic meters of gas were purified during the course of the experiment.

Method and Apparatus

The general procedure and the type of apparatus have been described by Bartlett and others.[1b,1d,e,3] The high pressure measurements were made in the following pipets

Pipet	Volume
Chrome vanadium steel pipet[4]	23.081
Chrome vanadium steel pipet	4.095
Copper alloy pipet	3.998

The copper alloy pipet was used principally at the lower temperatures. With the help of Bartlett's values,[1d] the pipets were calibrated at 0° with hydrogen at 100, 200, 500 and 1000 atmospheres. The compressibility factor for helium at 0° and 100 atmospheres based on this calibration was found to be 1.0523 when expressed in Amagat units. (Amagat unit is defined as the ratio of PV/P_0V_0 where P and V are the pressure and volume, respectively, at some particular temperature and P_0 and V_0 the corresponding values at 0° and one atmosphere.) The value, 1.0523, was used for checking the volumes of the pipet at frequent intervals. Temperature measurements were made by means of two thermocouples, a five-junction copper-constantan couple for the low-temperature range and a three-junction chromel–X–copel for temperatures above zero degrees centigrade. Both had been calibrated and checked at the Bureau of Standards. The e. m. f. was read on a Leeds and Northrup Type K potentiometer which, including the standard cell, had also been calibrated previously by the Bureau of Standards.

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[2] Courtesy of S. F. Pickering, Bureau of Standards.

[3] For a more detailed description of the apparatus see Dilley and Edwards, Dept. of Agriculture, Circular No. 61, 1929.

[4] Composition of chrome vanadium steel: Cr, 1.3%; V, 0.2%; C, 0.2–0.3%. Composition of copper alloy: Cu, 65.00%; Fe, 2.60%; Mn, 6.03%; Zn, 21.69%; Al, 5.72%; Pb, trace.

The old piston and cylinder of the 1000 atmosphere gage[1d] were replaced by new ones. The new piston diameter was 0.48824 cm. and that of the cylinder 0.48870 cm. at the point of equilibrium.

The newly equipped 1000 atmosphere gage was checked against the 200 atmosphere gage[1d] at 200 atmospheres and it was found that the calculated and experimental values checked better than 2 parts in 10,000 at 200 atmospheres. Temperatures were kept constant within 0.05". The accuracy of calibration of the high pressure pipets is estimated to be 0.03 of 1 . On the average at least three separate runs were made to determine each point. In the majority of cases the maximum deviation between the values obtained in each run was less than 0.05 of 1% ; but with the exception of three points at 200° (at 400, 600 and 800 atmospheres), where it was as high as 0.2, the maximum deviation did not exceed 0.1 of 1%. When plotting $\Delta \equiv V\left(\frac{PV}{RT} - 1\right)$[5] against temperature it was found that the above three points did not fall on a smooth curve, the first and third were about 0.2 of 1% too low while the second was the same amount too high. With the exceptions mentioned the general accuracy is estimated to be better than 0.1 of 1%. It is hoped at some later date to extend the measurements and determine the three points more accurately.

The experimental results of this investigation are presented in Table I and are expressed in Amagat units. Column 3 gives the direct experimental values; in Column 4 we have calculated the corresponding values from Equations 1–6 which were obtained from the experimental data by the method of least squares, throwing all the adjustment onto the measured volumes.[6] Finally in Columns 5 and 6 the values of Holborn and Otto[7] and Gibby, Tanner and Masson[8] are presented for comparison. The only other work at higher pressures was done by Bridgman,[9] who measured the compressibility of a known weight of 95.8% helium from 3000 to 15,000 kg./sq. cm. The absolute volume at 3000 kg./sq. cm. was unknown and the results given are relative to this unknown volume. He corrected his values for the impurity, assuming it to be nitrogen.

In conclusion the authors take pleasure in acknowledging the friendly cooperation of the staff of the Fixed Nitrogen Research Laboratory; especially we are indebted to Dr. R. T. Milner, who assisted us in the purification of helium.

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[5] For this method of plotting consult O. C. Bridgeman, THIS JOURNAL, 49, 1130 (1927).

[6] W. Edwards Deming, *Proc. Phys. Soc. London*, 42, 97 (1930); *Phil. Mag.*, 11, January, 1931.

[7] L. Holborn and J. Otto, *Z. Physik*, 33, 1 (1925).

[8] Gibby, Tanner and Masson, *Proc. Roy. Soc.* (London), A122, 283 (1929).

[9] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, 59, 173 (1924).

TABLE I

(1) $-70^\circ\ pv = 0.7438 + 0.0005322\ p - 0.00000004332\ p^2$
(2) $-35^\circ\ pv = .8721 + 0.0005296\ p - .00000004336\ p^2$
(3) $0^\circ = 1.00059 + 0.0005217\ p - .00000003876\ p^2$
(4) $50^\circ\ pv = 1.18480 + 0.00051043\ p - .000000035308\ p^2$
(5) $100^\circ\ pv = 1.3664 + 0.00050442\ p - .000000034889\ p^2$
(6) $200''\ pv = 1.73284 + 0.00047795\ p - .000000022518\ p^2$

Press., atm.	Temp., °C.	*pv* factors in Amagat units			
		Experimental	Calculated by Equations 1–6	Holborn and Otto[7]	Gibby. Tanner and Masson[8]
100	–70 ± 0 05	0.7964	0.7966	0.7964"	
200		.8490	.8485		
400		.9491	.9498		
600		1.0481	1.0475		
800		1.1417	1.1418		
1000			1.2327		
100	–50 ± 0 05	0.8699		.8696	
100	–35 ± 05	.9249	0 9246	.9245[a]	
200		.9759	.9763		
400		1.0769	1.0770		
600		1.1744	1.1743		
800		1.2682	1.2680		
900		1.3134	1.3136		
1000			1.3583		
100	0	1.0523	1 0524	1.0522	
200		1.1036	1.1027		
400		1.2026	1.2031		
600		1.3003	1.2996		
800		1.3924	1.3932		
1000		1.4838	1 4835		
100	50 ± 0.05	1.2348	1.2355	1.2346	1.2334
200		1.2859	1.2855		
400		1.3848	1.3833		
600		1.4768	1.4784		
800		1.5706	1.5705		
1000		1.6602	1.6599		
100	100 ± 0.10	1.4162	1.4165	1.4160	1.4141
200		1.4660	1.4659		
400		1.5635	1.5626		
600		1.6553	1.6565		
800		1.7481	1.7476		
1000		1.8359	1.8359		
100	200 ± 0 15	1.7803	1.7804	1.7806	
200		1.8283	1.8275		
400		1.9179	1.9204		
600		2.0152	2.0115		
800		2.0983	2.1008		
1000		2.1889	2.1883		

[a] Interpolated results.

Summary

The compressibility isotherms of helium have been measured at −70, −35, 0, 50, 100 and 200" up to 1000 atmospheres pressure.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

THE SYSTEM LITHIUM BROMATE-WATER

BY JOHN P. SIMMONS AND WILLIAM F. WALDECK

RECEIVED FEBRUARY 14, 1931 PUBLISHED MAY 6, 1931

According to A. Potilitzin,[1] crystallization of lithium bromate from aqueous solution results in the formation of a mixture of anhydrous and monohydrate crystals. On the other hand, P. Mylius and R. Funk[2] are of the opinion that the salt exists only in the anhydrous form. This conflict of opinion seemed to justify further investigation concerning the composition of solid phases which are capable of existence when lithium bromate and water are allowed to come to equilibrium at different temperatures.

Experimental

Preparation of Lithium Bromate.—Lithium bromate was made by bringing together solutions of lithium sulfate and barium bromate, titrating one against the other until a drop of either gave no precipitate. The filtrate from the barium sulfate was concentrated and upon cooling lithium bromate crystallized out. Analysis of the dried salt iodimetrically gave in duplicate analyses 99.50 and 100.0% lithium bromate.

Procedure

All solubility measurements were made by agitating lithium bromate with water in small Pyrex glass-stoppered tubes. Samples of from 0.5 to 1.5 cc. were drawn off by means of pipets into 15-cc. weighing bottles. The solutions were evaporated to dryness and the residues heated to constant weight at 110°.

Two sources of error occur in this method of analysis. The salt may suffer some decomposition during drying and there may be a loss of water by evaporation during the transfer of the solution from the solubility tube to the weighing bottle. These errors were shown to be negligible by the following experiments.

(1) 0.5909 g. of lithium bromate was placed in a weighing bottle, water added, then evaporated and the residue heated at 110° to constant weight. At the end of this treatment the weight of the residue was 0.5912 g.

(2) Water at 75° was transferred to a weighing bottle and allowed to stand exposed to the atmosphere for thirty seconds, during which time

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[1] Potilitzin, J. Russ. *Phys.-Chem. Soc.*, 22, i, 391 (1891).

[2] Mylius and Punk, *Ber.*, 30,1718 (1897).

there was a loss of 1.6 mg. Since ten seconds is the average time for transfer of a sample of solution, it is reasonable to assume that the loss in the case of pure water for this latter interval would be about 0.5 mg. Moreover, the solutions contained about one-third molar quantities of the salt, so that due to this fact evaporation ought to be reduced a further one-third or to about 0.2 mg. It is obvious then that errors due to the above sources may be considered negligible.

In the solubility measurements from 5 to 53° inclusive, automatically controlled water thermostats were used. At the higher temperatures a saturated solution of calcium chloride, covered with a layer of oil, was placed in a 3-liter beaker. The latter was placed in an oven heated by gas and controlled by hand, served as a thermostat. The calcium chloride solution and the system being studied were stirred by wind turbines until equilibrium was attained. The lower temperatures were maintained constant within 0.02° and the higher within 0.10°. Equilibrium appeared to be reached quickly, usually in about three hours. The metastable point shown on the curve at 30° was obtained by allowing a solution saturated at 100° to cool to 30° over a period of eight hours. This solution was kept at 30° for four hours without stirring and then analyzed. The point so obtained fell so well on a continuation of the anhydrous curve that it is reasonably certain that it is very close to the true value.

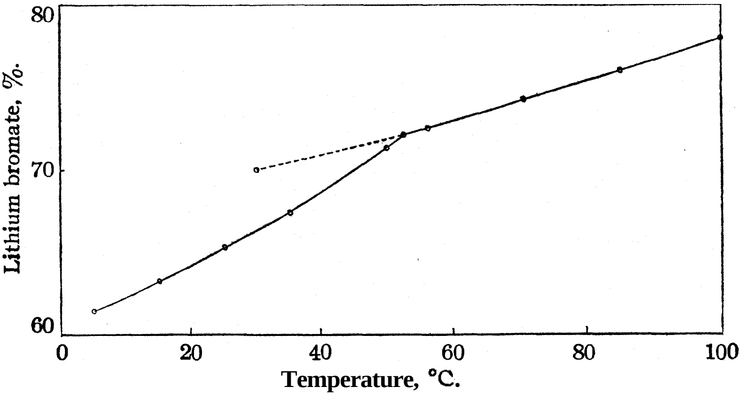

Fig. 1.—Solubility of lithium bromate in water.

The results of these measurements are given in the table and when plotted the curve of Fig. 1 is obtained.

Temp., °C.	% $LiBrO_3$	Temp., °C.	% $LiBrO_3$
5	61.6	53	72.4
15	63.3	56	72.6
25	65.4	70.5	74.3
35	67.5	85	76.2
50	71.5	100	78.0

An inspection of the curve in Fig. I shows a distinct break at about 52° and proves the existence of at least two solid phases. These results were obtained from the nndersaturated side only as the salt showed a great tendency to form supersaturated solutions.

To determine the composition of the solid phases, moist crystals which had come out of solution at room temperature were placed in a desiccator with anhydrous lithium bromate until no further loss was observed. Analysis of this material showed 0.995 and 1.008 molecules of water to one molecule of lithium bromate, in other words, the monohydrate. Crystals grown at 55° were small brilliant pyramids and upon analysis proved to be anhydrous lithium bromate. It is therefore evident that the two solid phases involved in this system are lithium brornate monohydrate, which is stable below 52°, and anhydrous lithium bromate stable above this temperature.

The determination of the transition point of lithium bromate–lithium bromate monohydrate was also made by cooling a solution saturated at 80° and, although supersaturation gave some difficulty, a number of results were obtained which gave an average figure of 50.8°. The agreement between this value and the one obtained by the solubility method may be considered good in view of the great viscosity of the solutions, the slight increase in solubility of the anhydrous lithium bromate with increase in temperature, and the marked tendency to form supersaturated solutions.

Attempts to determine the melting point of anhydrous lithium bromate by direct measurement gave an average of 248'. This, however, is low as some decomposition was observed. Extrapolation of the solubility curve indicated a melting point of 260'.

Summary

1. The solubility of lithium bromate in water has been determined over the range of temperature 5–100°.
2. Lithium bromate may exist in contact with its aqueous solutions as the monohydrate or as anhydrous salt.
3. The transition temperature lies between 50.8 and 52°.
4. The melting point of anhydrous lithium brornate lies between 248 and approximately 260°.

NEW YORK, N Y

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

THE ABSORPTION SPECTRUM AND PHOTOCHEMICAL DECOMPOSITION OF HYDRIODIC ACID

BY G. K. ROLLEFSON AND J. E. BOOHER

RECEIVED FEBRUARY 16, 1931 PUBLISHED MAY 6, 1931

The photochemical decomposition of hydriodic acid has been the subject of investigation from time to time for fifty years. The first mention of the reaction was by Lemoine[1] but the first detailed investigation was carried out by Bodenstein.[2,3,4] The quantum yield was determined by Warburg[5] for the wave lengths 2070, 2530 and 2820 Å. and found to be approximately two. This value was found to hold for wave lengths slightly greater than 3000 Å. by Bodenstein and Lieneweg. Coehn and Stuckardt[6] have investigated the reaction in quartz, uviol and Jena glass vessels using a quartz mercury arc as a source of light and found that the reaction occurred in all the vessels but was markedly slower in those of glass than in the quartz or uviol.

The absorption spectrum has been studied by several investigators,[6,7,8] who report essentially the same results, namely, a continuous absorption extending from 3340 Å. toward shorter wave lengths. Bodenstein and Lieneweg report slight absorption as far as 3600 Å.

These results have led to the decomposition being ascribed to the dissociation of an hydriodic acid molecule into a normal hydrogen atom and an iodine atom in the $^2P_1$ state followed by the reaction of the hydrogen atom with a second molecule of hydriodic acid. The iodine atoms produced combine to form molecules either by triple collision in the gas phase or at the walls. This explanation seems adequate for those wave lengths transmitted by quartz or uviol glass but in the case of decomposition in ordinary glass vessels we must assume either another mechanism, since the reported absorption is beyond the transmission limit of ordinary glass, or else the absorption must extend considerably beyond the limit given above. The observation of Salant and Sandow in their work on the Raman effect for hydriodic acid gas[9] that the 4047 Å. line of the mercury arc caused decomposition emphasizes this fact. The experiments described in this paper were designed to clarify the situation concerning this reaction in the long wave length region.

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[1] Lemoine, *Ann. chim. phys.*, [5], 12, 145 (1877).

[2] Bodenstein, *Z. physik. Chem.*, 22, 23 (1897); [3] 85, 329 (1913).

[4] Bodenstein and Lieneweg, *ibid.*, 119, 123 (1926).

[5] Warburg, *Sitzb. preuss. Akad. Wiss.*, 314 (1916); 300 (1918).

[6] Coehn and Stuckardt, *Z. physik. Chem.*, 91, 722 (1916).

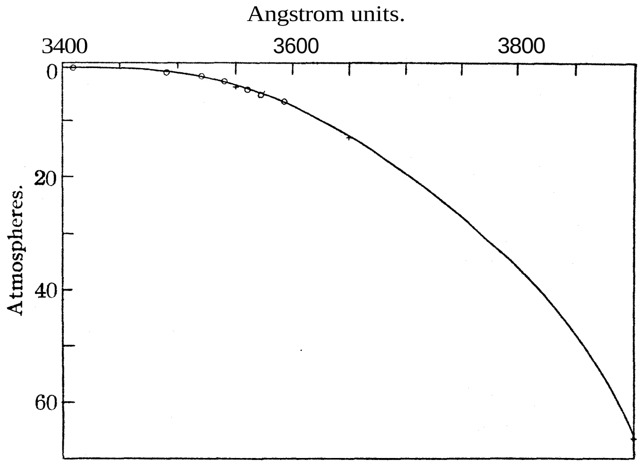
[7] Bonhoeffer and Steiner, *ibid.*, 122, 187 (1926).

[8] Tingey and Gerke, THIS JOURNAL, 48, 1838 (1926).

[9] Salant and Sandow, *Phys. Rev.*, 6, 1591 (1930).

The hydriodic acid used in the experiments we have performed was prepared by dropping a concentrated solution of the gas onto phosphorus pentoxide. The gas evolved was purified by passing it through a tube filled with phosphorus pentoxide and condensed with liquid air. It was distilled from the solid state, condensed in a tube the walls of which were covered with a film of mercury and this process was repeated several times. The final product was distilled into the reaction vessels or absorption tubes as needed. A water white product was obtained.

The first tests were to determine whether the decomposition could be sensitized by iodine. For this purpose several tubes of Pyrex glass were filled with the gas to one atmosphere pressure and various amounts of iodine added. These were illuminated by a bank of tungsten filament lamps for two days at a temperature of approximately 175° and the amount of decomposition determined by absorbing the iodine and hydriodic acid and measuring the residual hydrogen. The results showed no sign of any sensitization by the iodine, which is in agreement with the observation made by Bodenstein and Lieneweg at one pressure of iodine.



○, Gaseous hydriodic acid; +, liquid hydriodic acid.

Fig. 1.

In order to determine whether any decomposition was caused by visible light, three tubes were filled with pure hydriodic acid gas. One of these tubes was left in the dark and the other two were exposed to sunlight for about two weeks. One was surrounded by water and the other by a solution of quinine sulfate, which absorbed all light of wave length less than 4050 Å. On opening the tubes it was found that there had been no reaction in the tube left in the dark or in the one surrounded by the quinine sulfate solution, but the third one showed about 25% decomposition. This indicated that the decomposition must be attributed to absorption of light of wave length less than 4050 Å.; therefore we turned our attention to an investigation of the absorption in this region.

As we were primarily interested in determining whether the absorption extended to longer wave lengths than 3300 Å., it was possible to carry out the observations using vessels of Pyrex glass. The absorption spectrum of the gas was determined using a tube 175 cm. long with an internal diameter of 1.5 cm., and the pressure of the gas was varied from 1 to 8.5 atmospheres. The source of light was a 6-volt, 108-watt tungsten filament lamp which gives a continuous spectrum extending to approximately 2700 Å. The absorption tube, however, did not transmit wave lengths shorter than 3200 Å. The spectra were photographed with a Hilger quartz spectrograph. The absorption was perfectly continuous and at the highest pressure the edge of the blackening on the plate appeared at approximately 3550 Å. The variation in the absorption with pressure is shown in Fig. 1 by plotting the limit of the blackening on the photographic plate against the pressure. It is apparent that the absorption extends considerably beyond the limit of 3340 Å. given in the literature. Furthermore, it is obvious from the trend of the points that the limit of the absorption has not been reached even at the highest pressures used. The absorption for greater concentrations of hydriodic acid was carried out using the liquid. That such measurements could be used to extend the measurements on the gas was shown by comparing the absorption of a one-centimeter thick layer of liquid with the absorption of a layer of gas having the same value for the concentration times the thickness, *i.* e., a column 175 cm. long at a pressure of 4.4 atmospheres.

The absorption appeared to be identical for both conditions so the measurements were extended using the liquid up to a layer fifteen centimeters deep. The results were calculated to equivalent gas pressures in the long tube and plotted with the data on the gas in Fig. 1. The points plotted are for exposures of twenty seconds. From the curve we see that the absorption extends at least as far as 3900 Å. With shorter exposures a limit between 3950 and 4000 Å. was reached.

From the results which have just been given it is apparent that the absorption limit of 3340 Å. given in the earlier work is not a true limit characteristic of the gas. Such being the case, the interpretation of the absorption limit as corresponding to the energy of dissociation of the HI molecule into a normal hydrogen and an excited iodine atom becomes invalid. By this we do not mean that there is no absorption corresponding to such a process but rather that the observed absorption is due to a combination of this process with a dissociation into normal atoms. The value for the heat of dissociation of HI into normal atoms as calculated from thermal data is 69,000 cal. or 3 volts. The energy necessary to raise an iodine atom to the first stage of excitation is 0.95 volt. From these data it is readily calculated that the longest wave length which should dissociate the molecule into a normal hydrogen atom and an excited iodine atom is 3120 Å., whereas the value for both atoms in the normal state is 4120 Å. On this basis we should interpret the continuous absorption found between 3120 and 4000 Å. as causing a dissociation of the molecules into normal atoms, the excess energy going into kinetic energy of the atoms. The absorption at wave lengths less than 3120 Å. may be due partly to this process and partly to dissociation plus activation of the iodine, with the excess energy going into translational energy of the atoms.

The occurrence of two absorption processes of this type differing only in the excitation of the iodine atom is similar to the behavior of sodium iodide[10] except that in the latter case the intensity distribution was such that two well-defined maxima were readily distinguished. In the present case the

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[10] Franck, Kuhn and Rollefson, *Z. Physik,* 43, **155 (1927)**.

intensity distribution may be explained by assuming that the potential energy curves[11] for the normal and two excited states are as shown in Fig. 2. The curve A represents the normal state with a strong chemical binding, which is to be correlated with the relatively large value for the magnitude of the fundamental vibration quantum, ν (cm.$^{-1}$) = *2233,* found by Salant and Sandow[9] in the Raman spectrum of the gas. The upper states B and C represent much weaker bindings with the minima of the potential curves lying at a much greater separation of the nuclei than for A. Due to the magnitude of the vibration quantum in state A the absorption will be almost entirely from the zero or first vibrational states. On our diagram this is represented by the region between the vertical lines *ab* and *cd.* The portions of the curves B and C lying between these lines represent energies greater than the heats of dissociation of the respective states and therefore when absorption occurs we find it to the short wave length side of the minimum energy necessary for dissociation.

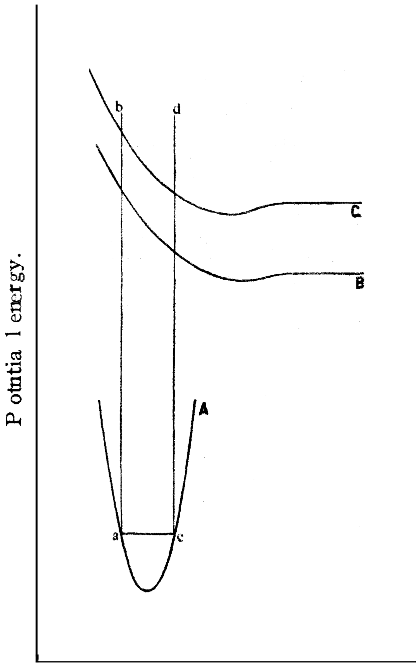

Fig. 2.

The dissociation products for curve B are normal atoms and for C a normal hydrogen atom and excited iodine atom. No dissociation products have been indicated for the lowest state, A, as the available evidence does not allow a definite decision. From the fact that HI shows an infra-red rotation and rotation–vibration spectrum in absorption, we may conclude that the binding is fairly polar in character. It is quite likely that in the zero and first vibrational levels the molecule may be considered as an example of ionic binding.

The mechanism of the photochemical decomposition is essentially the same for all effective wave lengths. The first step is

$$HI + h\nu = H + I \text{ or } I^*$$

followed by

$$H + HI = H_2 + HI$$

and the recombination of the iodine atoms. Since the iodine atoms do not enter into any reaction affecting decomposition, it makes no difference whether the iodine atom formed in the initial step is activated or not.

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

The slowness of the reaction in glass vessels is to be attributed to the small absorption coefficient for wave lengths transmitted by glass.

Summary

It has been shown that the continuous absorption of hydriodic acid extends up to a wave length of 4000 Å. instead of terminating at 3340 Å. as reported by others. The absorption on the long wave length side of 3120 Å. has been interpreted as due to the dissociation of the molecule into normal atoms and that on the shorter wave length side as due to a dissociation with the iodine atom excited. The intensity distribution of the absorption has been discussed with reference to the potential energy curves for the normal and excited states of the molecule. The photochemical decomposition of hydriodic acid has been shown to be due to this absorption and the mechanism of the reaction has been discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ELECTROMETRIC AND CATALYTIC DETERMINATION OF HYDROGEN-ION CONCENTRATION. THE MEAN ACTIVITY COEFFICIENTS OF THE IONS OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS[1]

BY MARTIN KILPATRICK, JR., AND ELWYN F. CHASE[1a]

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In connection with some work on the dissociation constants of indicators in aqueous salt solutions it became necessary to have buffer solutions of known hydrogen-ion concentration. Most buffer systems are standardized in terms of hydrogen-ion activity, the determination being based on certain non-thermodynamic assumptions regarding diffusion potentials. Where the classical dissociation constant is known in a given salt solution, the hydrogen-ion concentration can be calculated. However, accurate values of the dissociation constants are known for few acids except in very dilute solutions. The purpose of the present work is to determine the hydrogen-ion concentration of a series of benzoate–benzoic acid buffers in aqueous solutions of potassium chloride by two different methods. At the same time the mean activity coefficient $\sqrt{f_{H^+} f_{B^-}}$ will be obtained. The method of determining $f_{H^+} f_{B^-}$ the product of the activity coefficients, is as follows. The thermodynamic dissociation constant is equal to

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[1] Paper Presented at the Indianapolis Meeting of the American Chemical Society, April, 1931.

[1a] Abstracted in part from the thesis of Elwyn F. Chase to be presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

$$Ka = \frac{a_{\mathrm{H}^+}\,a_{\mathrm{B}^-}}{a_{\mathrm{HB}}} = \frac{C_{\mathrm{H}^+}\,C_{\mathrm{B}^-}}{a_{\mathrm{HB}}}\,f_{\mathrm{H}^+}\,f_{\mathrm{B}^-}$$

If at constant temperature the solutions are always saturated in respect to benzoic acid, the activity of the molecular benzoic acid is constant in all solutions and its value can be obtained from the solubility in pure water taking into account only that part of the benzoic acid which is present as molecules. At 25° the ionic strength of the saturated benzoic acid solution is approximately 0.001 and the activity of the molecular benzoic acid can be set equal to its concentration within the limits of the error of measurement. The hydrogen-ion concentration is determined by the electrometric and catalytic methods, and the benzoate concentration is calculated from the stoichiometric composition of the buffer. The dissociation constant at zero electrolyte concentration can be determined from conductivity measurements. From these data we calculate the product $f_{\mathrm{H}^+}\,f_{\mathrm{B}^-}$.

The Electrometric Method

The method employed is the same as that used by Güntelberg and Schiodt[2] and is based on the principle of Bronsted[3] which has been so useful in kinetic problems: "If a salt solution acts as a solvent for other salts, present in concentrations small compared with that of the solvent salt, the variation in the solute system keeping the medium or solvent salt unchanged will not, as in the case of pure water solutions, invalidate the ordinary gas laws and make the mass action law inapplicable." In other words, the activity coefficients of the substances present in small amount are independent of the small quantities of these substances and are determined solely by the salt present in large amount. Thus if we have a set of solutions of low hydrogen-ion concentration in potassium chloride solutions of relatively high concentration, we can assume that the activity coefficient of the hydrogen ion in these solutions of high constant potassium chloride concentration is constant. The assumption of practically complete ionization of the hydrochloric acid gives us a set of standards of known hydrogen-ion concentration. If the hydrogen-ion concentration in the above solutions is 0.01 molar, we do not have to take into account the possible alkalinity of the potassium chloride, which can be kept under 1 X 10^{-4} M. These standards at various potassium chloride concentrations from 0.01 to 3.0 M were compared with the benzoate–benzoic acid buffers by means of the quinhydrone electrode. The activity coefficient of the hydrogen ion was kept the same in both the standard and the unknown by keeping the ionic strength the same in each, where potassium chloride contributed from 90 to 99% of the ionic strength in practically all cases. The cell measured was

$$\mathrm{Pt}\,\Big|\,Q\quad \begin{matrix} c\ \mathrm{HCl\ and} \\ (m-c)\ \mathrm{KCl} \end{matrix}\,\Big|\,\begin{matrix}\mathrm{Satd.}\\ \mathrm{KCl}\end{matrix}\,\Big|\,\begin{matrix} (m-b)\ \mathrm{KCl\ and} \\ b\ \mathrm{NaOOCC_6H_5\ ratd.\ with\ C_6H_5COOH} \end{matrix}\quad Q\,\Big|\,\mathrm{Pt}$$

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[2] Giintelberg and Schiodt, *Z. physik. Chem.*, 135,393 (1928).

[3] Brönsted, *Trans. Faraday Soc.*, **23,430 (1927).**

Under the conditions of the experiment the diffusion potential would be small.

Experimental Part

The buffers were prepared by adding potassium chloride and carbonate-free sodium hydroxide solutions to pure benzoic acid in glass bottles and rotating the mixture in a thermostat at 25.15 ± 0.01° until saturated with benzoic acid. It was found that Kahlbaum benzoic acid could be used without further purification. The acid was rotated in the bath for twenty-four hours, a sample of the saturated solution was removed and the acid concentration determined by titration with sodium hydroxide in an atmosphere free from carbon dioxide, using phenol red as indicator. The residue of benzoic acid was then rotated with more water and the solubility redetermined. This was repeated several times and in all cases the determinations agreed within 0.5%. To be certain that twenty-four hours of rotation was sufficient, determinations were made on samples rotated for varying lengths of time up to two hundred hours, without an appreciable change in solubility. Table I summarizes the results of these determinations and Table II gives the values obtained by other workers.

TABLE I

SOLUBILITY OF BENZOIC ACID IN WATER AT 25.15°

Sample	Hours *rotated*	C_6H_5COOH, moles per liter	Remarks
1	..	0 02773	
2	..	.02776	
3	24	02783	Fresh sample
3	24	02773	Fresh sample
4	96	,02781	Fresh sample
4	96	,02778	Fresh sample
5	166	.02780	Fresh sample
5	166	,02780	Fresh sample
6	217	,02784	Residue from 4
6	217	.02788	Residue from 4
7	72	02778	Residue from 3
7	72	02782	Residue from 3
8	71	.02790	Twice extracted residue
8	71	02783	Twice extracted residue
	Av.	02781	

TABLE II

SOME PREVIOUS DETERMINATIONS OF THE SOLUBILITY OF BENZOIC ACID IN WATER AT 25°

Solubility, moles per liter	Observer
0.028082	Paul, Z. *physik. Chem.*, 14, 105 (1894).
.02793	Noyes and Chapin, THIS JOURNAL, 20,751 (1898).
,02796	Hoffmann and Langbeck, Z. *physik. Chem.*, 51, 385 (1905).
.02799	Freundlich and Seal, *Kolloid* Z., 11, 257 (1912).
.02791	Rørdam, *Thesis, University* of *Copenhagen,* 1925.
,02781	Larsson, *Z. anorg. Chem.*. 155,247 (1928).

The potassium chloride was Kahlbaum "with certificate of guarantee" and the small quantities of alkali present could be neglected in the well-buffered solutions. The standard hydrochloric acid solutions were prepared from weighed amounts of potassium chloride and constant boiling hydrochloric acid made according to Hulett.

The cell as shown in Fig. 1 consisted of two cylindrical electrode vessels A and A' of Pyrex glass connected through stopcocks B and B' to the reservoir C for the saturated potassium chloride solution. The electrodes D and D′ were pieces of bright platinum foil which were cleaned and heated to redness just before using. Constrictions at E and E′ served to hold cotton plugs on which the quinhydrone was placed. Through the inlets F and F′ nitrogen was passed into the solution to remove dissolved oxygen and to keep the solutions stirred, while the tubes G and G' served for adjusting the junctions H and H′ and for emptying the vessels. The apparatus was set in a thermostat at **25.15** ± 0.05°.

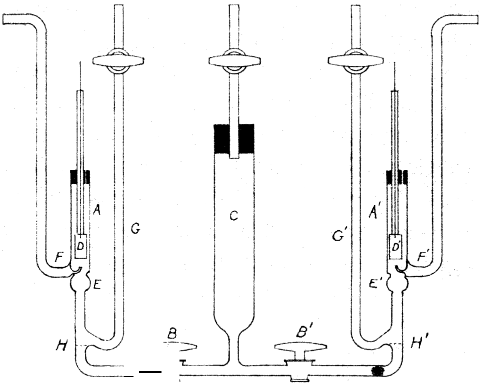

Fig. 1 –The *quinhydrone* **cell.**

The method of carrying out a determination was as follows. The standard hydrochloric acid solution in potassium chloride and the buffer solution were placed in **A** and A', respectively, and carbon dioxide-free nitrogen was bubbled through the solutions. By gentle suction at G and G′ the junctions were made at H and H'. Quinhydrone was added from a spatula and the electrodes were set in place. The potential difference was measured by means of a Type K Leeds and Northrup potentiometer and a suitable galvanometer. The readings were usually constant to 0.0001 volt for the first fifteen minutes. Over the range studied **0.0001** volt represents approximately **0.3%** in hydrogen-ion concentration. In general the results were reproducible to 1% in hydrogen-ion concentration.

The cell reaction is

$$\textit{Quinhydrone} + 2\mathrm{H}^+ + 2e \longrightarrow \textit{Hydroquinone}$$

and the potential is given by

$$E = E_0 + \frac{RT}{2F}\ln\frac{a_{\mathrm{Hy}}}{a_{\mathrm{Q}}|a_{\mathrm{H}}^2} = E - \frac{RT}{F}\ln a_{\mathrm{H}} + \frac{RT}{2}\ln\frac{f_{\mathrm{Hy}}}{f_{\mathrm{Q}}}$$

since $C_{\mathrm{Hy}} = C_{\mathrm{Q}}$. The last term is the salt error which cancels out in our experiments because the activity coefficients in both solutions are equal. Since at constant potassium chloride concentration we may replace the ratio of the activities of the hydrogen ion by the ratio of the concentrations and

$$AE = \frac{RT}{F} \ln \frac{C'_{H^+}}{C_{H^+}} = 0.05914 \log \frac{C'_{H^+}}{C_{H^+}}$$

and

$$\log C'_{H} = \frac{AE}{0.05914} + \log C_{H^+}$$

where C_{H^+} is the known concentration of the hydrogen ion in the standard solution of hydrochloric acid in potassium chloride and C'_{H^+} is the hydrogen-ion concentration of the buffer solution.

Table III gives the results of these determinations. The concentration of potassium chloride in each standard solution can be obtained by subtracting the hydrogen-ion concentration as given in Column **2** from the total electrolyte concentration as given in Column 1. Similarly the difference between Column 1 and the concentration of the sodium ion in Column 5 gives the concentration of potassium chloride for the buffer solutions.

TABLE III

THE ELECTROMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION (25.15')

Standard solution			Buffer				
Electrolyte $KCl + HCl$, moles per liter	H_3O^+, moles per liter × 10^5	E. m. f., volts	H_3O^+, moles per liter × 10^5	Na^+, moles per liter × 10^5	$C_6H_5COO^-$, moles per liter × 10^5	$C_{H^+}C_{B^-}$ × 10^7	Av.
0.1000	1035	0.07859	48.5	480.9	529.4	25.6	
.1000	1035	.08869	32.8	734.5	767.3	25.6	
.1000	1035	.09553	25.1	1000	1025	25.8	
.1000	1035	.11188	13.3	1852	1865	24.9	
.1000	1035	.11187	13.3	1852	1865	24.9	25.5
.2000	933.1	.08479	34.3	727.3	761.6	26.1	
.2000	933.1	.10452	15.9	1647	1660	26.4	
.2000	933.1	.12289	7.79	3293	3301	25.7	26.1
.3000	878.5	.10343	15.6	1647	1663	25.9	
.3000	878.5	.10395	15.0	1729	1744	26.1	
.3000	878.5	.11364	10.5	2470	2481	26.0	
.3000	878.5	.12082	7.94	3293	3301	26.2	26.1
.4000	1050	.10811	15.6	1647	1663	25.9	
.4000	1050	.10911	15.0	1729	1744	26.1	
.4000	1050	.11888	10.2	2470	2480	25.3	
.4000	1050	.12581	7.82	3293	3302	25.8	25.8
.5000	1002	.06490	80.1	240.4	320.5	25.6	
.5000	1002	.11183	12.9	1976	1989	25.8	
.5000	1002	.13265	5.72	4323	4329	24.8	
.5000	1002	.13241	5.78	4323	4329	25.0	25.3
.6000	999.3	.10779	15.0	1647	1662	24.9	
.6000	999.3	.10905	14.3	1729	1743	24.9	
.6000	999.3	.11818	10.0	2470	2480	24.8	
.6000	999.3	.11837	9.94	2470	2480	24.6	24.8

TABLE III (*Concluded*)

Standard solution			Buffer				
Electrolyte KCl + HCl, moles per liter	H_3O^+, moles per liter $\times 10^5$	E. m. f., volts	H_3O^+, moles per liter $\times 10^5$	Na^+, moles per liter $\times 10^5$	$C_6H_5COO^-$, moles per liter $\times 10^5$	$C_{H^+} C_{B^-} \times 10^7$	Av.
0.7000	1014	0.10944	14.3	1647	1661	23.7	
.7000	1014	.11953	9.64	2470	2480	23.9	
.7000	1014	.12742	7.09	3293	3300	23.4	
.7000	1014	.12761	7.04	3293	3300	23.2	**23.6**
.9000	1016	.11087	13.5	1647	1661	22.4	
.9000	1016	.12169	8.88	2470	2479	22.0	
.9000	1016	.12187	8.84	2470	2479	21.9	
.9000	1016	.12932	6.60	3293	3300	21.8	
.9000	1016	.12936	6.58	3293	3300	21.7	22.0
1.012	961.0	.09446	24.3	850	874.3	21.2	
1.012	961.0	.10551	15.8	1318	1334	21.1	
1.012	961.0	.11090	12.8	1647	1660	21.2	
1.012	961.0	.11606	10.5	1976	1987	20.8	
1.012	961.0	.13045	5.97	3293	3299	19.7	
1.012	961.0	.12885	6.36	3330	3336	21.2	
1.012	1067	.13950	4.66	4323	4328	20.2	
1.012	961.0	.13988	4.14	5000	5004	20.8	20.8
1.500	972.0	.07336	55.8	240.4	296.2	16.5	
1.500	972.0	.12026	8.98	1852	1861	16.7	
1.500	972.0	.12270	8.17	1976	1984	16.2	
1.500	972.0	.14387	3.58	4323	4327	15.5	
1.500	972.0	.14323	3.67	4323	4327	15.9	**16.2**
2.000	1122	.10201	18.3	617.5	635.8	11.6	
2.000	1122	.12106	10.1	1235	1245	12.6	
2.000	1122	.13213	6.53	1852	1859	12.1	
2.000	1122	.15408	2.78	4298	4301	12.0	
2.000	1122	.15380	2.81	4298	4301	12.1	12.1
2.500	996.5	.10815	14.8	617.5	632.3	9.35	
2.500	996.5	.12580	7.42	1235	1242	9.23	
2.500	996.5	.13884	4.47	1976	1980	8.86	
2.500	996.5	.13897	4.45	1976	1980	8.81	
2.500	996.5	.13842	4.54	1976	1981	8.99	9.05
3.000	1040	.11659	11.1	586.0	597.1	6.64	
3.000	1040	.12955	6.69	988	995	6.65	
3.000	966.1	.12792	6.63	988	995	6.60	**6.63**

The Catalytic Method

The catalytic method has been used for the determination of hydrogen-ion concentration in a number of cases but as in the case of the electrometric and colorimetric methods a proper consideration of the electrolyte effect is necessary for accurate determinations. In addition, in choosing a suitable reaction we have to consider, as well as the effect of the hydrogen ion, possible catalytic effects of acids other than the hydrogen ion. Both

TABLE IV

THE ELECTROMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION AT 20°

Standard solution			Buffer					
Electrolyte $KCl + HCl$, moles per liter	H_3O^+, moles per liter X 10^5	E. m. f., volts	H_3O^+, moles per liter X 10^5	Na^+, moles per liter X 10^5	$C_6H_5COO^-$, moles per liter × 10^5	C_{H^+} C_{B^-} X 10^7	Av.	G. + S. av.
1.000	200	00292	62.8	200.0	262.8	16.5		
1.000	500	.06918	32.3	500.0	532.3	17.2	16 9	
2.000	500	.0828	18.7	500.0	518.7	9.81	9 81	
3 000	200	.0538	23.7	200.0	223.7	5.30		
3.000	500	.0977	10 5	500.0	510.5	5.36	**5.33**	5.16
NaCl								
1.000	200	.0299	61.3	200.0	261.3	16.0		
1.000	500	.0703	309	500.0	5309	16.4	16.2	
2.000	200	.0425	37.1	200.0	237.1	8.43		
2.000	500	0855	17.0	500.0	517.0	8.79	8 61	
3.000	200	.0600	18.6	2000	218.6	4.07		
3.000	500	.1078	8.5	500.0	508.5	4.32	4.20	4.18
4.000	200	.0810	8.10	200.0	208.1	1.69		
4.000	500	.1249	3 60	500.0	503.6	1.81	1.76	1.82
5.000	200	.1015	4.57	200.0	203 6	0.733		
5.000	500	.1481	1.40	500.0	501.4	0702	0.717	0.741

NOTE.—Table IV gives some measurements carried out by Mr. W. H. Berry at 20° which are given for comparison with the results of Guntelberg and Schiodt and to complete the values over the whole concentration range. They are not to be considered as accurate as the measurements of Giintelberg and Schiodt.

of these factors have been discussed in the recent paper of Bronsted and Grove.[4]

Bronsted and Wynne-Jones[6] used the rate of hydrolysis of diethyl acetal to determine the hydrogen-ion concentration of formic acid buffer solutions *at* ionic strengths up to 0.05. They showed that this reaction was not catalyzed by acids weaker than the hydrogen ion (H_3O^+) and Bronsted has calculated that in all cases the effect of acids stronger than the hydrogen ion (H_3O^+), such as hydrochloric acid, will hardly be detectable in aqueous solution.[6] In order to know the proportionality between the rate of reaction and the hydrogen-ion concentration for a given medium, Bronsted and Wynne-Jones determined the rate of reaction in a solution of hydrochloric acid in potassium nitrate and assumed that the same proportionality factor could be used for formic acid-sodium formate buffer solutions. A similar assumption has been used by previous workers.' However, as further studies of primary salt effect have been made for these zero type reactions (a reaction between an ion and a non-electrolyte), it has been

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[4] Bronsted and Grove, THIS JOURNAL, 52, 1394 (1930).

[5] Bronsted and Wynne-Jones, *Trans. Faraday Soc.*, **25, 59** (1929).

[6] Bronsted, *ibid.*, 24,630 (1928).

[7] See Kilpatrick, THIS JOURNAL, 48, 2091 (1926)

realized that although the effect is linear in conformity with the theory the magnitude of the effect between $\mu = 0.01$ and $\mu = 0.10$ for uni-univalent electrolytes is in many cases much greater than the 2 to 4% stated for the reactions studied previous to 1922.[8] For the decomposition of nitrosotriacetonamine catalyzed by hydroxyl ion, the effect between $\mu = 0.01$ and $\mu = 0.10$ is 7% when sodium chloride is the solvent salt.[7] For the hydration of ethylene oxide catalyzed by hydrogen ion it is 9% for the solvent salt sodium perchlorate over the same range of concentration.[9] In the hydrolysis of diazoacetic ester catalyzed by hydrogen ion it is 14% for the same solvent salt and for the hydrolysis of diethyl acetal it is 11% for potassium chloride and approximately 13% for sodium chloride and potassium nitrate. The last two values are from Bronsted and Wynne-Jones[5] and are doubtful in that the concentration of strong acid used was only 0.0008 M. Bronsted and Grove[4] extended these studies to other acetals studied originally by Skrabal[10] and found that the primary salt effect is large and varies with the individual salt to such an extent that one is confined to the determination of the hydrogen-ion concentrations of unbuffered solutions of weak acids where the electrolyte concentration is below $\mu = 0.01$.[11]

Our problem was to determine the hydrogen-ion concentration of the benzoate buffers up to 3.0 molar concentration of potassium chloride. A search of the literature failed to reveal a suitable reaction with a small electrolyte effect, so the hydrolysis of diethyl acetal was used. As already pointed out, the primary salt effect cannot be studied at 25° because we must deal with such low concentrations of strong acids that the results are uncertain. Our method consisted of determining the electrolyte (salt) effect at 0° where the reaction is slow enough to permit the use of 0.01 to 0.005 molar hydrochloric acid. By determining accurately the temperature coefficient, which from previous experience would be expected to be independent of electrolyte concentration,[12,7] the proportionality of the rate to the hydrogen-ion concentration for the various concentrations of solvent salt at 25.15° was calculated. Then by determining the rate of reaction with the benzoate–benzoic acid buffer solutions we obtained the hydrogen-ion concentration.

Experimental Method

The experiments at 0° were carried out in a dilatometer previously used for the determination of the rate of hydration of acetic anhydride.[13] It was

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[8] Bronsted, *Z. physik. Chem.*, **102,** 169 (1922).

[9] Bronsted, Kilpatrick and Kilpatrick, THIS JOURNAL, 51, 420 (1929).

[10] Skrabal, *Z. Electrochem.*, **33,** 322 (1927).

[11] Grove, THIS JOURNAL, 52, 1404 (1930).

[12] Rice and Lemkin, *ibid.*, 45, 1896 (1923).

[13] Kilpatrick, *ibid.*, **50,** 2891 (1928).

found very convenient to have the whole apparatus in a refrigerator room which was kept a few degrees above the freezing point of water. Two samples of acetal were used and gave the same results. Preparation A boiled between 102 and 103° (760 mm.), while preparation B was very carefully fractionated and boiled at 103° (759 mm.). Preparation B was completely free from acidic impurities. Table V gives the results of the experiments in various concentrations of potassium chloride at 0°.

TABLE V

THE ELECTROLYTE EFFECT ($t = 0.0°$)

KCl, moles per liter	HCl, moles per liter	μ, ionic strength	k_{observed}	$\frac{k_{\text{obs.}}}{C_{HCl}} = k_{H_3O^+}$
0.0	0.01315	0.013	0.0326	2.48[a]
.087	.01315	.10	.0372	2.74
.20	.00933	.21	.02885	3.08
.40	.00933	.41	.0391	3.73[a]
.60	.00395	.60	.0174	4.51[a]
1.0	.01247	1.01	.0742	6.08
1.5	.00395	1.50	.03312	8.38
2 0	.00658	2.01	.0715	10.87
2.0	.00395	2.00	.0445	11.25

[a] = acetal sample B

The salt effect from 0.01 to 0.10 molar is 10% and over the range studied changes from 2.48 to 11.25, a four-fold increase. Experiments at higher concentrations of potassium chloride show an even greater effect between 2 and 3 molar but these results are more uncertain than the others, due to the lower hydrochloric acid concentrations, and are not given here. In Fig. 2 $k_{H_3O^+}$ is plotted against the electrolyte concentration. The electrolyte

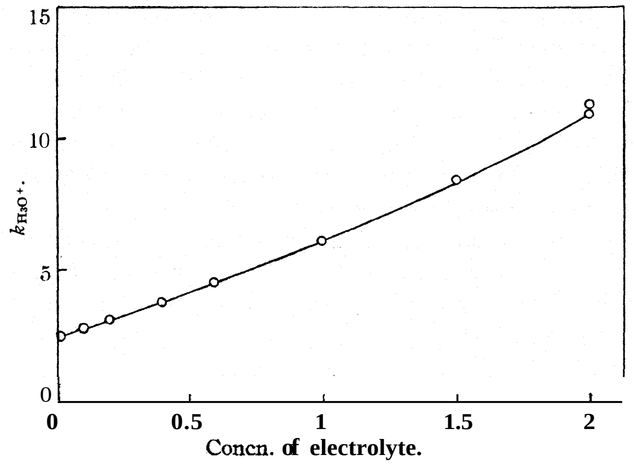

Fig. 2.—The electrolyte effect on $k_{H_3O^+}$.

effect is linear and for dilute solutions the experimental results can be expressed by the equation

$$k = 2.40 + 3.40\,c$$

where c represents the total equivalent electrolyte concentration. To emphasize again the dependence of the effect upon the individual nature of the salt, $k_{H_3O^+}$ for a solution 0.75 M in potassium nitrate is 4.34 as against 5.04 for the corresponding potassium chloride solution.

The temperature coefficient was determined by the two-thermostat method.[14] The reaction was followed dilatometrically, the reacting solutions being confined in two dilatometers similar in design to that used in the study of the hydration of ethylene oxide.[15] The dilatometers were placed in thermostats regulated to ±0.003° and at temperatures exactly five degrees apart as determined by a calibrated resistance thermometer. Portions of a solution of suitable acid concentration were placed in the mixing chambers of the dilatometers and after thermal equilibrium was established with the baths, acetal was added. The velocity constants were determined in the usual way. Although the hydrogen-ion concentrations were too small to be known accurately they were the same in both cases and the temperature coefficient was obtained directly from the velocity constants. The results are given in Table VI, which also contains the heat of activation E calculated from the Arrhenius equation.

TABLE VI

THE TEMPERATURE COEFFICIENT

KCl, moles per liter	0	0	0	0	1.0	2.0
$k_{25.00}/k_{20.00}$	1.870	1.893	1.887	1.894	1.923	1.944
E, cal. per degree	21,720	22,150	22,000	22,160	22,690	23,070

The temperature coefficient seems to increase slightly with increasing salt concentration but this may be due to experimental error and we have given E an average value of 22,300 calories from which we calculated $k_{25.15}/k_0 = 32.19$. An error of 1% in k_{25}/k_{20} means about the same percentage error in E, which would mean a possible error of 3% in $k_{25.15}/k_0$. The velocity constant $k_{H_3O^+}$ for 25.15' is determined by multiplying $k_{H_3O^+}$ for 0° for each electrolyte concentration by 32.19.

Table VII gives the results of the determinations of hydrogen-ion concentration in the buffer solutions. In Column 6 are given the hydrogen-ion concentrations as determined by the electrometric method.

The agreement between the two methods is fairly good, the catalytic method giving slightly lower values above 1 molar concentration of electrolyte. At higher electrolyte concentrations the deviations obtained are greater, apparently exceeding the experimental error. These differences

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[14] Rice and Kilpatrick, THIS JOURNAL, 45, 1401 (1923).

[15] Ref. 9, p. 428.

TABLE VII

THE CATALYTIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION

Total equivalent electrolyte, KCl + $C_6H_5COO^-$, moles per liter	Na^+, moles per liter × 10^5	k_{observed}	$k_{H_3O^+}$	$\frac{k_{\text{obs.}}}{k_{H_3O^+}}$ = H_3O^+, moles per liter × 10^6	E. m. f. method, H_3O^+, moles per liter × 10^6	$C_{H^+} C_{B^-}$ × 10^7
0.0013[a]	0.0	0.1017	7 7 4	131.6		17.0
.0998	734.5	.02960	88.3	33.6	32.8	25.8
.2000	741.0	.03510	99.2	35.4	35.5	27.4
.3000	1729	01730	112 7	15.4	15.0	26.8
.4000	1729	.01856	120.1	15.5	15.0	26.9
.5000	1976	.01688	135.2	12.5	12.9	24.9
.6000	1729	.02036	145 2	14.0	14.3	24.4
.8000	1729	.02166	167.8	12.9	13.3	22.5
1.012	3293	.01143	195.7	5.84	5.97	19.3
1.500	1976	.02070	270	7.69	8.17	15.3
2.000	4298	.00993	362	2.74	2.78	11.8

[a] Saturated solution of benzoic acid.

are being considered further in connection with the assumptions upon which both methods are based, in particular the assumption of practically complete ionization of the hydrochloric acid in potassium chloride solutions and the assumption that the reaction is a pure hydrogen-ion catalysis.

TABLE VIII

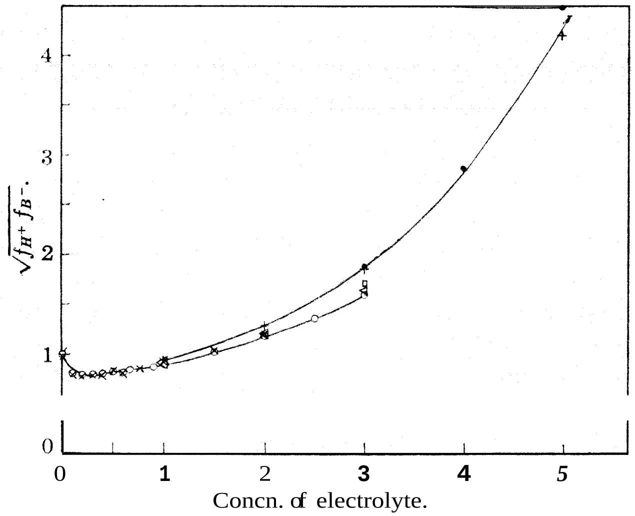
THE MEAN ACTIVITY COEFFICIENT OF THE IONS OF BENZOIC ACID

Total electrolyte concentration KCl + C_6H_5COONa	25° $\sqrt{f_{H^+} f_{B^-}}$ from e. m. f.	25° $\sqrt{f_{H^+} f_{B^-}}$ from catalysis	20° $\sqrt{f_{H^+} f_{B^-}}$ from e. m. f.. Berry	20° $\sqrt{f_{H^+} f_{B^-}}$ G. + S.
0.001	. .	0.98		
.1	0.81	.805		
.2	.80	.78		
.3	.80	.79		
.4	.805	.79		
.5	.81	.82		
.6	.82	.83		
.7	.84			
.8	. .	.86		
.9	.87	. .		
1.01	.90	.93	0.92	
1.5	1.02	1.04	. .	
2.0	1.18	1.19	1.21	
2.5	1.36		. .	
3.0	1.59		1.64	1.70
NaCl + C_6H_5COONa				
1.0			0.94	
2.0			1.29	
3.0			1.85	1.89
4.0			2.85	2.86
5.0			4.19	4.48

The values of the mean activity coefficients of the ions of benzoic acid can be calculated from the following equation

$$\sqrt{f_{H^+} f_{B^-}} = \sqrt{\frac{Ka\, a_{HB}}{C_{H^+}\, C_{B^-}}}$$

the product $C_{H^+} C_{B^-}$ being given in Tables III and VII. Ka is set equal to 6.31 × 10^{-5}.[16] The value for the activity of the molecular benzoic acid is obtained from the solubility of benzoic acid in water by subtracting the small part present as ions, a_{HB} being set equal to 0.0265. Table VIII gives the values of $\sqrt{f_{H^+} f_{B^-}}$ from the electrometric and catalytic methods at the various concentrations of electrolyte (potassium chloride and benzoate). For comparison we have included the values of Berry and those of Güntelberg and Schiodt in sodium chloride solutions.



⊙, E. m. f., 25°; X, catalytic, 25°; ◁, Berry, 20°; □, G. + S., 20° (in KCl); +, Berry, 20°; ●, G. + S., 20° (in NaCl); ♂, Simons.

Fig. 3.—Mean activity coefficients of the ions of benzoic acid in KCl and NaCl solutions.

From Table VIII and Fig. 3 it is to be noted that the mean activity coefficient is higher in solutions of sodium chloride than in the corresponding solutions of potassium chloride in all cases. Güntelberg and Schiodt[2] interpret this as being due to the predominance of the "salting out" effect over that of interaction.

In another communication will be given the activity coefficients of the molecular acid determined from solubility measurements and K_c, the

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[16] This value has been determined by J. K. Simons by conductance measurements and will be the subject of another communication.

classical dissociation constant. At that time a comparison will be made of the activity coefficients of benzoic acid and those of other acids.

Summary

The hydrogen-ion concentrations of benzoic acid–benzoate buffers saturated with benzoic acid in potassium chloride solutions have been determined by two independent methods.

The results obtained by the catalytic method are in agreement with those determined by the quinhydrone electrode.

In both cases "electrolyte effects" have been considered.

The mean activity coefficients of the ions of benzoic acid have been determined in potassium and sodium chloride solutions.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

THE SOLUBILITIES OF CERTAIN SLIGHTLY SOLUBLE ORGANIC COMPOUNDS IN WATER[1]

BY PAUL M. GROSS AND JOHN H. SAYLOR

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As part of a general investigation of solubility in relation to polar character, the solubilities of a number of slightly soluble organic compounds in water have been determined. Since the final interpretation of the data from this standpoint must await the completion of certain supplementary measurements now under way, it seemed advisable to publish the solubility data at this time since no reliable values for the solubilities of these substances are available in the literature.

Experimental

Method.—The saturated solutions of the substances were prepared by shaking in a thermostat and were analyzed by means of an interferometer. The instrument used was a combination liquid and gas interferometer made by Zeiss.

The procedure was a modification of that of Adams[2] and of Gross.[3] The standard or reference solutions were made by dissolving weighed amounts of the substance under investigation in approximately 1000 g. of water. In the case of liquids, a vial containing a weighed amount of the substance was dropped into the weighed sample of water contained in a glass stoppered bottle. During the weighing, the vial was closed with a cork stopper and care was taken that the liquid did not come in contact with the stopper. The stopper of the vial was removed, the vial quickly

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[1] Based upon a thesis submitted by John H. Saylor in partial fulfilment of the requirements for the Ph.D. degree at Duke University.

[2] Adams, THIS JOURNAL, 37, 1181 (1915).

[3] Gross, *ibid.*, 51, 2362 (1929).

dropped into the water and the bottle immediately stoppered. Solids were weighed out on a watch glass and quantitatively transferred to the bottle containing the water. The free space above the solutions was kept small enough to render negligible the error due to vapor losses. In most cases, this space was not more than 10 cc. per 1000 g. of solution. In the case of the less volatile liquids and solids, the vapor space was made somewhat larger in order to shorten the time of shaking necessary for complete solution. The bottles were placed in a shaker and shaken until all of the substance was dissolved. Inspection showed whether all of the drops of a liquid or particles of a solid had disappeared. The method, by which the proper concentrations to use for the standards were chosen, will be described below.

Three standard solutions, A, B and C were used whose concentrations were so chosen that the reading of the weakest against the strongest was not more than two hundred drum divisions. The concentrations of the standard solutions were usually about 0.25 or 0.3 that of the saturated solution. $\Delta C/\Delta R$, the value of a drum division in grams per 1000 g. of solution, was calculated from the difference between the concentrations of A and B and from the interferometer reading of A against B. $\Delta C/\Delta R$ obtained in the same fashion from A and C served as a check on the value obtained. In some cases B was also read against C. This gave not only an additional check on the value of $\Delta C/\Delta R$ but also checked the accuracy with which the solutions were prepared. An average value of $\Delta C/\Delta R$ was then used in the solubility measurements. Dry pipets were used for sampling the solutions. The interferometer chamber was dried after every determination by a stream of warm air.

The concentration difference between A and C was so chosen as to give a reading of not more than two hundred scale divisions, because for larger differences the drum reading is not a linear function of the concentration except in special cases.[4] In the present work the linearity of drum reading against concentration over the range of two hundred divisions was checked directly by plotting the readings of A against B and A against C against the corresponding concentrations. Within the limits of accuracy necessary, a straight line was obtained in all cases. Concordant values of $\Delta C/\Delta R$ also gave a direct test of the linear relationship.

The saturated solutions of a substance under investigation were prepared by shaking an excess of the liquid or solid with about 500 g. of water in thin-walled cylindrical flasks in a large water thermostat. The thermostat was regulated at 30 ± 0.01° and at 15 ± 0.02°. In all cases the flasks were shaken for at least twelve hours, and in most instances they were shaken for a longer period of time. Samples were then withdrawn from two or three different saturation flasks and read against water in the interferom-

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[4] Adams, This Journal, 37, 1181 (1915); Gans and Bose, *Z. Instrumentenk.*, 36, 137 (1916).

eter. Equilibrium was usually reached in less than twelve hours, as shown by the constancy of the readings of the saturated solutions at different time intervals. It was possible in most cases to reproduce the readings of the saturated solutions within two or three scale divisions of the interferometer drum. The values of $\Delta C/\Delta R$ were of the same order of magnitude for all aliphatic compounds. Also the values of $\Delta C/AR$ were of the same order of magnitude for all aromatic compounds.

The value of $\Delta C/AR$ in the case of a given aromatic compound could be employed to calculate approximately the amounts of substances necessary to make up the standard solutions of all other aromatic compounds. Likewise, the value of $\Delta C/\Delta R$ in the case of a given aliphatic compound could be used to calculate the amounts of substances needed to make up the standard solutions of all aliphatic compounds. The only other quantities needed were the readings of the saturated solutions of the substances in question. These readings when multiplied by $\Delta C/\Delta R$ would give the approximate concentrations of the saturated solutions. Then the amounts of substances which would give standard solutions of the desired concentrations could be calculated.

From the reading of the saturated solution and the average value of $\Delta C/\Delta R$, it was possible to calculate the extent to which the saturated solution would have to be diluted in order to give a reading of less than two hundred divisions when read against one of the standard solutions as a reference. Usually this difference was made about one hundred rather than two hundred divisions. The weight of water necessary for the dilution was put in a 500-cc. glass-stoppered volumetric flask. A two-holed rubber stopper carrying a glass siphon fitted with a stopcock was then placed in the saturating flask in the thermostat. The siphon was started by gently blowing into the flask. Enough of the saturated solution was allowed to siphon over and discarded to insure thorough rinsing of the siphon. Then a sample large enough to fill the volumetric flask to the mark was run into it. The sample was run in beneath the surface of the water in the volumetric flask in order to prevent loss by evaporation. The volumetric flask was immediately stoppered and weighed, thus giving the weight of the saturated solution added. The dilution of the saturated solution could then be calculated. A sample of this diluted solution was read in the interferometer against a sample of the standard solution. The standard solution chosen was usually the one whose concentration was between the standard with the lowest and the standard with the highest concentration, as the bottle containing this intermediate standard had had fewer samples removed from it. The concentration of the saturated solution was calculated from the reading of the dilution against the standard, the concentration of the standard, the value of $AC/$ AR and the dilution of the saturated solution.

In the case of some substances whose saturated solutions did not give a reading of over five or six hundred scale divisions against water, the values of $\Delta C/\Delta R$ were obtained by reading the standards directly against water. The saturated solutions were then diluted so as to give a reading of less than two hundred when read against water.

In all cases, duplicate determinations were run on samples from at least two different saturated solutions of the same substance. The 80-mm. chamber of the interferometer was used throughout except for the saturated solutions of some of the more soluble substances. In those cases, the 40-mm. chamber was employed.

The method used has several advantages. As mentioned above, it is not necessary to correct for the non-linearity of drum reading as a function of concentration since no reading exceeds two hundred divisions. Also, errors in dilution, reading of the interferometer, etc., will have a small effect on the precision of the final result since the reading is a difference measurement between the dilution and the reference solution. The reference solution can be prepared with a high degree of precision.

The method as used has the further advantage that it affords a check on the purity of the organic substances. Since varying amounts of the same substance were used in preparing different saturated solutions of the substance, if any soluble impurities were present, the interferometer readings for these saturated solutions would not agree with each other.

Materials

The chloroform, carbon tetrachloride and toluene were Baker's c. P. analyzed grade. All of the other organic substances were Eastman Kodak Co. best grade. The substances were purified by fractional distillation unless otherwise stated. For this purpose, two all-glass stills of the type described by Gross and Wright[5] were so designed that the thermometers were totally immersed in the vapor, eliminating exposed thread corrections. The large still had a capacity of one liter and had a fractionating column a meter long. The small still had a capacity of 250 cc. and had a column 0.5 meter long. Pressures were read on an accurate barometer. Temperatures below 105° were read on thermometers calibrated by the Bureau of Standards. For higher temperatures, a set of Anschiitz thermometers of good quality were used. Boiling points were corrected to 760 mm. by means of Craft's rule when dT/dP was not given in the literature. Unless otherwise stated, melting points were taken in open tubes on 5- or 10-g. samples.

Chloroform.—Two kilos were shaken for one hour with sodium hydroxide solution, washed twice with distilled water, shaken three times with concd. sulfuric acid, twice with distilled water, once with mercury and finally washed with distilled water and dried over calcium chloride as recommended by Harris.[6] The dried product was fractionated in the large still. A fraction of about 700 g. which boiled from 61.07-61.09" was used. Timmermans[7] gives a boiling point of 61.09–61.21'.

Carbon Tetrachloride.—This was purified according to the method of Williams and

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[5] Gross and Wright, *J. Ind. Eng. Chem.*, 13,701 (1921)

[6] Harris, *J. Chem. Soc.*, 127, 1063 (1925).

[7] Timmermans, *Bull. soc. chim. Belg.*, **24**, 244–269 (1910).

Krchma.[8] One kilo was refluxed for eight hours over mercury, shaken twice with coned. sulfuric acid, shaken with dilute sodium hydroxide, washed with distilled water and dried over calcium chloride. It was then fractionated in the large still. A fraction of about 800 g. boiling at 76.74 ± 0 02" was used. Timmermans[7] gives a boiling point of 76.74–76.76°.

Benzene.—This material was a sample of benzene purified for another purpose according to the method of Richards and Shipley.[9] Baker's C. P. crystallizable benzene was shaken successively with sulfuric acid, water, sodium hydroxide solution, water and mercury; dried over calcium chloride and then over sodium, distilled through a long all-glass column and a fraction of about one liter boiling between 80.05–80.07° collected. This was then recrystallized three times by freezing, resulting in a sample of about 700 cc. with m. p. 5.40". This was dried over sodium in a glass-stoppered distilling flask for two years and was distilled directly from this flask into carefully dried bottles whose necks were sealed off after distillii the benzene into them.

Toluene.—The material was purified according to the method of Beal and Souther.[10] A fraction of 600 g. all of which came over at 110.74 ± 0.02" was used. Timmermans[11] gives a boiling point of 110.7°. "International Critical Tables" gives a boiling point of 110.5°.

Monochlorobenzene.—A fraction of approximately 700 g. all of which came over at 131.83 ± 0.02' was used. Timmermans[7] gives a boiling point of 131.99–132.01°.

Monobromobenzene.—A fraction of 700 g. boiling from 155.88 to 155.93° was used. Timmermans[7] gives a boiling point of 156.14–156.16".

Nitrobenzene.—A sample containing 700 g. of this material was distilled under reduced pressure using cork stoppers as recommended by Roberts and Bury.[12] The first and last portions were discarded. The distillate was fractionally frozen twice. A fraction of 400 g. melting at 5.7" was used. "International Critical Tables" gives a melting point of 5.7°.

Ethylene Bromide.—Two different samples were purified. The first sample, containing 250 g., was fractionally frozen five times according to the method of Biron.[13] A fraction of 125 g. melting at 9.7" was used. The second sample had a slightly yellow color before it was purified. Four hundred grams of it was fractionated. A sample containing 250 g. boiling from 131.19–131.29° was used. "International Critical Tables" gives a boiling point of 131.7". This fraction melted at 9.7°. Biron[13] gives a melting point of 10.012°.

Methylene Bromide.—Two samples were used. The first containing 100 g. was fractionated through a Hempel column. Nearly all distilled over at 97.2°. The second sample containing 300 g. was distilled in the small glass still. A fraction of 200 g. boiling from 97.13 to 97.23° was used. "International Critical Tables" gives a boiling point of 97.8°. Timmermans[14] gives a boiling point of 96.5°.

Normal **Butyl** Bromide.—Two hundred grams of this material was fractionated three times through a Hempel column. A fraction containing about 75 g. boiling from 101.52 to 101.72° was used. "International Critical Tables" gives a boiling point of 101.6°.

***p*-Dichlorobenzene.**—A sample melting at 52.7' was recrystallized twice from ethyl

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[8] Williams and Krchma, THIS JOURNAL, 48, 1888 (1926).

Richards and Shipley. *ibid.*, 36, 1828 (1914).

[10] Beal and Souther, *ibid.*, 49, 1994 (1927).

[11] Timmermans, *Bull. soc. chim. Belg.*, 25, 300–27 (1911).

[12] Roberts and Bury, *J. Chem. Soc.*, 123, 2038 (1923).

[13] Biron, *Z. physik. Chem.*, 81, 590 (1913).

[14] Timmermans, *Bull. soc. chim. Belg.*, 28, 392 (1919).

alcohol. The product melted at 52.84°. "International Critical Tables" gives a melting point of 52.9'.

Bromoform.—A sample containing 500 g. was partially frozen once as recommended by Cauwood and Turner.[15] A fraction of about 350 g. melting at 7.7° was used. "International Critical Tables" gives a melting point of 7.7°.

Ethylene Chloride.—This was a portion of material previously purified.'

Ethyl Iodide.—The fraction used, which contained 125 g., boiled at 72 42°. Timmermans[16] gives a boiling point of 72.30°.

Normal Propyl Bromide.—A fraction of about 300 g. boiling from 70.97–71.08° was used. Timmermans[17] gives a boiling point of 71.0'.

Methylene Iodide.—A sample containing 300 g. of this material was shaken with sodium thiosulfate solution in order to decolorize it. It was then washed with distilled water, dried over potassium carbonate and fractionally frozen twice. A fraction of about 200 g. melting at 5.85' was used. "International Critical Tables" gives melting points of 5.2 and 5.7°.

Normal Propyl Iodide.—The sample of 200 g. was highly colored with iodine. It was decolorized by shaking with sodium thiosulfate solution. It was then washed twice with distilled water and dried for ten days over aluminum oxide. The dried substance was fractionated. A fraction of 100 g. boiling from 102.28 to 102.58° was used. Timmermans[11] gives a boiling point of 102.4°.

Carbon Tetrabromide.—This material was recrystallized once from ethyl alcohol and once from petroleum ether. It was found impossible to obtain a sharp melting point. Melting point determinations were carried out in an open tube using a 10-g. sample; in a capillary tube and in a sealed bulb. "International Critical Tables" gives a melting point of 91.1°. However, according to Biltz and Meinecke,[18] it is impossible to obtain a sharp melting point in an open tube due to partial decomposition of the carbon tetrabromide. In a capillary tube, the above authors found that the melting point was 92.5'. Our experience in the present work indicates a slight decomposition at the melting point.

***m*-Dinitrobenzene.**—This material was recrystallized three times from ethyl alcohol. The product used melted at 89.5'. "International Critical Tables" gives a melting point of 89.7".

***p*-Nitroaniline.**—This was recrystallized successively from ethyl alcohol, methyl alcohol, a mixture of ethyl and methyl alcohols, ethyl alcohol and finally from water. It was found to be impossible to obtain a sharp melting point. Melting points were taken in an open tube, a capillary tube and in a sealed bulb. In the capillary tube, all of the solid had disappeared at 147' but the sample did not melt sharply. The indications point to decomposition at the melting point. "International Critical Tables" gives 148° for the melting point. The value quoted in Beilstein and found in most of the literature is 147°.

Water.—Distilled water of good quality was obtained from the laboratory supply.

Results

The following substances were also purified with the intention of measuring their solubility: methyl iodide, trichloroethylene, ethylidene bromide, benzyl benzoate, isopropyl bromide, nitromethane and ethyl bromide. However, all of these substances were found to hydrolyze. The following

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[15] Cauwood and Turner, *J. Chem. Soc.*, 107,280 (1915).

[16] Timmermans, *J. chim. phys.*, 25,418 (1928).

[17] Timmermans, *ibid.*, 23,776 (1926).

[18] Biltz and Meinecke, *Z. anorg. allgem. Chem.*, 131, 14 (1923).

materials were available as Eastman Kodak Co. best grade: isopropyl iodide, tetrachloroethane, and tetrachloroethylene. These were found to hydrolyze. They were not further purified as from their nature and from the extent of hydrolysis it seemed likely that the existence of this hydrolysis was attributable not to impurities but to the substances themselves.

Hydrolysis was readily detected by the fact that constant interferometer readings of the saturated solutions could not be obtained, the readings continuing to increase over a period of time. Hydrolysis was confirmed in the case of the halogen compounds by appropriate tests for acid and halogen in the aqueous solutions. Nitromethane solutions showed increasing interferometer readings over a period of time. This was probably due to the formation of the pseudo acid as postulated by Hantzsch.[19]

TABLE I

SOLUBILITIES IN WATER AT 30°

Substance	G./1000 g. water	Moles/1000 g. water	% Estimated error
Ethylene chloride	9.00	0.0909	0 3
Methylene bromide	11.93	0680	0.5
Chloroform	7 71	.0646	1.0
Ethyl iodide	4 04	.0259	0.5
Benzene	1 85	0237	1 0
Ethylene bromide	4.31	0229	0.5
n-Propyl bromide	2 31	.0188	1 0
Nitrobenzene	2 05	.0167	0.5
Bromoform	3.19	.0126	1.0
Toluene	0.57	0062	2.0
n-Propyl iodide	1.04	00618	3.0
Carbon tetrachloride	0.81	0053	2.0
p-Nitroaniline	0.728	00527	1.0
Methylene iodide	1 24	00463	2 0
n-Butyl bromide	0.608	00444	1 5
Monochlorobenzene	.488	00433	1.0
m-Dinitrobenzene	.654	00389	2.0
Monobromobenzene	446	00284	2.0
Carbon tetrabromide	24	00072	8 0
p-Dichlorobenzene	.U77	00052	5 0

TABLE II

SOLUBILITIES IN WATER AT 15°

Substance	G./1000 g water	Moles/1000 g. water	% Estimated error
Ethylene chloride	8.72	0.0882	0.5
Chloroform	8 52	,0713	1 0
Methylene bromide	11.70	,0673	0 5
Ethylene bromide	3.92	.0209	1 0
Nitrobenzene	1.78	0145	1 0
Bromoform	3 01	0119	1.5
Carbon tetrachloride	0 77	0051	2 5

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[19] Hantzsch and Schultze, *Ber.*, 29,699,2251 (1896).

The solubilities of all the substances measured and the estimated errors of all determinations are given in Tables I and II. The error was estimated from values of duplicate determinations.

Rex[20] gives values for the solubilities of several of the substances measured in this investigation. Most of his values are higher than those obtained in the present work. As previously suggested by one of us,[3] this may be due to the possible loss of liquid in Rex's measurements. Also several of the compounds which he measured have been shown to hydrolyze in the present work, thus making the validity of his results doubtful in these cases. However, hydrolysis may not have introduced *a* significant error in his work if the determinations were completed in a sufficiently short interval of time.

Discussion

Attention may be drawn to a number of points of interest in connection with these data. The magnitude of some of the solubility values is surprisingly large for substances such as chloroform and ethylene chloride which are commonly thought of as "insolublc" in water. In view of this it would seem that water should at least be thought of when considering solvent media in which to carry out reactions involving such substances.

The existence of appreciable hydrolysis in the cases of a number of the compounds mentioned above, whose solubility we wished to determine, is of interest in connection with the statements found in the standard organic references that such hydrolysis does not occur. This indicates that the criteria commonly used to detect such hydrolysis are inadequate.

Lastly, this method of analysis or some modification of it would seem to have considerable promise as a method for studying reaction rates. We plan to investigate some of these hydrolyses from this point of view.

Summary

1. A modification of the existing methods for using the interferometer in the determination of the solubility of difficultly soluble liquids and solids in water and aqueous solutions is described.

2. The solubilities of a number of organic compounds in water at 30 and 15° are given.

DURHAM, NORTH CAROLINA

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[20] Rex, *Z. physik. Chem.*, **55**, 355 (1906).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

EQUILIBRIUM IN SYSTEMS COMPOSED OF SULFUR DIOXIDE AND AMMONIUM OR AN ALKALI IODIDE[1]

BY H. W. FOOTE AND JOSEPH FLEISCHER

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Systems composed of sulfur dioxide and an alkali iodide have been investigated chiefly by Walden and Centnerzwer,[2] Ephraim and Kornblum,[3] and De Forcrand and Tabouris.[4] All the investigators mentioned have obtained solid addition products of the two components, but there is much disagreement as to their composition, due partly to the fact that the existing equilibrium conditions have not been sufficiently studied. The pressure–temperature data in the various systems are also incomplete and many results which are comparable do not agree closely.

We have determined the composition of the solid phases and the vapor pressure relations in the two component systems consisting of sulfur dioxide with sodium, potassium, rubidium, cesium and ammonium iodides between the maximum limits of −25 and +25°. The invariant points within this temperature range have also been determined. At room temperature, a slow reaction takes place between the components which results in the liberation of iodine. The reaction only becomes noticeable after several days, and it is not sufficiently rapid to offer difficulty in determining vapor pressures.

Method, Apparatus and Procedure

In two component systems like those under consideration, composed of a volatile and a non-volatile component, the equilibria involved, as well as the composition of existing compounds, can be readily studied through the medium of the vapor pressure relations, which are entirely analogous in principle to those in a system composed of a salt and water. A complete vapor pressure-composition isotherm of a system formed of sulfur dioxide and a salt with which it forms an addition product exhibits a sharp change in pressure at the composition of the pure compound, while constant vapor pressures are exhibited by the univariant systems on either side of the pure compound regardless of the relative amounts of the phases present. The determination of the vapor pressures of these univariant systems as a function of temperature fixes the limits of pressure and temperature between which the compounds formed are stable. The intersection of the

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[1] An abstract of a dissertation presented by Joseph Fleischer to the Graduate School, Yale University, 1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Walden and Centnerzwer, *Z. physik. Chem.*, 39,513 (1902); 42,432 (1903).

[3] Ephraim and Kornblum, *Ber.*, 49,2007 (1916).

[4] De Forcrand and Tabouris, *Compt* rend., 168, 1253 (1919); 169, 162 (1920).

vapor pressure curves fixes the invariant points existing in the temperature range studied. If no addition products form, the vapor pressure relations are correspondingly simplified.

The measurements were carried out with an apparatus, the essential features of which are illustrated in Fig. 1 (not drawn to scale). The volume of the bulb was 29.3 cc. Tubes A, B, and C were each provided with a well-ground, mercury sealed stopcock. Tube A was attached to a manometer through a fused joint. The manometer was of the open type and was therefore used in conjunction with a calibrated barometer. The final pressures were rounded off to the nearest millimeter after the usual corrections. Tube B was connected with a two-liter suction flask which served as a vacuum reservoir. By means of a three-way stopcock, the reservoir could be connected with a pump, shut off, or opened to the air. Tube C connected with the supply of sulfur dioxide, which was dried by means of concentrated sulfuric acid.

A silvered Dewar flask of two liters' capacity served as a thermostat. Temperatures somewhat below 0° were obtained by mixtures of ice and sodium chloride. The lowest temperatures were produced by the additional use of ammonium chloride. The variation in temperature could be kept within about 0.1° for the time necessary for the systems to reach equilibrium. The thermometer used had been calibrated with considerable care.

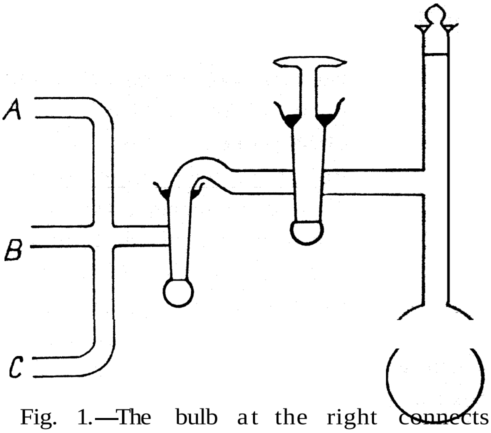

Fig. 1.—The bulb at the right connects through mercury-sealed stopcock and detachable ground-glass joint with the tubes A, B and C.

The salts were dried at 100° either in a vacuum or in a stream of dry air free from carbon dioxide. When necessary, the salts were purified by customary methods and in every case the purity was checked by analysis.

The experimental procedure was, in general, as follows. A weighed quantity of salt was introduced into the bulb, the stopper sealed in and the bulb and contents weighed. The bulb was then attached to the apparatus, the joint being sealed with mercury. The entire apparatus was then alternately evacuated and filled with sulfur dioxide to remove air. Twenty to thirty grams of sulfur dioxide was then allowed to condense in the bulb at a temperature of about −20°.

Before making any measurements, it was essential to insure the complete conversion of the original salt into its highest addition product. With salts rather insoluble in liquid sulfur dioxide, this was accomplished by allowing the finely ground iodide to stand for twelve hours or more in the presence of an excess of liquid. In all cases where the solubility allowed, the solid was brought completely into solution by removing the bulb from the bath and warming. The addition product was then crystallized from the solution by cooling and, if necessary, by evaporating a portion of the solvent. A vapor pressure–composition isotherm was usually carried out on this material at a temperature approximating −20° with the object of determining the univariant systems of three phases and the composition of any addition products. A temperature constant within several tenths of a degree was sufficient for this purpose. After the vapor pressure of

the saturated solution was determined, sulfur dioxide was allowed to evaporate at a pressure of some thirty or forty millimeters below this value until the material in the bulb was in equilibrium with this pressure, as indicated by the absence of any trend in the meniscus of the manometer when the system was closed. This procedure left a homogeneous solid in the bulb which was of necessity the highest addition product which could form at the temperature of the isotherm or at a higher temperature, and its composition could be calculated after weighing the bulb and making the proper small correction for the weight of sulfur dioxide present as vapor in the bulb at known temperature and pressure. If a second addition product existed, its composition was next determined in a similar manner.

The behavior of a compound as it warmed to room temperature in the bulb gave helpful information concerning the relations existing in the system. Decomposition into a liquid and a solid indicated the existence of a transition temperature between the temperature of the bath and that of the room; melting to a clear liquid indicated a congruent melting point; while the absence of any change showed that no invariant point existed in this temperature range.

In determining the vapor pressure curves of the three-phase univariant systems, the pressure reached the equilibrium value rapidly whenever a liquid phase were present if the bulb were shaken thoroughly. In such a case, the presence of the solid phase could be confirmed both visually and by checking for constant vapor pressure after withdrawing a portion of the sulfur dioxide. Such mixtures were allowed to stand for at least a half hour at constant temperature before the pressure was measured. In cases where two solids were present, instead of solid and liquid, equilibrium pressures were established rather slowly, more so when approached from higher pressures than from lower. The determinations were therefore made by averaging the value obtained from an initially lower pressure on standing for several hours with that reached from an initially higher value, a procedure which, on duplicating, proved to give satisfactory results.

When the vapor pressure curves had been determined for a system, it was frequently possible to determine the composition of a compound in the following simple manner which was applicable whenever the temperature could be adjusted to a value such that atmospheric pressure was intermediate between the vapor pressures of the saturated solution of the compound and that of the next lower univariant system. The bulb containing the saturated solution was immersed in a bath at such a temperature, and sulfur dioxide allowed to evaporate until the contents of the bulb were in equilibrium with a pressure of one atmosphere of sulfur dioxide; this could occur only when the liquid had disappeared. The evaporation was conveniently carried out by bubbling the gas through a thin layer of mercury serving as a trap, contained in a small vessel open to the air. By means of this contrivance, only the sulfur dioxide exerting a pressure greater than one atmosphere could escape and the point where evaporation was complete was indicated by cessation of bubbling. The composition of the compound could then be determined by weighing the bulb, Similarly, the composition of a lower addition product could be determined by repeating the same process at a higher temperature, where atmospheric pressure was intermediate between the pressure of the two univariant systems which limit the formation of the lower compound.

The vapor pressure data, with a few exceptions, were found to satisfy equations of the form

$$\log p = \frac{A}{T} + B$$

The exceptions all consisted of the saturated solutions of the compounds the solubility of which increased with temperature sufficiently to cause a divergence from the usual curve of vapor pressure. The heat of vaporization per mole of sulfur dioxide was calculated for the normal cases by the relation $\Delta H = 2.303$ AR, where R is the gas constant in calories, and A is the constant in the equation above.

Sodium Iodide and Sulfur Dioxide.—This system was first studied by Ephraim and Kornblum[3] and later by De Forcrand and Tabouris.[4] The former described two compounds, one yellow and the other red, to which they assigned the formulas $NaI \cdot 4SO_2$ and $NaI \cdot 2SO_2$, respectively. The latter found but one compound to which they gave the formula $NaI \cdot 3SO_2$.

In the present investigation it was found that on standing in contact with liquid sulfur dioxide below 0°, sodium iodide is converted to a bright yellow solid, $NaI \cdot 4SO_2$. The compound is rather insoluble in the liquid, to which it imparts, however, a pale red color. On evaporating the solvent, the compound crystallizes in the form of transparent pale yellow cubes. If heated in a closed system above a transition temperature of 1.4°, the compound melts incongruently and forms a bright red compound, whose composition as shown below corresponds to the rather unusual formula $3NaI \cdot 8SO_2$. The reverse change takes place readily on cooling below the transition point.

The composition of both compounds was determined as previously described, by evaporating sulfur dioxide at atmospheric pressure from the saturated solutions at temperatures where the vapor pressure data given below showed that only the pure compounds were stable. The temperature adopted for the higher compound was −8°, and for the lower, +8°.

The following results were obtained:

$NaI \cdot 4SO_2$			$3NaI \cdot 8SO_2$		
NaI, g.	SO_2, g.	Ratio $NaI:SO_2$	NaI, g.	SO_2, g.	Ratio $NaI:SO_2$
3.698	6.377	1:4.04	3.698	4.268	3:8.10
6.933	11.759	1:3.97	4.898	5.638	3:8.07
4.989	8.616	1:4.04	8.725	9.907	3:7.98
			9.778	11.248	3:8.07
			4.989	5.704	3:7.94

The compound to which we have assigned the unusual formula $3NaI\cdot8SO_2$ is undoubtedly the red compound to which the formula $NaI\cdot3SO_2$ was assigned by De Forcrand and Tabouris, and $NaI\cdot2SO_2$ by Ephraim and Kornblum. The former investigators prepared the compound by starting with a saturated solution at a low temperature and allowing the excess sulfur dioxide to evaporate at 0° and atmospheric pressure. While this method should, in principle, yield the lower compound ultimately in pure condition, it involves the primary formation of the higher 1:4 compound, followed by its subsequent decomposition, and the latter process is slow. The writers repeated this experiment of De Forcrand and Tabouris at 0° and after two hours the escape of sulfur dioxide nearly ceased and the empirical composition of the residue corresponded to $NaI\cdot2.96SO_2$. On raising the temperature to +3°, which is just above the transition point (1.4°), the excess of sulfur dioxide was converted to liquid and escaped in a few minutes, leaving a residue corresponding closely to the 3:8 ratio. Ephraim and Kornblum obtained the same red compound by passing sulfur dioxide over the iodide at 0° and atmospheric pressure, a procedure which should yield the pure compound. The experimental data reported by them (5.86 g. of sulfur dioxide absorbed by 5.15 g. of sodium iodide) yield the formula $3NaI\cdot7.98SO_2$, almost exactly the 3:8 ratio, and indicate that the pure compound was obtained, but that the results were misinterpreted, as the formula $NaI\cdot2SO_2$ was assigned.

The following vapor pressure data were obtained on the three univariant systems. Here and in all subsequent cases pressure is given in centimeters of mercury. Whenever applicable, the equation for calculating the vapor pressures is given, as well as AH.

I. $NaI\cdot4SO_2$–Solution–Vapor

T, °C.	p, cm.
–20.20	47.2
15.75	58.4
13.10	65.8
10.70	72.8
7.50	84.0
5.10	92.9
3.20	100.8
0.0	115.8

$$\text{Log}\, p = 6.944 - \frac{1332.9}{T}$$

AH = 6100 cal.

II. $NaI\cdot4SO_2$–$3NaI\cdot8SO_2$–Vapor

T, °C.	p, cm.
–18.65	29.9
14.15	42.4
9.20	60.1
7.00	70.0
4.00	85.2
0.0	111.9

$$\text{Log}\, p = 9.776 - \frac{2110.3}{T}$$

AH = 9650 cal.

III. $3NaI\cdot8SO_2$–NaI–Vapor

T, °C.	p, cm.
–24.35	4.4
–10.90	13.3
0.0	28.6
9.90	55.9
18.40	96.4
19.40	102.4

$$\text{Log}\, p = 8.811 - \frac{2281.7}{T}$$

AH = 10,450 cal.

The vapor pressure curves of systems I and II above intersect at +1.4°, a transition point where the four phases in equilibrium are the two addition products, solution and vapor. This temperature was also determined directly by immersing a bulb containing the compound $NaI\cdot4SO_2$ with its saturated solution in a bath of slowly rising temperature contained in a transparent Dewar flask and observing the temperature at which the red 3:8 compound first appeared. This temperature was found to be +1.5°, in close agreement with the result obtained from the vapor pressure curves.

Above the transition point, another univariant system exists, but the pressures were too high to be determined with safety in our apparatus. It consists of the phases $3NaI{\cdot}8SO_2$–solution–vapor.

The vapor pressure curves of the three systems are shown in Fig. 2.

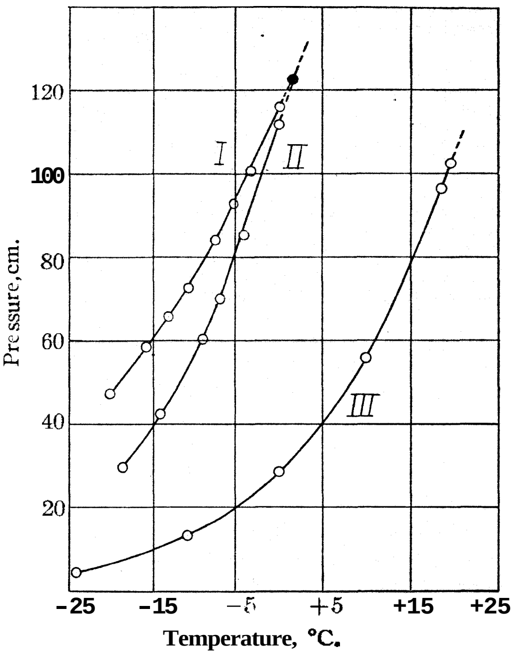

Fig. 2.—NaI–SO_2. Curves I. II and III represent, respectively, the systems $NaI{\cdot}4SO_2$–solution–vapor; $NaI{\cdot}4SO_2$–$3NaI{\cdot}8SO_2$–vapor; and $3NaI{\cdot}8SO_2$–NaI–vapor. The black dot represents the invariant system of four phases.

Potassium Iodide and Sulfur Dioxide.—Walden and Centnerzwer[2] have investigated the freezing point diagram of this system over a wide range of temperature and have described the compounds $KI{\cdot}4SO_2$ and $KI{\cdot}14SO_2$. The latter compound only exists at very low temperatures, below the range we have investigated. Pechard[5] and Fox[6] claim the existence of the compound $KI{\cdot}SO_2$, and Kistiakowsky,[7] the compound $2KI{\cdot}SO_2$. We have found no evidence that either of these compounds exists.

Isothermal evaporation of unsaturated solutions at pressures slightly below those of the saturated solutions between —20 and —5° left residues corresponding to the formula $KI{\cdot}4SO_2$, thus confirming Walden and Centnerzwer's formula. The following results were obtained

KI, g.	SO_2, g.	Ratio KI:SO_2	Temp., °C.
5.491	8.419	1:3.98	-18.3
5.159	7.951	1:3.99	-15.0
7.113	11.003	1:4.01	-12.0
6.680	10.352	1:4.02	- 7.6

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[5] Pechard, *Compt. rend.*, 130, 1188 (1900).

[6] Fox, *Z. physik. Chem.*, 41, 458 (1902).

[7] Kistiakowsky, *J. Russ. Phys.-Chem. Soc.*, 34, 24 (1902).

The compound has a pale red color and crystallizes in cubes. The saturated solution has a pale yellow color at −20°, but due to the rapidly increasing solubility, the color deepens and the viscosity increases as the temperature rises. Withdrawal of sulfur dioxide from the compound at 0° results in the appearance of white potassium iodide, the pressure remaining constant until the sulfur dioxide is almost completely removed, thus showing the non-existence of compounds containing less sulfur dioxide. The vapor pressure curves of the three univariant systems are given in the following table and are plotted in the diagram (Fig. 3).

The three curves intersect at about +0.2°, which is the invariant point where the two solid phases, liquid and vapor, coexist. Walden and Centnerzwer[2] also determined this temperature (+0.26°) and considered it a transition point rather

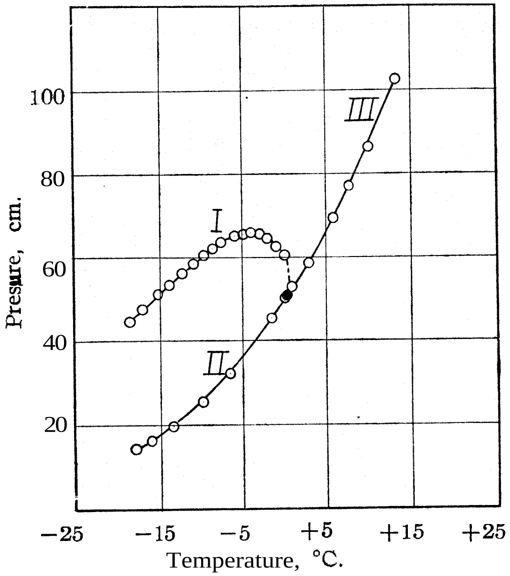

Fig. 3.—KI-SO_2. Curves I, II and III represent, respectively, the systems KI·$4SO_2$–solution–vapor, KI·$4SO_2$–KI–vapor, and KI–solution–vapor. The black dot represents the invariant system of four phases.

I. KI·$4SO_2$-Solution–Vapor

T, °C.	p, cm.
−18.7	44.9
17.05	47.8
15.25	51.2
13.90	53.5
12.25	56.3
10 80	58.7
9.60	60.8
8.50	62.5
7.55	63.7
5 85	65.2
4.80	65.8
4.05	66.1
2.95	65.7
2.00	64.8
1.00	62 7
0.00	60.6

II. KI·$4SO_2$–KI–Vapor

T, °C.	p, cm.
−18.20	14.3
16.05	16.3
13.30	19.9
9.85	25.7
6.50	32.3
1.50	45.7
0.00	50.2

$$\text{Log } p = 9.534 - \frac{2139.3}{T}$$

$$\Delta H = 9800$$

III. KI–Solution Vapor

T, °C.	p, cm
0.95	53.1
2.85	58.9
5.85	69.4
7.80	77.0
10.00	86.4
13.30	102.4

$$\text{Log } p = 8.345 - \frac{1814.3}{T}$$

$$\Delta H = 8300$$

than a eutectic, so that the melting point was incongruent. We found the pure compound, however, melted congruently to a clear liquid and the form of the vapor pressure curve (Fig. 3, I) also indicates that the pure compound melts slightly above the invariant point, which is therefore a eutectic rather than a transition point. In either case, the composition of the liquid at the invariant point is very close indeed to that of the compound $KI{\cdot}4SO_2$.

Rubidium Iodide and Sulfur Dioxide.—Rubidium iodide dissolves readily in liquid sulfur dioxide to give an orange-red solution. On evaporating this solution at 0° and atmospheric pressure, using the mercury bubbler, a solid residue of transparent yellow needles remained, the composition of which corresponded to the formula $RbI{\cdot}3SO_2$.

RbI, g	SO_2 g.	Ratio RbI:SO_2
4.376	4.045	1:3.06
4.971	4.577	1:3.05
4.608	4.217	1:3.03
5.125	4.719	1:3.05

Removal of sulfur dioxide from the solid compound caused the appearance of white rubidium iodide, and the pressure remained constant until the sulfur dioxide was almost completely removed; therefore, no lower compound exists. At room temperature the compound decomposed to a very viscous orange-brown liquid and solid rubidium iodide, indicating the existence of a transition temperature.

The vapor pressures of the univariant systems are shown in the following tables and Fig. 4. The vapor pressure curve of the saturated solution of the compound in liquid sulfur dioxide could not be determined over the entire range, as, at the higher temperatures, the pressures became too high for the apparatus, but the curve must display a maximum as indicated. The intersection of

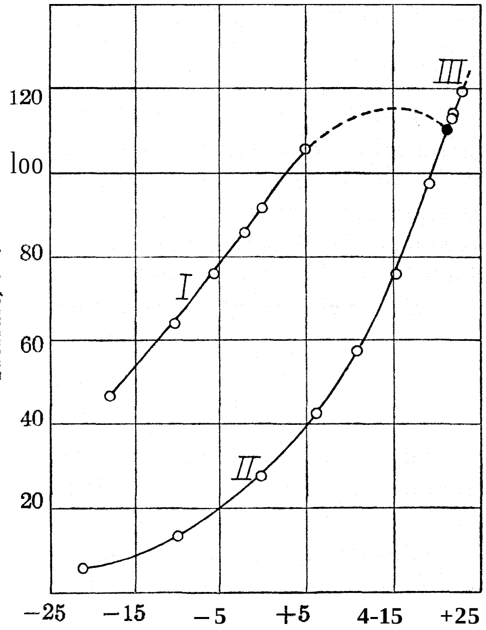

Fig. 4.—RbI–SO_2. Curves I. II and III represent, respectively, the systems $RbI{\cdot}3SO_2$–solution –vapor; $RbI{:}3SO_2$–RbI–vapor and RbI–solution –vapor. The black dot represents the in-variant system of four phases.

Curves II and III places the transition temperature at +21.3°; Curve I must meet the other curves at this point.

I. $RbI \cdot 3SO_2$–Solution–Vapor

T, °C.	p, cm.
−18.10	46 8
10.30	64.0
5.60	76.0
2 00	85.7
0 0	91.5
+5.00	1059

II. $RbI \cdot 3SO_2$–RbI–Vapor

T, °C.	p, cm.
−21.30	5.5
10.00	13.4
0.00	27.35
+6.30	42.6
10.90	57.2
15.30	75.8
19.20	97.4

$$\text{Log } p = 9\,836 - \frac{2294.0}{T}$$

$$\Delta H = 10{,}500$$

III. RbI–Solution–Vapor

T, °C.	p, cm.
+21.75	113.0
22.0	114.1
23.0	119.4

De Forcrand and Tabouris[4] found the same composition for the compound that we have found. Their result for the vapor pressure of the saturated solution at 0° is 82 cm., a value almost 10 cm. below ours, which was repeatedly checked on different samples of salt. Ephraim and Kornblum[3] state that rubidium iodide absorbed 4.4 moles of sulfur dioxide per mole of salt at 0°—an inexplicable result—and therefore assigned the formula $RbI \cdot 4SO_2$ to the compound.

Cesium Iodide and Sulfur Dioxide.—Cesium iodide dissolves readily in liquid sulfur dioxide, giving a pale red solution. Evaporation of the latter at 0° and atmospheric pressure left a residue of pale yellow needles of composition corresponding to the formula $CsI \cdot 3SO_2$, confirming the formula of De Forcrand and Tabouris.[4] Ephraim and Kornblum[3] assigned the formula $CsI \cdot 4SO_2$ to this compound.

The following results were obtained

CsI, g.	SO_2, g.	Ratio $CsI:SO_2$
5.144	3.946	1:3.05
4.844	3.693	1:3.03

Removal of sulfur dioxide from the compound resulted in the appearance of white cesium iodide and the pressure remained constant until the sulfur dioxide was nearly all removed, showing the absence of lower compounds.

The increasing solubility of the compound in liquid sulfur dioxide with rising temperature causes the vapor pressure curve of the saturated solution to diverge considerably from that of pure sulfur dioxide, although its form can be expressed by an equation of the usual type over the temperature range studied. At somewhat higher temperatures, the curvature probably reverses and the curves of the two univariant systems intersect. Following are the results of the vapor pressure determinations. The results are plotted in Fig. 5.

I. $CsI\cdot3SO_2$–Solution–Vapor

T, °C.	p, cm.
−21.60	42.7
18.45	48.8
16.30	63.9
11.50	65.8
8.10	75.5
4.25	87.1
0.0	102.5

$$\text{Log } p = 6.440 - \frac{1209.7}{T}$$

$$\Delta H = 5550$$

II. $CsI\cdot3SO_2$–CsI–Vapor

T, °C.	p, cm.
−19.60	5.3
15.90	8.5
10.90	12.3
5.25	18.4
0.0	26.65
+7.50	43.8
12.40	60.3
17.10	80.8
20.25	98.2

$$\text{Log } p = 9.629 - \frac{2240.6}{T}$$

$$\Delta H = 10,250$$

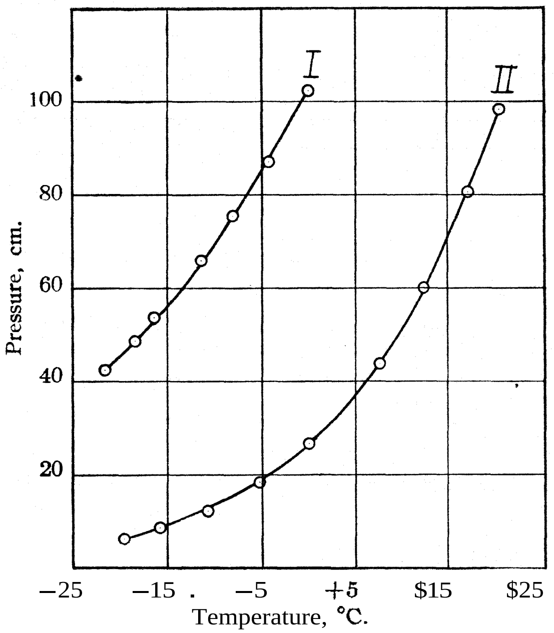

Fig. 5.—CsI–SO_2. Curves I and II represent, respectively, the systems $CsI\cdot3SO_2$–solution–vapor and $CsI\cdot3SO_2$–CsI–vapor

Ammonium Iodide and Sulfur Dioxide.—There appear to be no data in the literature on this system. Ammonium iodide dissolves readily in liquid sulfur dioxide forming a red solution. Evaporation of sulfur dioxide from unsaturated solutions to a pressure somewhat below that of the

NH_4I, g.	SO_2, g.	Ratio $NH_4I:SO_2$	Temp., °C.
4.883	6.647	1:3.08	−22
3.383	4.636	1:3.10	−19
5.980	8.160	1:3.09	−20

saturated solution, at three temperatures, left in each case a residue of yellow needles having the composition corresponding to $NH_4I \cdot 3SO_2$.

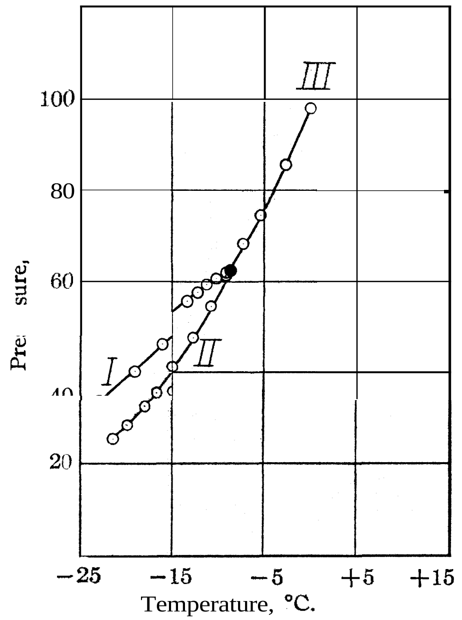

Fig. 6.—NH_4I–SO_2. Curves I, II and III represent, respectively, the systems $NH_4I \cdot 3SO_2$–solution–vapor; $NH_4I \cdot 3SO_2$–NH_4I–vapor; and NH_4I–solution–vapor. To avoid confusion, the results in the metastable region of curve III are omitted. The black dot represents the invariant system of four phases.

The existence of lower compounds was disproved by the fact that withdrawal of sulfur dioxide from the compound caused the appearance of white ammonium iodide and the pressure remained constant until sulfur dioxide was almost completely removed.

The existence of a transition temperature was indicated by the fact that on removal from the freezing bath, the compound $NH_4I \cdot 3SO_2$ decomposed to yield a liquid and a solid. The intersection of the vapor pressure curves of the three univariant systems placed the transition temperature at −8.8°. At this temperature, the phases in equilibrium are $NH_4I \cdot 3SO_2$–NH_4I–solution–vapor.

The vapor pressure data are given below and plotted in Fig. 6. It was possible to obtain some measurements on the system NH_4I–solution–vapor at temperatures below the transition point, a region in which the system is

I. $NH_4I \cdot 3SO_2$–Solution–Vapor

T, °C.	p, cm.
−24.40	36.5
23.05	39.0
19 35	45.6
16.10	51.3
13.45	55.6
12.25	57.6
11.25	59.1
10.20	60.6
9.00	62.0

II. $NH_4I \cdot 3SO_2$–NHJ–Vapor

T, °C.	p, cm.
−21.50	25.5
20.00	28.2
18.05	32.6
16.80	35.7
14.90	41.1
12.70	47.6
10.80	54.5
9.15	61.2

$$\text{Log } p = 9.537 - \frac{2045.8}{T}$$

$$\Delta H = 9350$$

III. NH_4I–Solution–Vapor

T, °C.	p, cm.
−13.85[a]	48.2
12.35[a]	52.3
10.45[a]	57.4
7.20	68.1
5.45	74.3
2.65	85.5
0.0	97.6

$$\text{Log } p = 7.781 - \frac{1581.6}{T}$$

$$\Delta H = 7250$$

[a] Metastable system.

metastable. As in the case of all the simple alkali iodides (as distinct from the addition products) the solubility of ammonium iodide in sulfur dioxide decreases with rising temperature.

Summary

The composition of the solid addition products and the vapor pressure curves limiting the stability of these compounds have been determined between the maximum limits of -25 and $+25°$ for the 2-component systems of sulfur dioxide with sodium, potassium, rubidium, cesium and ammonium iodides.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE KINETICS OF THE DECOMPOSITION OF AMMONIA ON COPPER

BY J. K. DIXON[1]

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The decomposition of ammonia on the surfaces of certain metals has been studied by Hinshelwood and Burk, Schwab and Kunsman.[2] In each case the metal in the form of a hot filament has been used to decompose the ammonia. In order to obtain a true conception of a heterogeneous reaction a knowledge of the following is necessary: (1) the heats of adsorption of the gases involved in the reaction; (2) the amount of each gas adsorbed, as a function of its pressure; (3) the rates of adsorption of the gases; and (4) the law expressing the relation between the velocity of reaction and the pressures of the gases above the surfaces.[3] Except at low pressures, the use of a filament as a surface precludes any attempts to make measurements on the first three quantities. The object of the present work has been to study the kinetics of the decomposition of ammonia on copper, using enough of the metal to make later measurements on the first three factors possible.

Elod and Banholzer[4] have studied the decomposition of ammonia on copper and iron by a dynamic method. Their results on copper agree with those given here and can now be interpreted in a quantitative way.

Experimental

About fifty experiments on the decomposition of ammonia on forty grams of granular copper (see below) were performed in a static system.

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[2] (a) Hinshelwood and Burk, *J. Chem. Soc.*, *127*, 1105 (1925); (b) Schwab, *Z. physik. Chem.*, *128*, 161 (1927); (c) Schwab and Schmidt, *ibid.*, **B3**, 337 (1929); (d) Kunsman, THIS JOURNAL, 50, 2100 (1928); 51, 688 (1929).

[3] Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford University Press, 1929.

[4] Elod and Banholzer, *Z. Elektrochem.*, 32, *556* (1926).

The experiments were reproducible, but it was not possible to obtain an equation which would explain the rate of decomposition correctly. As only the general conclusions and a possible explanation of these experiments will be reported here, the details of the experiments will be omitted.

Experiments were then carried out in a dynamic system, from which it has been possible to set up an equation which expresses the rate of decomposition correctly.

Materials.—Ammonia from a tank was passed over fused potassium hydroxide and then through two tubes of anhydrous barium oxide. The latter removes water efficiently and does not react with ammonia. The gas obtained was completely absorbed by dilute sulfuric acid. Tank nitrogen (99.9%) was passed over copper turnings at 450°, then over solid potassium hydroxide and finally through phosphorus pentoxide. Tank hydrogen was passed over copper turnings at 350°, over potassium hydroxide and over phosphorus pentoxide.

Copper oxide, Kahlbaum's "pea-size," was sieved to 10–16 mesh and reduced in oxygen-free hydrogen. Since the temperature range studied in the catalytic reaction was 500–625°, the final twelve hours of reduction was made at 700°. The copper was strongly sintered, characterized by a true copper color.[5]

Apparatus and Experimental Procedure.—Ammonia passed from its purification train through a flowmeter and then over the copper catalyst. Hydrogen, nitrogen, or both, were added to the ammonia stream, as desired, before the latter entered the catalyst chamber. The amounts of added nitrogen and hydrogen were determined by suitable flowmeters. The amount of ammonia escaping decomposition in a definite length of time was found by absorbing it in dilute sulfuric acid of known concentration and titrating the excess acid with sodium hydroxide. The quantity of ammonia entering the catalyst chamber was known from the calibration of the ammonia flowmeter; hence, the percentage decomposition was easily calculated. It was possible to divert the "off" gases to a gas analysis apparatus by means of a three-way stopcock. The entire apparatus was constructed of Pyrex glass, the only rubber connection being used to lead the exit gases to the absorbing bottle.

Fig. 1.

The type of capillary used in the flowmeters is shown in Fig. 1. It is recommended because it is easily made, does not become clogged, gives a gas flow proportional to the pressure head and can be made to give small flow rates when the pressure head (mercury) is appreciable. For each of the gases, the pressure head on the flowmeter was kept constant by means of an overflow in the gas purification train. The hydrogen and nitrogen flowmeters were standardized by "displacing" water and, in the case of small flow rates, by using mercury in place of water. The accuracy was ±1.0%. The ammonia flowmeter was standardized by titration, the accuracy being ±0.3%. Since the ammonia flow rate decreased as the room temperature increased, the flowmeter was calibrated three or four times a day and hence it was unnecessary to calculate the corrections to be applied on account of these temperature variations.

Thirty-five grams of the copper catalyst, with an apparent volume of 15 cc., was held in an unfused quartz vessel, whose volume was 25 cc. and to which were attached inlet and outlet tubes. Connection with the rest of the apparatus was made by means of graded quartz to Pyrex seals. The inlet gases passed down through the furnace

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[5] When the oxide is reduced at 180–200°, it has a purple appearance.

and then entered at the bottom of the catalyst chamber. A furnace, wrapped with nichrome wire and electrically heated, was drawn up about the catalyst tube and the free space in the furnace filled with iron rods in order to equalize the temperature. A chromel–alumel thermocouple was fixed against the catalyst tube at the mid-point of the catalyst and the temperature determined in this way has been taken as that of the catalyst. The furnace was well insulated with asbestos; consequently the maximum temperature variation during an experiment was ±1°.

The experimental procedure was, first, to pass a suitable gas mixture over the catalyst for ten to fifteen minutes at the temperature of the experiment in order to assure constant conditions above the surface. Then the ammonia in the "off" gases was absorbed in approximately 50 cc. of standard sulfuric acid for a suitable length of time and the excess acid determined by titrating back with sodium hydroxide, using methyl orange as indicator. A small correction was determined and made for the amount of ammonia escaping absorption in the acid. This correction proved to be negligible except for high rates of flow of nitrogen or hydrogen. Three or four runs were performed for each gas mixture and the mean of these results has been used in subsequent calculations. In any experiment the values of the percentage decomposition vary among themselves by not over 1%. When the mean is compared with that for the same experiment performed at a different date, the variation is not over ±5%.

Results and Interpretation

The rate of decomposition has been studied at 495.5, 542.5, 581.5 and 619.5°. In Table I are given the results of the experiments at 542.5 and 581.5°; the results at 495.5 and 619.5° are analogous. The flow rates throughout are expressed in cc. per minute reduced to 25° and 760 mm. pressure. In the first column is given the experiment number, in the second the temperature in degrees centigrade, and in the third the volume of ammonia entering the catalyst tube per minute. The fourth column gives the percentage of ammonia decomposed, the fifth the hydrogen inlet flow rate and the sixth the inlet flow rate of nitrogen.

If we consider any small element of length of the catalyst tube containing an amount of surface, dA, then the rate of disappearance of ammonia per minute is proportional to this surface area. The composition of the gas above this surface is assumed to be constant. If we let V be the total flow rate of gas over dA, v the flow rate of ammonia, v_{H} the flow rate of hydrogen and v_{N} that for nitrogen, each in cc. per minute, then

$$V = v'_{\mathrm{H}} + v'_{\mathrm{N}} + 2v' - v \tag{1}$$

The primed quantities refer to the flow rates of the inlet gases. The pressures of ammonia, hydrogen and nitrogen are

$$p = \frac{v}{V}P \qquad p_{\mathrm{H}} = \frac{v_{\mathrm{H}}}{V}P \qquad p_{\mathrm{N}} = \frac{v_{\mathrm{N}}}{V}P \tag{2}$$

where P is the total pressure, which is the barometric pressure in this case. The experiments indicate that the rate of decomposition of the ammonia is proportional to p and inversely proportional to p_{H}. If dv is the amount of ammonia decomposed per minute on the surface dA, then

$$-\mathrm{d}v = k\,\mathrm{d}A\,\frac{p}{p_{\mathrm{H}}} = k\,\mathrm{d}A\,\frac{v}{v_{\mathrm{H}}} \quad \text{or} \quad -\frac{v_{\mathrm{H}}\mathrm{d}v}{v} = k\,\mathrm{d}A$$

TABLE I

THE DECOMPOSITION OF AMMONIA ON COPPER

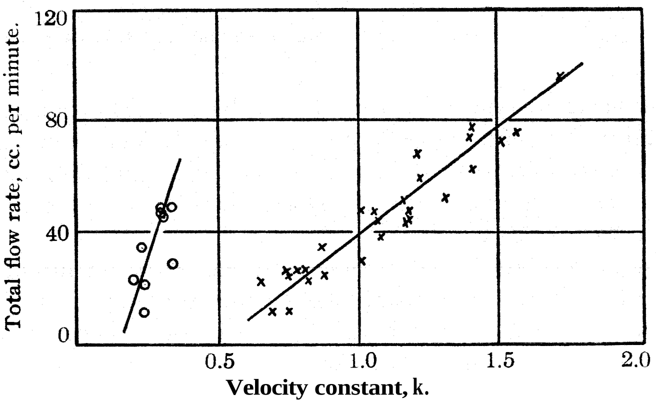
Expt.	Temp., °C.	Inlet NH_3, cc./min.	% NH_3 decomposed	Inlet H_2, cc./min.	Inlet N_2, cc./min.	Barometric pressure, cm.	kt
1	580.5	20.2	23.50	0.00	0.00	75.3	0.65
3	581.0	20.2	13.60	8.30	.00	75.3	1.01
4	581.0	20.2	26.00	0.00	.00	75.1	0.52
7	581.5	20.2	14.45	4.80	.00	75.9	.74
8	581.5	22.0	19.25	2.40	.00	75.9	.81
10	581.5	31.7	21.60	0.00	.00	75.7	.87
11	581.5	43.2	20.10	.00	.00	75.2	1.06
16	581.5	21.7	19.95	4.80	14.5	74.2	1.19
17	581.5	21.7	23.95	2.40	16.9	74.4	1.18
18	581.5	21.7	28.10	0.00	18.6	74.5	1.07
19	581.5	21.7	29.95	.00	43.0	75.4	1.21
20	581.5	21.7	27.80	.00	22.9	75.8	1.06
21	581.5	22.0	23.85	.00	0.00	76.0	0.75
29	581.5	43.2	21.65	.00	.00	76.3	1.18
33	581.5	43.2	23.50	.00	25.4	75.8	1.40
34	581.5	43.2	17.45	5.30	25.4	75.7	1.41
35	581.5	43.2	16.65	5.30	0.00	75.6	1.31
37	581.5	43.2	2.35	52.9	.00	75.6	0.84
39	580.5	10.4	33.25	0.00	.00	75.5	.75
42	581.5	10.4	40.85	.00	47.1	75.8	1.22
45	581.5	22.0	32.65	.00	47.0	74.2	1.52
47	582.0	43.3	25.90	.00	47.3	75.2	1.72
51	581.5	22.0	5.68	25.3	0.00	77.1	1.01
52	581.5	22.0	3.08	40.2	.00	77.0	0.85
12	543.5	43.2	10.80	0.00	.00	75.0	.30
13	542.0	43.2	8.43	2.40	.00	74.6	.34
14	542.5	43.2	6.33	4.80	.00	74.5	.30
23	542.5	22.0	13.40	0.00	11.4	75.8	.23
24	542.5	22.0	12.80	.00	0.00	75.8	.20

k representing the number of cc. of ammonia decomposed per minute on unit surface when $p = p_H = 1$ atmosphere. When $A = 0$, $v = v'$, $v_H = v'_H$ and $v_N = v'_N$; when $A = A_1$, the total area of the catalyst, then $v = v_f$, which is calculated from the percentage decomposition. Therefore

$$-\int_{v'}^{v_f} \frac{v_H dv}{v} = -\int_{v'}^{v_f} \frac{(2/3\, v'_H + v' - v)\, dv}{v} = 2/3\, kA_1, \text{ or} \qquad (3)$$

$$(2/3\, v'_H + v') \ln \frac{v'}{v_f} - v' + v_f = 2/3\, kA_1 = k_1$$

The barometric pressure is given in the seventh column of Table I and the calculated values of k_1 in the eighth column. The latter are not quite constant, but increase with the flow rate, as illustrated in Fig. 2. If the velocity of decomposition is assumed to be proportional to $p/(1 + k_2p)$ instead of p, it is possible to account for the increase of k_1 as we add nitrogen, that is, increase the total flow rate. Since the activity of the catalyst increased slightly with time and the experimental accuracy of the determination of the percentage decomposition was about ±5%, the introduction of a second constant, k_2, is not warranted. If, for example, in Expt. 10, Table I, we assume that the percentage decomposition is 23.6, then k_1 becomes 1.06. That is, an error of 10% in the percentage decomposition makes an error of 20 to 25% in k_1. In Expt. 37, where the amount of added hydrogen is large and the percentage decomposition small, the experimental error may be greater than 5%, hence the agreement of the constant with those from other experiments is satisfactory.



⊙, 542.5"; X, 581.5 °.

Fig 2.—The dependence of the velocity constant on the total flow rate.

In Expts. 11, 37 and 42 the average ammonia pressures are 62, 22 and 10 and the average hydrogen pressures 10, 53 and 3.7, respectively, in centimeters of mercury. The pressure range for ammonia is from 10 to 60 cm. and the range of hydrogen pressures 4 to 50 cm.

The results of the experiments in the static system agree in some respects with those of the dynamic method. Nitrogen had no effect on the rate of decomposition of the ammonia. A number of experiments were made with the same initial pressure of ammonia, but varying initial pressures of added hydrogen. The results are given in Table II, in which the first column gives the initial pressure of ammonia, the second the *initial* pressure of hydrogen, and the third the initial slope of the pressure–time curve.

The reaction velocity is seen to be very nearly inversely proportional to the hydrogen pressure. The velocity constants, k, calculated from the results of the static experiments by means of the equation

$$-\frac{d\,p_{NH_3}}{dt} = \frac{k\,(p_{NH_3})^n}{(p_{H_2})^m} \qquad (4)$$

with $n = m = 1$, drop off as the reaction proceeds. It would be necessary to assume that $n > 2$ and $m > 1$, and neither a whole number, in order to obtain a true constant. Such a procedure has been adopted by Schwab and

TABLE II

THE EFFECT OF HYDROGEN ON THE RATE OF DECOMPOSITION OF AMMONIA ON COPPER IN A STATIC SYSTEM

$t = 619°$

p_0, NH_3, cm.	p_0, H_2 cm.	$\underline{p}$ (initial), cm. per minute
10.5	0.0	(3.50)[a]
10.8	5.4	1.32
10.2	9.9	0.74
9.7	24.7	.40
11.2	34.0	.30

[a] When (p_0, H_2) is zero the rate at the start is so fast that this value has very little significance.

Schmidt in order to explain their results on the decomposition of ammonia on a platinum filament, above 25 mm. pressure.[2c] They were the first to point out the complexity of the reaction mechanism and their experiments showed the same rapid decrease in velocity with time which we have observed in a static system.

It seems more plausible to assume a simpler reaction mechanism and that the falling off in rate is partly due to a covering of the surface by an unstable nitride or other compound. In the case of copper it is known that copper oxide and ammonia react to form a nitride,[6] and Beilby and Henderson[7] report the formation of copper nitride by the action of ammonia on copper at high temperatures. The question of a nitride formation was investigated in the dynamic system. An analysis of the "off gas from the catalyst was carried out at various times during the kinetic studies. Table III shows that the ratio of the hydrogen formed to the sum of hydrogen and nitrogen is that which we would expect if none of the nitrogen were disappearing to form a nitride.

TABLE III

ANALYSIS OF THE "OFF" GAS FROM THE DECOMPOSITION OF AMMONIA ON COPPER

$N_2 + H_2$, cc.	H_2, cc.	$H_2/(H_2 + N_2)$
37.85	28.50	0.753
39.00	29.00	.743
36.30	27.65	.763
35.10	25.80	.735

Theoretical, 0.780

Since the amount of nitrogen held by the copper might have been very small compared with the total set free by decomposition or since the nitride might have formed and remained in a nearly constant amount,[8] a different procedure was adopted to detect a possible nitride formation under the conditions of the kinetic studies. A sample of Kahlbaum's

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[6] Guntz and Bassett, *Bull. soc. chim.*, [3] *35*, 201 (1906).

[7] Beilby and Henderson, *J. Chem. Soc.*, *79*, 1245 (1901).

[8] Compare with Mittasch, Kuss and Emert, *Z. Elektrochem.*, 34, *829* (1928).

copper oxide, 17.7756 g., was reduced completely in pure hydrogen at 300°. The weight of copper expected was 14.201 g. and the value found was 14.229 g. Pure ammonia was then passed over this heated catalyst, decomposition beginning at 410°. The temperature was raised to 500–550°, where the rate of decomposition of the ammonia was high. The copper with its containing tube was cooled from time to time and weighed, but there was no increase in weight. Finally, the ammonia was passed over the copper continuously for three days and the weight was again determined and found to be the same. During the course of the treatment with ammonia the weight of the copper decreased 0,002 g.

The negative results of these experiments do not disprove that a trace of some compound might be formed on the surface which would inhibit the reaction considerably. Experiments of the type described by Mittasch and Frankenburger[9] might yield information with regard to compound formation.

The Temperature Coefficient.—The heat of activation, E, of the decomposition on copper has been determined from the reaction velocity constants at 495.5, 542.5, 581.5 and 619.5°. E in calories per mole has been calculated by means of the equation

$$E = 2.303 \left(\log_{10} \frac{k_2}{k_1}\right) \left(\frac{T_1 \times T_2}{T_2 - T_1}\right) \qquad (5)$$

R is the gas constant expressed in calories per mole per degree; k_2 and k_1 are the velocity constants at the absolute temperatures, T_2 and T_1, respectively. The values of $\log_{10} k$ corresponding to a certain total flow rate of gas have been plotted against $1/T$, the resulting curve being a straight line. The slope of the curve was used to calculate E. In Table IV the first column gives the temperature in degrees centigrade, the second the total gas flow rate, the third the velocity constant and the fourth column the energy of activation, E.

Table IV

The Energy or Activation for the Decomposition of Ammonia on Copper

t, °C.	V, cc./min.	k	E, cal./mole
542.5	12	0.20	42,000
581.5	12	.65	
495.5	25	.041	
542.5	25	.24	46,500
581.5	25	.82	
619.5	25	2.80	
495.5	50	0.041	
542.5	50	.32	47,500
581.5	50	1.15	
619.5	50	3.90	

The most probable value of E is 46,000 ± 2000 calories per mole.

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[9] Mittasch and Frankenburger, *Z. physik. Chem.*, A139, 386 (1928).

The Results of Elöd and Banholzer

Eldd and Banholzer[10] have made measurements on the decomposition of ammonia on copper by a dynamic method which was essentially the same as we have used here. Their results may now be explained by assuming the same reaction mechanism, that is, by using equation (3) to calculate velocity constants. A few typical calculations of their results are given in Table V. The first column gives the table number and the second column the experiment number from their paper. The notation in the other columns is consistent with that used in our Table I, except that the flow rates are in terms of cc. per hour, hence k_1 is expressed in these units.

TABLE V

THE DECOMPOSITION OF AMMONIA ON COPPER ACCORDING TO ELÖD AND BANHOLZER

$t = 700°$[a]

Table	Expt.	v'	v'_H	v'_N	k_1	Table	Expt.	v'	v'_H	v'_N	k
2	1	180	0.0	0.0	28	3	1	1191	0.0	0	26
2	4	2260	.0	.0	33	3	3	1292	.0	1000	35
2	7	5340	.0	.0	37	3	4	1292	.0	5000	31
2	8	7700	.0	.0	23	3	5	1353	.0	10000	35
2	9	11400	.0	.0	35	3	6	1212	.0	16000	31[b]

[a] The temperature is not given, but a comparison with their Table VIII shows that it is probably 700°.

[b] Experiments 7–10 give values of $k_1 = 15$–20, but the value for the percentage decomposition in Erpt. 9, with $v'_N = v'_H = 0$, does not agree with Expt. 7 of Table II.

The heat of activation calculated from the values of k_1 at 600 and 700" is 63,000 calories per mole (Ref. 4, Expts. 5 and 6, Table VIII). The percentage decomposition measured at 600° was 3.7, too small to be accurate, and this may account for the high value of the heat of activation.

In Table VI are given some of the values of k_1, according to Equation 3, calculated from the experiments of Elöd and Banholzer for the decomposition of ammonia on an iron catalyst in a flowing system.

TABLE VI

THE DECOMPOSITION OF AMMONIA ON IRON ACCORDING TO ELÖD AND BANHOLZER

$t = 700°$

Table	Expt.	v'	v'_H	k_1[a]	Table	Expt.	v'	v'_H	k_1
1	2	554	0.0	826	6	7 and 8	1135	10000	1495
1	4	2438	.0	1055	7	2	2229	2000	1070
1	6	4480	.0	1365	7	5 and 4	3504	3500	1005
1	9	10015	.0	1805	7	6 and 7	5513	5500	1275
6	2	1063	1000	1150	7	8	8333	8000	1320
6	5 and 6	1129	5000	1305					

[a] Nitrogen has no effect.

The heat of activation calculated from the values of k_1 at 600 and 700° is 37,900 calories per mole. It should be noted that k_1 increases as the flow rate increases in the same general way as we have found for copper.

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[10] Elöd and Banholzer, *Z. Elektrochem.*, **32,** 555 (1926).

The Poisoning Effects of Carbon Monoxide

It is known that carbon monoxide has a higher heat of adsorption an copper than hydrogen and ammonia[11] and, therefore, in small traces, should have a pronounced inhibiting effect on the decomposition of ammonia. Carbon monoxide from formic acid and sulfuric acid was purified and dried carefully and then added to the ammonia stream before the latter reached the copper catalyst. The percentage decomposition of the ammonia was determined in the usual way. Carbon monoxide reacts with ammonia to form hydrogen cyanide and water. The "effect" of carbon monoxide which has been measured is due to the sum of the effects of carbon monoxide, water and hydrogen cyanide. The results of the experiments are given in Table VII and are interesting because the first trace of carbon monoxide produced an appreciable lowering of the rate of decomposition; but subsequent increase in the amount had little added effect.

TABLE VII

THE EFFECT OF CARBON MONOXIDE ON THE DECOMPOSITION OF AMMONIA ON COPPER

$t = 581.5°$

NH_3 per minute, cc	CO per minute, cc	% NH_3 decomposed	Expt.
32.3	0.00	21.60	1
32.3	.30	18.00	2
32.3	.79	18.20	3
32.3	1.34	18.00	4
43.8	0.00	18.40	5, 9, 10, 12
43.8	.35	15.65	8, 11
43.8	.70	15.40	7
43.8	1.20	14.86	13
43.8	1.35	14.85	6

The copper used had been sintered at 700° (see Materials) and consequently possessed a nearly uniform surface. A very small partial pressure of carbon monoxide was sufficient to cover the few active patches remaining on the catalyst; but further increase in its pressure required that the carbon monoxide compete for a portion of the uniform surface and its effect was then necessarily very similar to that of adding hydrogen. The discussion which follows throws some doubt on this explanation, but it is presented nevertheless.

Discussion

Since the rate of decomposition of ammonia has been found to be proportional to the ammonia pressure and inversely proportional to the hydrogen pressure, we can say that the surface of the copper is almost completely covered with hydrogen and that the amount of surface available for ammonia adsorption is small. The fraction of this available surface which is covered with ammonia is proportional to the ammonia pressure.

[11] Taylor, *Z. Elektrochem.*, 35, 542 (1929).

It is surprising that this simple explanation fits the facts over wide ranges of pressures. The observed heat of activation of 46,000 calories per mole is probably the true value since Beebe and Taylor,[12] and Dew and Taylor,[13] have found nearly the same values for the heats of adsorption of hydrogen and ammonia on copper, 9600 and 9200 calories per mole, respectively. The results of the experiments with carbon monoxide, which show a small fraction of the surface is abnormally active, will not alter this conclusion materially.

The use of heats of adsorption to predict catalytic activity meets with serious objections in the light of recent experimental work. When pure ammonia was passed over copper at 581.5°, the average ammonia pressure above the metal was about 60 cm. and the average hydrogen pressure about 10 cm. In the ratio of 6:1, the hydrogen nearly completely covers the surface of the metal. Hence, if the accommodation coefficients of the two gases are the same, the rate of evaporation of hydrogen from the surface must be very much smaller than that of ammonia. To consider this particular case more closely, let k_2 and k_2' be the rates of evaporation of ammonia and hydrogen, respectively, at 581.5°, each for unit area of covered surface. It is easily shown that k_2'/k_2 has the values 1/54, 1/114, 1/594 when the ratio of the fraction of the total surface covered by hydrogen to that covered by ammonia has the values 9:1, 19:1 and 99:1, respectively.[14] The pressure of hydrogen has been taken as one-sixth that of the ammonia. Hinshelwood[15] assumes that

$$k_2 = b_2e^{-\lambda/RT} \quad \text{and} \quad k_2' = b_2'e^{-\lambda'/RT} \tag{6}$$

where λ and λ′ are the heats of desorption and the b's are constants. Using the ratios of k_2'/k_2 as given above and letting $b_2 = b_2'$, it is found that $\lambda' = \lambda + 2200$, $\lambda + 8100$ and $\lambda + 10{,}900$, respectively. The constant b_2 must be 10^3 to 10^4 times as large as b_2' in order for λ′ to equal λ. Although measurements cannot be made at high temperatures, it does not seem probable that the heats of adsorption differ by such values at high pressures. For practical purposes at least the use of equation (6) is doubtless incorrect.

Further evidence that these equations are not correct has been discussed by Taylor.[16] In some cases a gas with a higher heat of adsorption can be pumped off a metal much more easily than a gas with a lower heat of adsorption. Unless the constant b varies enormously from gas to gas, the rate of evaporation is influenced by some other factors besides the heat of adsorption. Recently Benton and White[17] have reached the conclusion that when

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[12] Beebe and Taylor. THIS JOURNAL. 46, 45 (1924).

[13] Dew and Taylor, J. *Phys. Chem.*, *31*, 277 (1927).

[14] Hinshelwood. "Kinetics of Chemical Changes in Gaseous Systems," p. 206.

[15] Ref. 14, p. 233.

[16] G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, *34*, 799 (1930).

[17] Benton and White, THIS JOURNAL, 52, 2325 (1930).

hydrogen is adsorbed by nickel above −100° the adsorbed gas is activated, possibly existing as atomic hydrogen. In this ease the rate of evaporation would not be determined solely by the heat of desorption. The same conclusion is probably true for copper.

From three different viewpoints we are led to the conclusion that the equations (6) are not correct and, therefore, it is not correct to assume that the true heat of activation of a heterogeneous reaction is equal to the observed heat of activation, minus the heats of adsorption of the reactants, plus the heats of adsorption of the products which retard. Experiments on the rate of adsorption of gases by copper are in progress, from which we should be able to draw more definite conclusions with regard to various points in the foregoing discussion.

I wish to thank Professor Hugh S. Taylor for suggesting this problem and for his constant advice and criticism.

Summary

The kinetics of the decomposition of ammonia on copper have been studied by a dynamic method. The experiments were made on a large amount of catalyst between 495 and 620° with ammonia and hydrogen partial pressures between 4 and 50, and 10 and 60 centimeters of mercury, respectively. The rate of decomposition was proportional to the ammonia pressure and inversely proportional to the hydrogen pressure. Experiments in a static system confirmed the facts that the rate was inversely proportional to the hydrogen pressure and independent of the nitrogen pressure. There was no appreciable formation of copper nitride under the conditions of the experiments. The heat of activation of the reaction was 46,000 ± 2000 calories per mole. Carbon monoxide in small amounts poisoned the surface of the copper; the first amount had the greatest inhibiting effect.

Some objections to the use of heats of adsorption in calculating true heats of activation of heterogeneous reactions have been pointed out. Measurements on rates of adsorption of gases by copper are in progress.

PRINCETON, NEW JERSEY

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

THE USE OF BUFFERED AMMONIA IN THE IODIMETRIC THIOCYANATE DETERMINATION

BY H. ARMIN PAGEL AND HERMAN J. KOCH

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The suitability of borax as a non-volatile alkaline buffer to accelerate the oxidation of thiocyanate with iodine was shown by Pagel and Ames.[1] **A.** Schwicker[2] used a solution of ammonium borate as buffer (synthetically prepared by adding approximately the equivalent amount of boric acid to ammonia). Both methods give accurate results.

In case, however, it is desired to determine borate in the same sample, both of the above methods would be undesirable. Schwicker suggests that dilute ammonia accelerates the oxidation, but that there is danger of the formation of insoluble iodides of nitrogen unless the ammonia is added with extreme care; hence he discourages its use.

We have found, however, that the proper amount of dilute ammonia containing about an equivalent amount of ammonium salt does not react irreversibly with iodine, even with a large excess of iodine on long standing. Furthermore, a fixed volume of this solution gives accurate results independent of a wide range of volume and of thiocyanate (Table III). From the oxidation reaction in alkaline medium

$$NCS^- + 4I_2 + 8OH^- \longrightarrow SO_4^{=} + 7I^- + 4H_2O + ICN \qquad (A)$$

it is apparent that equivalent amounts of hydroxyl and iodine are required, Upon acidification the iodocyanogen again reacts with iodide, liberating free iodine; hence the net reaction used as a basis of computation is

$$NCS^- + 3I_2 + 4H_2O \longrightarrow SO_4^{=} + CN^- + 8H^+ + 6I^- \qquad (B)$$

With this in view an amount of ammonia was chosen which should contain sufficient reserve hydroxyl to provide for the oxidation of a large amount of thiocyanate, and still not be too alkaline in case only small amounts of thiocyanate were present. Thus, for instance, 20 cc. of 1 N ammonia should provide for 150 cc. of titration with 0.1 N iodine and still leave in excess 5 cc. of 1 N ammonia to insure complete oxidation. It should also be noted that large amounts of additional ammonium salts do not interfere with either the accuracy or the time required for complete oxidation.

Materials and Apparatus.—The preparation of solutions and type of apparatus used in this work was in general identically as described in a previous publication.[1] The additional reagents used were all "Highest Purity;" nevertheless blanks were run in all cases to detect traces of thiocyanate or other interfering impurities.

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[1] Pagel and Ames, THIS JOURNAL, 52,2698, 3093 (1930).

[2] A. Schwicker, Z. *anal. Chem.*, 77,278 (1929).

Experimental

Various amounts of ammonium sulfate (ranging from 1 to 6 g.) were dissolved in 20 cc. of 1 N ammonia and the resulting solution diluted with water to 150 cc. Then 35 cc. of 0.1 *N* iodine was added and the mixture allowed to stand from five to fifteen minutes in a dark cupboard. After acidifying with 5 cc. of 6 *N* hydrochloric acid, the iodine was immediately titrated slowly with thiosulfate, using starch indicator after the iodine color had been almost completely discharged. The equivalent amounts of iodine were also prepared from pipetted portions of standard iodate and 3 g. of potassium iodide, treated with a slight excess over the calculated amount of hydrochloric acid. The buffered ammonia solution was then added to the liberated iodine and the procedure completed as above. In both cases the thiosulfate titrations agreed identically with values obtained in the iodine–thiosulfate ratios determined in the usual manner. Ammonium chloride and nitrate substituted for the sulfate likewise gave perfect results. The analyses of known amounts of thiocyanate (tabulated in Tables I, II and III) were carried out according to the method given in the procedure below.

Procedure

The solution containing the thiocyanate in a volume of 150 to 300 cc. should be practically neutral to litmus. Any excess of strong acid or base should be neutralized. Slight acidity or alkalinity due to hydrolysis of salts may be ignored. If heavy metals which produce insoluble hydroxides are present, ammonia is added until faintly alkaline to litmus. The buffer solution containing 1 g. of ammonium salt (sulfate, chloride or nitrate) dissolved in 20 cc. of 1 N ammonia is then added and the mixture treated with standard iodine with a minimum excess of 5 cc. This excess is determined with sufficient accuracy by comparing colors with 5 cc. of iodine in a similar volume of water. (This reference solution should be prepared before starting the titration.) A larger excess of iodine does no harm. After standing for four to five minutes the solution is acidified with an excess of about 5 cc. of 6 *N* hydrochloric acid and the excess iodine immediately titrated with standard thiosulfate.

In case standard iodate is used as a source of iodine, certain modifications may be necessary. If the salts of heavy metals or of weak acids are absent, the iodate and potassium iodide may be added directly to the neutral solution of thiocyanate. A small excess of hydrochloric acid (1 or 2 cc. of 1 *N*) in addition to the calculated amount is then added. (A large excess of acid must be avoided since this would unnecessarily neutralize large amounts of the ammonia buffer.) The ammonia buffer solution is then added, the mixture allowed to stand for four to five minutes and the determination completed as stated above.

In case heavy metals or salts of weak acids are present, the iodine must be liberated in a separate flask, and the faintly alkaline mixture containing the thiocyanate is added to the liberated iodine. The ammonia buffer may be added either to the liberated iodine or the faintly alkaline thiocyanate mixture.

Table I shows the results obtained using standard iodine, with 20 cc. of 1 N ammonia and 6 g. of the given ammonium salt as buffer. The volume during oxidation was approximately 150 cc. Five minutes was allowed for complete oxidation. Identical results were obtained in fifteen minutes. The excess iodine to that required for reaction (A) ranged from approximately *5.3* to 6.5 cc. (namely, the difference between "iodine added" and $^4/_3$ times "calcd. iodine").

TABLE I

RESULTS USING STANDARD IODINE

0.07278 *N* KSCN, cc.	Buffer salt	G.	Iodine, 0.0998 N Added, cc.	Reduced, cc.	Calcd., cc.	Error, %
50	$(NH_4)_2SO_4$	6	55.00	36.38	36.46	−0.2
50	$(NH_4)Cl$	6	55.00	36.40	36.46	− .2
50	$(NH_4)Cl$	6	55.00	36.37	36.46	− .2
25	$(NH_4)_2SO_4$	6	30.00	18.20	18.23	− .2
25	$(NH_4)_2SO_4$	6	30.00	18.21	18.23	− .1
25	$(NH_4)Cl$	6	30.00	18.22	18.23	.0
25	$(NH_4)Cl$	6	30.00	18.20	18.23	− .2
10	$(NH_4)Cl$	6	15.00	7.28	7.29	− .1
10	$(NH_4)Cl$	6	15.00	7.28	7.29	− .1

Table II shows that accurate results are obtained in large or small oxidation volumes, using iodate as a source of iodine with 1 g. of ammonium salt.

TABLE II

RESULTS USING STANDARD IODATE

0.07078 *N* KSCN, cc.	Vol., cc.	Buffer salt	Iodate, 0.1000 N Added, cc.	Reduced, cc.	Calcd., cc.	Error, %
50	150	$(NH_4)_2SO_4$	55.00	36.36	36.39	−0.1
50	150	$(NH_4)_2SO_4$	55.00	36.38	36.39	.0
50	350	$(NH_4)_2SO_4$	55.00	36.34	36.39	− .1
50	150	NH_4Cl	55.00	36.34	36.39	− .1
50	350	NH_4Cl	55.00	36.33	36.39	− .2
25	350	$(NH_4)_2SO_4$	30.00	18.15	28.19	− 2
25	350	$(NH_4)_2SO_4$	50.00	18.18	18.19	− .1
25	150	NH_4Cl	30.00	18.15	18.19	− .2
25	350	NH_4Cl	30.00	18.15	18.19	− .2
25	150	NH_4NO_3	30.00	18.15	18.19	− .2
25	350	NH_4NO_3	30.00	18.14	18.19	− .3
10	150	$(NH_4)_2SO_4$	15.00	7.26	7.28	− .3
10	350	NH_4Cl	15.00	7.25	7.28	− .4

As previously stated, Table III shows that 20 cc. of 1 N ammonia even in the presence of large amounts of ammonium salt provides for large amounts of thiocyanate. Borax does not interfere; furthermore, large amounts of precipitated hydroxides have no effect on the completeness of oxidation. In a series of comparable determinations (not shown), it was found that the oxidation was apparently complete in two minutes, but four to five minutes is recommended in all cases.

In Table III, 20 cc. 1 N ammonia containing 1 g. of ammonium sulfate was used as buffer. The additional salts added are listed.

TABLE III

EFFECT OF SALTS ADDED

0 07278 *N* KSCN, cc.	Vol., cc.	Salts added G.	Salt	Iodate, 0.1000 N Added, cc.	Reduced, cc.	Calcd., cc.	Error, %
100	250	5	$(NH_4)_2SO_4$	105.00	72.72	72.78	−0.1
100	250	5	$(NH_4)_2SO_4$	105.00	72.71	72.78	− .1
50	150	5	$(NH_4)_2SO_4$	60.00	36.37	36.39	− .1
50	350	5	$(NH_4)_2SO_4$	55.00	36.32	36.39	− .2
25	350	9	$(NH_4)_2SO_4$	30.00	18.13	18.19	− .3
25	350	9	$(NH_4)_2SO_4$	30.00	18.11	18.19	− .4
25	350	2	$NaNO_3$	50.00	18.17	18.19	− .1
25	350	2	$NaNO_3$	50.00	18.18	18.19	.0
10	350	5	$(NH_4)_2SO_4$	15.00	7 29	7.28	+ .1
10	350	5	$(NH_4)_2SO_4$	15.00	7.28	7.28	.0
25	200	2	$ZnSO_4{\cdot}7H_2O$	50.00	18.15	18.19	− .2
25	200	2	$ZnSO_4{\cdot}7H_2O$	80.00	18.13	18.19	− .3
25	200	2	$MgCl_2{\cdot}6H_2O$	30.00	18.15	18.19	− .2
25	200	4	$Al_2(SO_4)_3{\cdot}18H_2O$	30.00	18.16	18.19	− .2
25	250	3	$Na_2B_4O_7{\cdot}10H_2O$	30.00	18.17	18.19	− .1
25	250	3	$Na_2B_4O_7{\cdot}10H_2O$	30.00	18.14	18.19	− .3
25	250	3	$NaC_2H_3O_2{\cdot}3H_2O$	50.00	18.14	18.19	− .3

Nickel, cobalt and manganese, even in relatively small amounts, produced very erratic results.

Summary

It has been shown that the proper amount of ammonia treated with ammonium salts gives the proper alkalinity for the rapid iodimetric determination of thiocyanate, over a wide range of conditions.

Data, and the details of procedure, and also a citation of some interfering metallic radicals, have been included.

LINCOLN, NEBRASKA

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

EQUILIBRIA IN THE IRON–NITROGEN SYSTEM

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In a previous paper[1] the values of the equilibrium constants for the reaction

$$2Fe_4N + 3H_2 = 8Fe + 2NH_3 \quad K_1 = (P_{NH_3})^2/(P_{H_2})^3 \tag{1}$$

were reported at various temperatures and with their help the dissociation pressures of Fe_4N were calculated. While these experiments were being extended to iron nitrides of higher nitrogen content, Lehrer,[2] Eisenhut and Kaupp[3] and Lehrer[4] published exhaustive studies of both the iron–NH_3–iron nitride–H_2 and the iron–nitrogen system by magnetometric and x-ray methods. The investigations in the present paper have been restricted to (1) the extension of our equilibrium data on the above reaction to 400 and 575°; (2) a determination of the equilibrium constants for the conversion of Fe_4N into the higher nitrides by NH_3–H_2 mixtures at 400, 444 and 500°; and (3) a study of the equilibria at 400 and 444° within the solid solutions formed by the higher nitrides. Some additional information has also been obtained relative to the purity of the Fe and Fe_4N phases involved in reaction (1). In the designation of the solid phases we have adopted the nomenclature of Hägg.[5] Iron containing only as much nitrogen as may dissolve in it below the P_{NH_3}–P_{H_2} ratio necessary for its conversion into Fe_4N constitutes the a-phase. The nitride approximating Fe_4N in composition over the temperature range studied is the γ'-phase. The ϵ-phase is the series of solid solutions ranging in composition from approximately that of Fe_3N to that of Fe_2N in our experiments.

Apparatus and Experimental Procedure

A dynamic system similar to that described in our previous paper was used. Hydrogen–ammonia mixtures of definite compositions were passed over a sample of iron at a fixed temperature. The gases were obtained and purified in the manner previously described.[1] Calibrated water-jacketed flowmeters permitted mixing the two gases accurately in any desired proportion immediately before passing them over the sample. All readings were corrected to the temperature and pressure at which the flowmeters were originally calibrated.

The iron used was obtained by the reduction in hydrogen of C. P. ferric

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[1] Emmett, Hendricks and Brunauer, THIS JOURNAL, 52, 1456 (1930).

[2] Lehrer, *Z. Elektrochem.*, *36*, 383 (1930).

[3] Eisenhut and Kaupp, *ibid.*, *36*, 392 (1930).

[4] Lehrer, *ibid.*, *36*, 460 (1930).

[5] *Hagg*, Nature, 121, 826 (1928).

oxalate. Iron reduced from ferric oxide has also been tried, but it cracked ammonia appreciably at 444°.

The glass reaction vessel was similar to that described in the previous paper. An attached side tube which was kept outside the furnace had three arms: one for taking samples for x-ray powder photographs, one for samples for chemical analysis, and one for mixing x-ray samples with reference substances. The reaction tube was heated by a nichrome wound furnace controlled by hand adjusted rheostats. An aluminum block was used inside the furnace as a temperature equalizer. The variation in temperature was not more than ±1.5° during a run. In the experiments carried out at 444° the furnace was replaced by a sulfur bath; the temperature in these runs was constant within ±0.5°. All temperatures were determined with chromel–alumel thermocouples in conjunction with a Leeds and Northrup Type K potentiometer. The thermocouples were calibrated against a platinum–platinum–rhodium thermocouple, calibrated by the U. S. Bureau of Standards.

In a typical experiment a charge of about 20 g. of ferric oxalate was completely reduced in the reaction tube in a stream of hydrogen at about 450°. Various mixtures of ammonia–hydrogen were then passed over the iron for definite periods of time at a fixed temperature. The composition of the gaseous mixture was checked by titration before and after it passed over the iron. At a flow of approximately 100 cc. of gas per minute no cracking occurred at 400 and 444°; slight cracking took place, however, with high P_{NH_3}–P_{H_2} ratios from 500 to 575°. Equilibrium was usually reached in ten to twenty hours at 400°, in five to ten hours at 444° and in five hours or less at 500° and higher temperatures.

At the end of each experiment pure nitrogen was run over the hot sample for a few seconds to flush out the NH_3–H_2 mixtures; the reaction tube was then removed from the furnace and the sample cooled quickly with the stream of nitrogen still passing over it. When the tube was cool an x-ray sample was taken and three samples were sealed off for analysis. These samples were then dissolved without exposure to air by breaking their containers under sulfuric acid. The nitrogen and iron contents of the samples were then determined by the Kjeldahl and the Jones reductor methods, respectively.

The x-ray data were obtained from powder diffraction photographs taken with iron K radiation in a camera of about 3.46 cm. radius. For determining the lattice dimensions the nitride samples were mixed with sodium chloride. In each case measurements were made on at least three photographs.

Results and Discussion

A. Equilibrium Runs.—The equilibrium runs for the Fe–Fe_4N system at 400 and 575° are given in Table I. From them it can be concluded that at 1 atmosphere pressure an NH_3–H_2 mixture need not contain more than 37% NH_3 to convert Fe into Fe_4N at 400, and 14.5% at 575°.

TABLE I

SUMMARY OF EQUILIBRIUM RUNS IN THE SYSTEM $Fe–NH_3–Fe_4N–H_2$ AT 400 AND 575°

Run	Temp.. °C.	NH_3 in NH_3–H_2 gas mixture, %	N_2 by weight in samples (average), %	X-ray diffraction pattern
M1	400	35	0.09	No photograph
M2		37	.14	No photograph
M3		39	.17	No Fe_4N, only Fe
M4		41	.48	Fe_4N present
P1		37	.09	Presence of Fe_4N doubtful
P2		37	.10	Very faint Fe_4N
P3		37	.11	Very faint Fe_4N
A3	575	11.5–13	.13	Only Fe
A4		12–14	.13	Only Fe
A5		14–15	.31	Very faint Fe_4N
A6		14.6–16	2.46	Strong Fe_4N

The results of the equilibrium runs in the system γ'–NH_3–ϵ–H_2 are given in Table II. The equilibrium constants were determined at 400, 444 and 500°. At temperatures of 550° and higher the cracking of ammonia made the determination of the constants impracticable.

TABLE II

SUMMARY OF EQUILIBRIUM RUNS IN THE SYSTEM γ'–NH_3–ϵ–H_2

Run	Temp., °C.	Starting material	NH_3 in NH_3–H_2 gas mixture, %	N_2 by weight in samples (average), %	X-ray diffraction pattern
P6	400	γ'	75	5.91	Only Fe_4N
P8		γ'	77	5.93	Only Fe_4N
P11		γ'	79	6.15	Presence of ϵ besides Fe_4N
F1		ϵ	79	8.78	No photograph
F2		ϵ	77	8.47	Only ϵ
F3		ϵ	75	8.22	Only ϵ
F4		ϵ	75	8.07	Presence of Fe_4N besides ϵ
III 4	444	γ'	75	6.83	Presence of ϵ and γ'
III 5		$\epsilon + \gamma'$	70	5.99	Presence of ϵ and γ'
III 12		γ'	70	6.03	Only Fe_4N
III 13		γ'	72	5.85	Only Fe_4N
III 14		γ'	72	6.14	Faint lines of ϵ besides Fe_4N
IV 2		γ'	70	6.05	Very faint lines of ϵ
IV 3		γ' (trace ϵ)	70	6.13	Very faint lines of ϵ
IV 4		γ' (trace ϵ)	72	6.20	ϵ lines stronger
B2	500	ϵ	59	7.89	Only ϵ
B3		ϵ	58	7.89	Only ϵ
B4		ϵ	56	7.63	Distinct Fe_4N lines
B5		ϵ (some γ')	54	7.30	No photograph
B6		$\epsilon + \gamma'$	58	7.45	No photograph

The errors in these experiments consist of those involved **(1)** in obtaining a constant and definite NH_3–H_2 mixture, (2) in measuring the temperature of the reacting material, and **(3)** in determining the composition and amounts of the solid phases at the end of each run. Errors **(1)** and (2) are considerably less than in the previous paper because of **(1)** the correction for variation of pressure and temperature of the flowmeter capillaries from the temperature and pressure at which they were calibrated, and **(2)** better temperature regulation. The ammonia percentages given are accurate to ± 0.5; we accordingly estimate that the percentage of ammonia in an NH_3–H_2 mixture at 1 atm. necessary to convert Fe to Fe_4N is 37 ± 2 at 400, and 14.5 ± 1 at 575°. The equilibrium percentage of ammonia for the conversion of Fe_4N into the a-phase is 77 ± **2** at 400, 70 ± 2 at 444, and 57 ± 1.5 at 500°.

It should be pointed out that the "equilibrium" values deduced from Table I above, as well as those presented in Table I of the previous publication from this Laboratory, for the Fe–Fe_4N system in reality represent only the upper limit of the true equilibrium values for two reasons. In the first place, because of the sluggishness with which NH_3–H_2 mixtures slightly below equilibrium reduced the nitride, experiments approaching equilibrium from the high nitride side were impracticable. Furthermore, any thermal decomposition of the Fe_4N formed in these experiments would tend to increase the apparent percentage ammonia necessary to convert Fe into Fe_4N. The thermal decomposition rate of the nitride samples used **was** very low. No satisfactory method of correctly estimating the influence of this factor on the equilibrium constant has as yet been devised. The slowness of the thermal decomposition compared to the rate of nitride formation makes it highly probable, however, that this influence is small.

The equilibrium measurements on the γ'–ϵ system were approached from both the high and low nitride sides. These values, however, are still susceptible to any influence that the thermal decomposition of the a-phase may have on them, and must in a strict sense also be regarded as upper limits of the true equilibrium values.

In Fig. 1 curve **A** is a plot of log K_1, the equilibrium constant for reaction (1), against $1/T$. Of the six points in the plot, four were reported in the previous paper, two were determined in the present experiments. The dotted line shows the curve obtained by Lehrer[2,4] in this region by the magnetometric method. The agreement between the two sets of experiments seems well within the combined experimental errors.

The equilibrium constant for the conversion of Fe_4N into a nitride of the solid solution region ϵ may be calculated from the equation

$$8Fe_xN + 3(4 - x)H_2 = 2xFe_4N + 2(4 - x)NH_3 \quad K_2 = (P_{NH_3})^{2(4-x)}/(P_{H_2})^{3(4-x)} \qquad (2)$$

In the temperature region studied the composition of the nitride of lowest nitrogen content of the a-phase is such as to make the value of x approximately equal to **3.** Consequently as a convenient means of comparing our results with those of Lehrer we have plotted in Fig. 1, curve B, $1/T$ against log K_3 corresponding to the reaction

$$8Fe_3N + 3He = 6Fe_4N + 2NH_3 \quad K_3 = (P_{NH_3})^2/(P_{H_2})^3 \qquad (3)$$

The dissociation pressure of Fe_4N into Fe and nitrogen is as previously pointed out approximately 5000 atmospheres at about 450°. Similar calculations from data of Table II indicate that the dissociation pressure of the ϵ-phase containing about **7.9%** nitrogen into Fe_4N and nitrogen is of the order of 3×10^5 atmospheres at 450°.

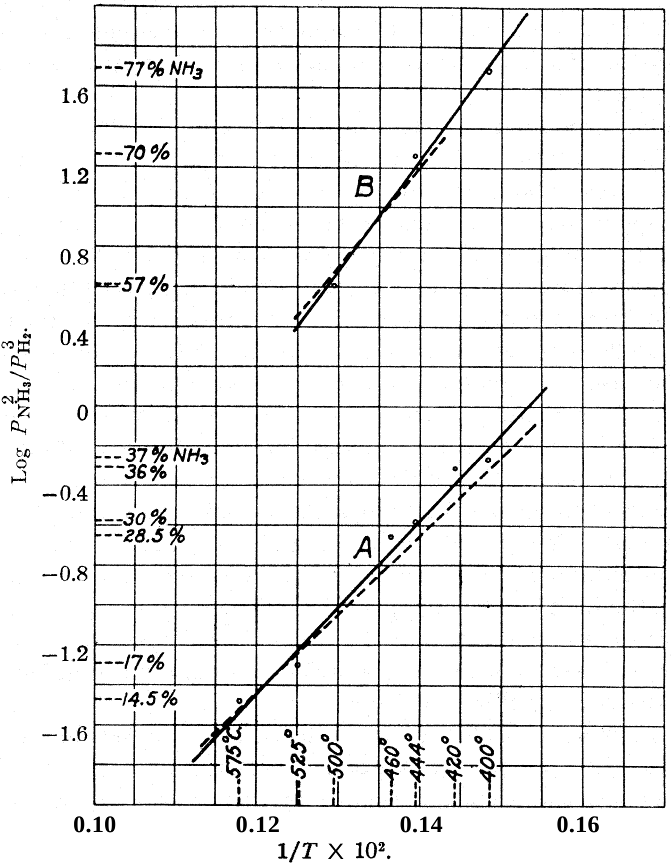

Fig. 1.—Variation of log K_1 and log K_3 with $1/T$.

B. Composition of **the** Phases

The a-Phase.—An exhaustive investigation of the amount of nitrogen taken up by iron when exposed to NH_3–H_2 mixtures containing less ammonia than corresponds to the Fe–Fe_4N equilibrium has not been included in the present experiments. However, in twelve experiments at temperatures between **400** and **575"** and at ammonia concentrations only a few per cent. below equilibrium, no more than 0.2% nitrogen could be put into the iron samples in five to ten hours' exposure. The probable error in the analytical determination was ± **0.02%** nitrogen. X-Ray diffraction patterns obtained did not show a change in the lattice constant of α-iron taking up 0.2% nitrogen.

The γ'-Phase.—In agreement with the results of Eisenhut and Kaupp our experiments indicate a variation in the composition of the γ'-phase from about **5.65** to 5.95% nitrogen. The probable analytical error in this region was ±0.05% nitrogen. The magnitude of the error in this narrow solid solution region made it impracticable to determine accurately the variation of composition of the γ'-phase as a function of the P_{NH_3}/P_{H_2} ratio used in its formation. X-Ray diffraction patterns did not show a variation in the lattice constarit of the γ'-phase with increasing nitrogen content.

The ϵ-Phase.—The variation in the composition of the ϵ-phase with increasing P_{NH_3}/P_{H_2} ratios was investigated at **400** and 444°. The summary of these experiments is given in Table III. At temperatures of 500° and higher an appreciable decomposition of the nitride prevented us from making similar investigations.

TABLE III

COMPOSITION OP THE ϵ-PHASE IN EQUILIBRIUM WITH VARIOUS NH_3–H_2 MIXTURES

	Composition of the t-phase. % N_2 by weight in nitride					
	400°			444°		
NH_3 in NH_3–H_2 gas mixtures. %	High nitride side	Low nitride side	Best average value	High nitride side	Low nitride side	Best average value
72	..	..	..	7.9	..	7.9
75	..	..	..	8.1	..	8 1
80	8.4	..	8 4	8.8	..	8.8
85	..	..	..	9.2	..	9 2
90	9 45	9.25	9 4	9.7	9.7	9.7
95	10.15	10.15	1015	1025	10.4	10.35
98	..	..	..	10.95	10.85	10.9
100	11.05	..	11.05	11.2	..	11.2

The probable analytical error varied between ±0.06% nitrogen for the lower limit of the e-phase to ±0.10% nitrogen for the upper limit. As the table shows, equilibrium was approached from both high and low nitride sides whenever the reaction rate permitted it. This was possible only with gas mixtures containing over **85%** of ammonia. Below this value equilibrium could be conveniently approached from the high nitride side only.

Figure 2 represents the variation in the composition of the various iron nitrides with increasing P_{NH_3}/P_{H_2} ratios at **400** and **444".** The slopes of the curves representing the variation in the composition of the phases α and y' are uncertain; for this reason they were drawn with dotted lines.

Errors in the determination of the lattice dimensions of the ϵ-phase by means of x-ray powder photographs might arise from systematic errors inherent in the method and from accidental errors of measurements. The technique ordinarily used consists in mounting a small sample coaxial with a cylindrical film. If the sample is too thick, the diffraction cones will not have apexes on the same line. If the sample is not accurately centered, each line on the film will be at a different distance from it. Divergence of the x-ray beams also introduces an error into the measurements. For a cubic substance these errors can partially be corrected for by extrapolating to $\Theta = 90°$ a curve obtained by plotting the values of A_K, the measured values of a_0, against the corresponding values of Θ.[6] The determination by this method of two parameters defining the dimensions of a hexagonal lattice must depend upon a relationship between them. In either case considerable error can be introduced by the extrapolation, particularly so if values of A_K are not determined for large values of Θ. This method was used by Eisenhut and Kaupp[3] in the determination of a and c for various samples of the ϵ-phase.

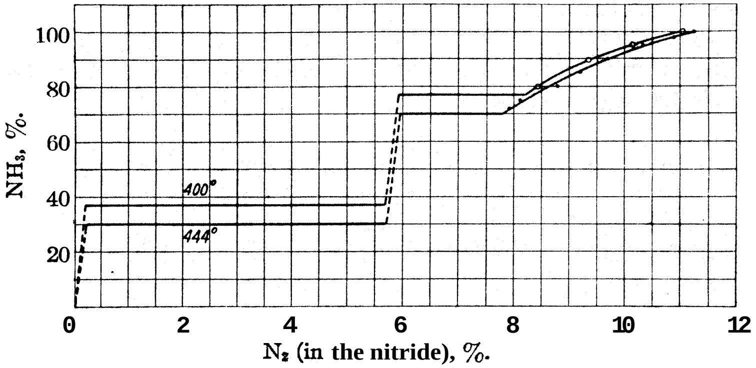

Fig. 2.—Equilibrium diagram showing the variation of the percentage nitrogen in the iron nitrides with the percentage ammonia in the ammonia–hydrogen mixtures.

In our work we effectively eliminated these sources of error by reducing the sample to very small cross sectional area, approximately the half value thickness, and by using only those films that had constant radii, determined from the sodium chloride reference lines. This method approximates the ideal case given by Kettmann.[6] The probable limits of error for the a values given in Table IV are ±0.002 Å., for the c values ±0.003 Å.

The x-ray data obtained from the ϵ-phase are summarized in Table IV. The values of a and c corresponding to various compositions of the solid phase are listed in this table and are shown in Fig. 3 in comparison with the values of Eisenhut and Kaupp and Hägg.[7] The three sets of results, although closely similar, show variations that we believe to be greater than

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[6] Kettmann, Z. *Physik*, 53, 198 *(1929)*.

[7] Hagg, *Z. physik. Chem.*, 8B, *455* (1930).

TABLE IV

SUMMARY OF X-RAY DATA FOR THE 6-PHASE

Plane	1 100% NH_3 400°	2 95% 444°	3 9590 400	4 90% 444°	5 90% 400°	6 85% 444°	7 80% 444°	8 80% 400°
(100)	2 397	2.383	2.380	2.393	2.372	2.369	2.359	2.358
(002)	2.202		2.202		2.197			2.194
(101)	2.108	2.096	2.096	2.091	2.090	2.082	2.079	2.074
(102)	1 624	1.621		1.619	1.810	1.606	1.604	1.599
(110)	1.384	1.374	1.389	1.371	1.368	1.365	1.361	1.359
(112)	1.172	1.166	1.164	1.163	1.162	1.160	1.157	1.156
(103)	1.256	1.249	1.248	1.246	1.246	1.244	1.242	1.241
(201)	1.156				1.144	1.142	1.138	1.138
(004)	1.105	1.101					1.095	
a_0	2.764	2.750	2.746	2.742	2.737	2.732	2.723	2.722
c_0	4.424	4.402	4.400	4.391	4.397	4.386	4.382	4.376
% N	11.06	10.35	10 14	9.65	9.4	9.3	8 8	8.47
At. Fe /At. N	2.02	2.16	2.25	2.35	2.42	2.44	2.60	2.72

our experimental error. Eisenhut and Kaupp indicated that both a and *c* of the e-phase are linear functions of the nitrogen concentration expressed

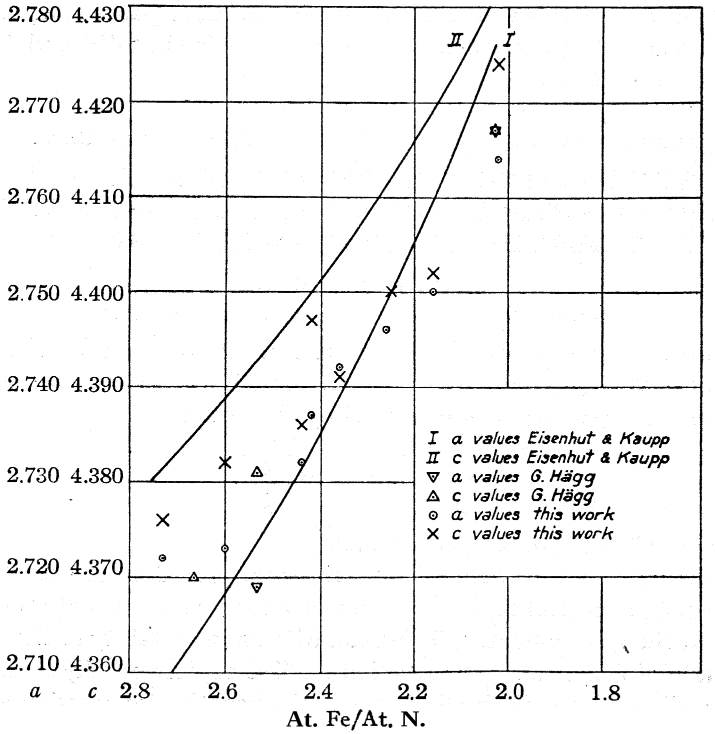


Fig. 3.—Variation in the lattice constants a and *c* of the e-phase with increasing atomic ratios Fe:N.

as per cent. by weight. Within the limits of our experimental error it is possible for a to be a linear function either of the nitrogen concentration expressed as per cent. by weight, or of the ratio of the number of iron to nitrogen atoms. The values of c, however, are not linear functions of either of these variables. We do not believe that any of the results thus far obtained are sufficiently accurate to warrant the deduction of empirical equations expressing either *a* or *c* as functions of the nitrogen concentration.

We wish to acknowledge the excellent cooperation of Miss Ellen Z. Kibbe, who analyzed all the nitride samples, and Mr. Leonardo Testa, glass blower.

Summary

1. The equilibrium data for the reaction $2Fe_4N + 3H_2 = 8Fe + 2NH_3$ have been extended to 400 and 575'; they indicate that the percentage of NH_3 in an NH_3–H_2 mixture at 1 atmosphere necessary to convert Fe to Fe_4N is 37 ± 2 at 400, and 14.5 ± 1 at 575'.

2. The percentages of ammonia in an NH_3–H_2 mixture in equilibrium with the solid phases γ' and ϵ were found to be 77 ± 2 at 400, 70 ± 2 at 444 and 57 ± 1.5 at 500°.

3. The composition and lattice dimensions of the e-phase in equilibrium with various NH_3–H_2 mixtures have been determined at 400 and 444'.

WASHINGTON, D. C

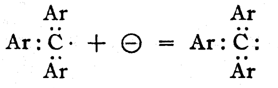
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTRON AFFINITY OF FREE RADICALS. II. DIPHENYL-ALPHA-NAPHTHYLMETHYL DIPHENYLBIPHENYL AND PHENYLBIPHENYL-ALPHA-NAPHTHYLMETHYL

BY HENRY E. BENT

RECEIVED MARCH 2, 1931 PUBLISHED MAY 6, 1931

The work to be described in this paper is a continuation of the study of the effect of various groups on the electron affinity of organic free radicals.[1] The type reaction may be represented by the equation



$$\mathrm{Ar}:\overset{\mathrm{Ar}}{\underset{\mathrm{Ar}}{\ddot{\underset{\cdot\cdot}{C}}}}\cdot + \ominus = \mathrm{Ar}:\overset{\mathrm{Ar}}{\underset{\mathrm{Ar}}{\ddot{\underset{\cdot\cdot}{C}}}}: \quad (1)$$

Ar, in general, being an aromatic group.

The details of the method and experimental procedure are described in the first paper on triphenylmethyl, in which it was shown that its electron affinity in the gaseous state is 59 kg. cal. with an uncertainty of the order of magnitude of 5 kg. cal. The reaction studied experimentally is the addition of sodium to the free radical to give the negative ion in ether solution

$$Na + R = Na^+ + R^- \quad (2)$$

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[1] H. E. Bent, THIS JOURNAL, 52, 1498 (1930).

in which R is the free radical. It is possible to determine the free energy change for this reaction by shaking a solution of the sodium salt with mercury. This partially reverses the reaction and from the equilibrium data the free energy change for Reaction 2 is obtained. By combining appropriate equations an estimate is then obtained for Reaction 1 in the gaseous phase.

This paper describes the work on three more free radicals which were chosen because of the large dissociation of the corresponding ethanes and because of their increasing complexity. The large dissociation of the ethane makes it possible to assume in the dilute solutions used that all of the material is in the form of the free radical.

Procedure

The experimental technique has been improved in two or three respects. The final crystallization of the chloride, which is sensitive to moisture, is carried out in an atmosphere of carbon dioxide. A convenient apparatus is made by cutting the bottom from a ten-liter bottle, inverting, and supporting a glass shelf at the beginning of the constriction of the neck. This shelf is put in place by fastening corks to the inside of the bottle with sealing wax melted onto the glass with a soldering iron. Dry carbon dioxide is then passed steadily into the neck of the bottle during recrystallization. Analysis of the gas shows that objects may be moved in and out of the bottle without introducing as much as 1% of air. The purified chloride is transferred to a small bottle without coming in contact with air. This small bottle, Fig. 1, may be evacuated for removal of the last traces of solvent and permits removal of a sample without introducing air a steady stream of carbon dioxide preventing downward diffusion while the sample is removed with the aid of a long silver spatula.

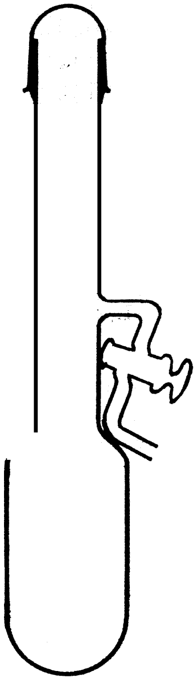

Fig. 1.—Sample bottle.

The alundum disks used for filtering the solutions have been replaced by sintered Pyrex disks, which give tighter seals to Pyrex and less adsorption of water or other reactive compounds.[2]

Materials

α-**Naphthyldiphenylchloromethane.**—This compound was prepared from the corresponding carbinol, obtained from the Eastman Kodak Co., by treating with hydrogen chloride. The chloride so formed melted at 169–171° and the analysis for chlorine by the Carius method gave 10.65 and 10.89; calcd., 10.79.

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[2] W. F. Bruce and H. E. Bent, THIS JOURNAL, 53, 990 (1931).

Diphenylbiphenylchloromethane.—Dr. R. B. Whitney very kindly furnished this compound. The preparation of benzophenone[3] was carried as far as the chloride stage as the first step. This was then isolated[4] and the final Friedel and Crafts reaction carried out according to the directions of Schlenk.[5] After recrystallization, analysis for chlorine gave 9.75; calcd., 10.0.

Phenylbiphenyl-α-naphthylchloromethane.—Phenylbiphenyl ketone was prepared[6] and converted into the carbinol by means of α-naphthylmagnesium bromide.[7] The chloride was then treated with hydrogen chloride gas as usual and after recrystallization analysis for chlorine gave 8.45 and 8.47; calcd., 8.76.

Experimental Results

The experimental data are given in Table I, the last column giving the mean value of log K for Reaction 2. In the sixth column the calculation is made assuming the salt to be completely ionized, an assumption which,

TABLE I

EQUILIBRIUM CONSTANTS FOR THE ADDITION OF SODIUM TO FREE RADICALS

Compound	G. atoms of Na removed × 104	G. atoms of Na left × 104	Moles of ether	G. atoms of mercury	Log K_2		Mean
					$K_3 = \infty$	$K_3 = 10^{-4}$	
Diphenyl-α-naphthylmethyl	0.750	2.305	0.145	1.01	14.71	13.40[b]	
	.626	1.024	.107	1.387	14.43	13.31	
	.287	0.540	.119	1.250	14.46	13.61	
	.142	.232	.119	1.190	14.31	13.72	
	.137	.234	.120	1.238	14.37	13.78	13.6
Diphenylbiphenylmethyl	1.608	3.642	.129	1.200	14.58	14.04	
	1.211	2.424	.126	1.151	14.46	14.08	
	0.343	1.203	.143	1.115	14.87	13.80	
	.226	0.749	1	1.070	14.84	13.91	
	.125	.287	.106	1.560	14.78	14.09	14.0
Phenylbiphenyl-α-naphthylmethyl	.560	6.39	.102	1.493	16.17	14.32	
	.284	1.693	.117	1.192	15.45	14.17	
	.274[a]	1.948	.079	1.829	15.96	14.48	
	.223[a]	1.203	.099	1.065	15.38	14.17	
	.178[a]	1.219	.095	1.106	15.63	14.39	
	.112	0.373	.128	1.437	14.99	14.27	14.30

[a] These runs were made by Mr. M. E. Dorfman on a fresh sample of chloride. [b] The large values of log K_2 arise from the large free energy change accompanying the solution of sodium in dilute amalgam. Log a_2/N_2 for these amalgams is -12.89; see Bent and Hidebrand, THIS JOURNAL, 49, 3011 (1927).

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[3] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 26.

[4] Gomberg, THIS JOURNAL, 37, 2677 (1915).

[5] Schlenk, Ann., 372, 18 (1910).

[6] Norris, Thomas and Brown, *Ber.*, 43, 2956 (1910).

[7] Schlenk, *Ann.*, 394, 196 (1912).

of course, is not correct. The data of this column are given for the purpose of showing to what extent the assumed ionization constant influences the final results. In the seventh column the value of K_3, the ionization constant of the sodium salt, is taken as 10^{-4}. This is the same value that was used in the first paper and gives the most concordant results for K_2. One would hardly expect a variation of more than a power of ten among such similar compounds and anything smaller than this is not significant for these calculations. Although the assumption that the mass law may be applied to the ionization of these electrolytes in ether solution, using concentration for activities, is certainly not accurate,[8] it probably introduced no significant error which would alter the conclusions. Only if these compounds deviated widely in their behavior, not only from the simple mass law but also from each other, would the conclusions drawn from these experiments be in error.

Discussion of Results

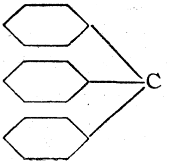
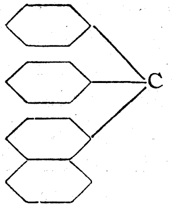
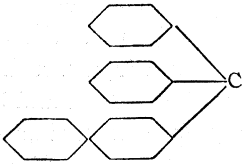
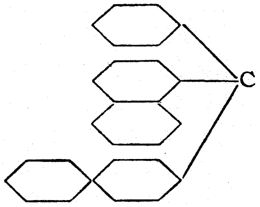
The equilibrium constants corresponding to the addition of sodium to four different free radicals have been determined experimentally. For sodium the standard state is taken as the metal at 25°. For the radical and the two ions the activity is taken as equal to the mole fraction. The total reaction may be considered to be the sum of two reactions: first, sodium metal giving sodium ion and an electron; second, free radical plus an electron giving the methide ion.

$$\begin{array}{llll} \mathrm{Na} & & = \mathrm{Na}^+ & + \ominus \\ \ominus & + \mathrm{R} & = \mathrm{R}^- & \\ \hline \mathrm{Na} & + \mathrm{R} & = \mathrm{Na}^+ & + \mathrm{R}^- \\ \textbf{solid} & \textbf{ether} & \textbf{ether} & \textbf{ether} \end{array} \qquad (2)$$

The equilibrium constants given in Table I are for this total reaction. In discussing the results it is perhaps more convenient to express them as free energies with the aid of the equation $AF = -RT \ln K$. Table II gives the values in kilogram calories for AF of Reaction 2.

TABLE II

THE FREE ENERGY OF ADDITION OF SODIUM TO FREE RADICALS IN ETHER SOLUTION

Triphenylmethyl	Diphenyl-α-naphthylmethyl	Diphenylbiphenylmethyl	Phenyl-α-naphthylbiphenylmethyl
			
AF, −17.9	AF, −18.6	ΔF, −19.1	AF, −19.5

Ziegler and Wollschitt, Ann., 479, 123 (1930).

The free energy data given in Table II are, therefore, the sums of the free energy changes for the two parts which go to make up reaction (2). Since, in every case, sodium ion is being formed in ether solution, the energy change corresponding to this part of the reaction will be a constant and any changes in ΔF in Table II must be due to the changing electron affinity of the free radical. In the first paper of this series an estimate of 59 kg. cal. was obtained for the electron affinity of triphenylmethyl in the gaseous state. As far as possible comparisons should be made in the gaseous state in order to eliminate the effect of the solvent. When this is done the variation of 1.6 kg. cal. in the electron affinities of the free radicals studied becomes a little less than **3%** of the energy change in the gaseous state. One may say, then, that to a rather rough first approximation the electron affinity of the four free radicals studied is the same.

Further examination of the data leads to the conclusion that within this 3% variation in the electron affinity there are regularities which are significant. An increase in the size of the molecule causes an increased electron affinity. Thus, substitution of an α-naphthyl group for the phenyl group produces a change in ΔF of **0.7** kg. cal., while a substitution of biphenyl for phenyl produces a change of 1.2 kg, cal. The two groups substituted in the same molecule produce an effect which, within the accuracy of the experiments, is the sum of their effects individually, namely, 1.6 kg. cal. The experimental error is about 0.2 kg. cal.

The fact just noted, that the larger molecules have the greater electron affinity, is very surprising when considered in conjunction with the data on the dissociation of the corresponding ethanes. If the energy change accompanying the process of joining two carbon atoms is determined by the behavior of the electrons entering into the bond, then a larger electron affinity might be expected to give rise to a greater strength of chemical bond. For polar compounds this may readily be demonstrated by breaking up the whole process of compound formation into several steps, as has been done by Born, one of which is the addition of an electron to the negative element. It becomes evident in this case that a greater electron affinity, other factors remaining constant, causes the resulting compound to be more stable. The same fact may be observed when considering a series of compounds such as the halogen derivatives of a number of metals. The fluorides are most stable, then the chlorides, bromides and iodides. This is the same order found in measuring the electron affinities of the halogens, fluorine having the greatest and iodine the least electron affinity. The oxides and sulfides show a similar connection. In fact, the phenomenon that the greater electron affinity is associated with the more stable compound seems to be quite general. When we turn to non-polar compounds we find that it is not quite so easy to break up the process of compound formation into a number of steps which are known experimentally. However, here also stability seems to be associated with a large electron affinity. The best illustration is probably to be found in the stability of the halogen molecules, iodine, which dissociates readily, having a small electron affinity and fluorine, which has a large heat of dissociation, having a high electron affinity.

It would appear, therefore, that the electron affinity of an atom or molecule is a measure of the energy change accompanying a process which is very intimately related to chemical valence and the stability of chemical compounds. The two processes, of course, have much in common. In the case of the electron affinity the process involved is the bringing of an electron to a carbon atom which has seven electrons around it, six of which are shared In the case of the formation of a carbon-carbon bond an electron is brought to the same carbon but, in this case, is not a free electron but is an odd electron of another carbon atom. From the standpoint of these relations one would expect the larger free radicals to be the least dissociated, judging by their electron affinities, which are the greatest. What one finds is that these are the free radicals which are most dissociated. Walden[9] has summarized the various data which all lead to the conclusion that the larger free radicals studied in this work are those which are most dissociated.

The way out of this difficulty seems to be with the aid of the concept of steric hindrance. If we assume that the strength of the bond is determined not alone by the behavior of the electrons forming the valence pair but also by the rest of the molecule, then it is possible to understand the above facts. In Fig. 2, a schematic curve, we may indicate very roughly the potential energy of a system of a free radical and an electron as a function of the distance, r, between them. We may also assume that a free electron approaches to about the same distance from the central carbon atom regardless of the bulk or exact position of other groups attached to it, the depth of the valley in this potential energy curve being the 59 kg. cal. determined in this investigation. If, however, the electron were attached to a bulky group of atoms we might not be surprised to find that it could approach only to a distance corresponding to the position (A) on the curve, and the decrease in the energy of the system would be correspondingly less. The fact that the

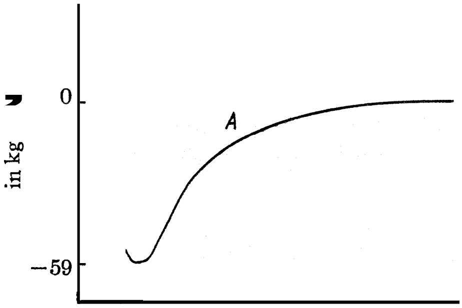


Fig. 2.—The electron affinity as a function of the distance of the electron from the equilibrium position in the molecule.

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[9] P. Walden, "Chemie der freien Radikale," Verlag von S. Hirzel, Leipzig, 1924.

larger free radicals have somewhat deeper potential energy curves, therefore, has little effect on the firmness of a weak bond, this being determined primarily by the closeness of approach of the two atoms. Thus, the biphenyl and α-naphthyl groups prevent the central carbon atoms coming as close together as they do when phenyl groups are involved, and the bond is correspondingly weaker.

This idea also explains the fact that the heat of dissociation of the normal aliphatic carbon–carbon bond is about 73 kg. cal.,[10] while the heat of dissociation of the bond in hexaphenylethane is about 11 kg. cal.[11] These figures indicate that the steric effect prevents the two carbon atoms approaching closer than the distance which corresponds to about one-seventh of the way down the potential energy curve for two aliphatic carbon atoms. The fact that the heat of dissociation of ethane is about the same as the value calculated for a single bond in diamond[10] indicates that the hydrogen atoms in ethane introduce, as might be expected, no steric effect.

Two questions remain to be considered: first, the significance of the solvent in these equilibria, and, second, the use of free energy data in discussing the potential energy curve in Fig. 2. Although the conclusions discussed above are found not to be altered by either of these considerations, they can hardly be dismissed without careful attention.

The solvent undoubtedly has a very great effect on the equilibrium studied experimentally. In the paper on triphenylmethyl it was shown that the solvent affected the free energy change of the reaction to the extent of about 77 kg. cal. Since most of this 77 kg. cal. comes in the solvation of the sodium ion, the effect of the ether on the electron affinity of the free radical is very much less. The significant problem, however, is to determine to what extent the effect of the solvent will vary from one compound to another. Considering the reaction

$$R + \ominus = R^-$$

it is necessary to discover in what way the activities will change in passing from the standard state for the solution to the standard state for the gas reaction, and in particular how this change will vary with radicals of varying size. The effect of the solvent may be divided into three parts: first, the change in activity in passing from the standard state in solution to the standard state in the gas resulting from the van der Waals' forces; second, a similar effect resulting from more specific valence forces centering around the unsaturation in the free radical; third, the effect of the solvent resulting from the charge on the ion. The first of these factors, that of van der Waals' forces, does not have to be considered inasmuch as it will be the same for the ion as for the free radical and will, therefore, cancel out.

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[10] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1931, p. 328.

[11] Ziegler and Ewald, Ann., 473, 163 (1929).

The second, the effect of valence forces, probably is not significant, inasmuch as Ziegler and Ewald[11] have shown that the change in the dissociation constant and the heat of dissociation of hexaphenylethane, in passing through a series of eight widely varying solvents, varies less than 2 kg. cal. In considering the third factor, the effect of the solvent resulting from the charge on the ion, we find that there is an increase in the free energy in passing from the ion in solution to the ion in the gaseous state. The amount may be calculated by Born's equation

$$AF = \frac{e^4}{2r}(1 - 1/D)$$

which gives 27 kg. cal. for an ion of radius 4.6 Å. An increase of 33% in the volume of the ion would cause a decrease of about 2.7 kg. cal. in this free energy change. This would also result in $-AF$ for the electron affinity of a large free radical in the gaseous state being larger than for a small one as compared with the values in ether solution. Therefore, we are led to the conclusion that the solvent affects the comparison of free energies to a small extent, 3–5 kg. cal., and that the observation that the larger molecule has the greater electron affinity would be still more marked in the gaseous state.[12]

The second question to be considered is the relation between the free energy change of the gas reaction and the heat of the reaction. Since the free radical and its ion are of the same mass, by the Sackur–Tetrode equation they will have the same entropy. The change in entropy for the reaction will be just the entropy of the electron gas which is of the order of three entropy units. Therefore, for this reaction AF equals ΔH to within 1 kg. cal., making use of the equation $AF = AH - TAS$. Hence for practical purposes we can interchange free energy and heat of reaction in discussing these reactions.

In conclusion, the writer takes pleasure in acknowledging the work of Mr. M. E. Dorfman in making measurements on one of the compounds and the assistance of Dr. R. B. Whitney in preparing another.

[12] A somewhat different way of treating the same problem of the effect of the solvent on the equilibrium is to consider the changes in heat content and entropy of the reactants and products in passing from the solution to the gaseous state. The changes in entropy of the ion were calculated by the method used by Latimer and Kasper[13] for water solutions taking the experimental data of Bridgeman for the coefficient of thermal expansion of ether and integrating graphically. The change in entropy of the free radical was estimated from Hildebrand's modification of Trouton's rule and from his definition of regular solutions as being those for which there is no entropy change on mixing, The heat change for the ion was calculated by the equation of Born given above, which is for either heat or free energy change. The heat of solution of the free radical would be practically the same for both and was estimated from Hildebrand's modification of Trouton's rule and the specific heats. The result was approximately the same as from the more direct procedure and offers confirmation of that result.

[13] Latimer and Kasper, THIS JOURNAL, 51, 2293 (1929)

Summary

1. As a first approximation the electron affinity in the gaseous state of the four free radicals studied is 60 kilogram calories.

2. The substitution of larger groups for phenyl slightly increases the electron affinity. The effect of substituting two groups is approximately the sum of the effects of the groups individually.

3. The fact that the larger free radicals have the greater electron affinity and the smaller tendency to form ethanes suggests that due to steric hindrance the carbon atoms cannot approach each other as closely and, therefore, the energy liberated is smaller.

4. The effect of the solvent on the equilibrium is considered and found to be essentially the same for the four free radicals studied.

CAMBRIDGE, MASSACHUSETTS

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

THERMODYNAMIC PROPERTIES OF FUSED SOLUTIONS OF SODIUM BROMIDE IN SILVER BROMIDE

BY EDWARD J. SALSTROM

RECEIVED MARCH 2, 1931 PUBLISHED MAY 6, 1931

The following investigation represents a contribution to the general program begun by Hildebrand and Ruhle[1] of gathering data upon the free energy of dilution of fused salt solutions. The system selected, solutions of sodium bromide in silver bromide, is a continuation of the more recent study by Salstrom and Hildebrand[2] of investigating the influence of the size of the cation of the diluting salt upon the activity of the solvent. The freezing point–composition diagram obtained for this system by Sandonnini and Scarpa[3] shows no evidence of complex salt formations which might add complexity to any interpretation of the results.

Experimental Part

The sodium bromide was from commercial sources of high purity The remaining materials, apparatus and procedure involved in this investigation were essentially the same as those described for the previous study of lithium bromide in silver bromide.[2,4] In short, the method consists of removing hydrolysis and oxidation products from the cell by bubbling a stream of dry hydrogen bromide gas through the fused salts for at least two hours. Bromine gas generated by electrolysis of fused lead bromide

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[1] Hildebrand and Ruhle, THIS JOURNAL, 49, 722 (1927).

[2] Salstrom and Hildebrand, *ibid.*, 52, 4650 (1930).

[3] Sandonnini and Scarpa, *Atti. accad. Lincei*, II, 22, 517 (1913).

[4] Salstrom and Hildebrand, THIS JOURNAL, 52, 4641 (1930).

was then bubbled through the melt over a graphite rod dipping into the solution. Equilibrium was attained in about two hours. Readings were then taken at certain temperature intervals over the whole permitted temperature range several times. Ascending and descending series were in complete agreement.

TABLE I

Ag/AgBr, NaBr/Br_2

Mole fraction of AgBr	Temp., °C	E. m. f. obsd., volt	Mole fraction of AgBr	Temp., °C.	E. m. f. obsd., volt
1 000 A	442 3	0 8031	0 6045 C	569.3	0.7955
1.000 A	453 6	8000	.6045 C	577.0	.7936
1 000 A	456 0	.7989	.6045 C	588.9	.7910
1.000 A	467.0	.7956	.6045 C	597.9	.7889
1.000 A	490.9	.7887	,6045 C	598.4	.7888
1 000 A	499 9	.7866	.6045 C	598.5	.7887
1 000 A	521.4	.7803	.6045 C	604.3	.7874
1.000 A	524 4	.7795	.6045 C	604.4	.7873
1.000 A	531.7	.7769	.6045 C	616.3	.7844
1.000 A	538 3	.7751	.6045 C	618.0	.7840
1.000 A	556.2	.7702	.5130 D	605.8	.7966
1.000 A	565.0	.7680	.5130 D	608.3	.7960
0.7486 B	481.6	8056	,5130 D	609.7	.7957
7486 B	507.3	.7985	.5130 D	611.8	.7953
.7486 B	526.4	.7936	.5130 D	613.0	.7950
.7486 B	526.7	.7935	.5130 D	613.3	.7949
.7486 B	527 2	7934	.5130 D	614.3	.7948
.7486 B	551 7	7874	.5130 D	615.5	.7945
.7486 B	553.1	.7869	.5130 D	616.5	.7944
7480 B	605.8	.7735	5130 D	617.7	.7942
.7486 B	607.0	.7732	5130 D	618.7	.7940
7486 B	807.9	.7730	5130 D	618 8	.7939
.7486 B	615.8	.7711	5130 D	621 3	.7934
			.5130 D	621.7	.7933

The results of the e. m. f. measurements of the cell, Ag(s)/AgBr(l), NaBr(l)/Br_2(g), are given in Table I and plotted in Fig. 1. The values for pure silver bromide are those obtained in the silver bromide–lithium bromide investigation.[2] Because of the high melting point of solutions rich in sodium bromide, measurements on cells beyond a half mole fraction of this salt could not be obtained with the Pyrex containers used. The study of cells containing increasing fractions of sodium bromide was also increasingly limited as to temperature range. The extreme deviations of the observed values from the straight lines drawn through them in Fig. 1 is 0.4 millivolt, and the average deviation is less than 0.15 millivolt.

Since the theoretical treatment of the results will ultimately require a knowledge of the interionic distances, it was considered desirable to measure the density of a solution containing a half mole fraction of each salt. The method consisted in weighing a tungsten-weighted quartz bulb in air, in water and then at various temperatures in the fused salt solution, correcting[5] each time for the expansion of quartz. The bulb was sharply tapped before each reading to remove any adhering bubbles of gas. The densities observed are given in Table II.

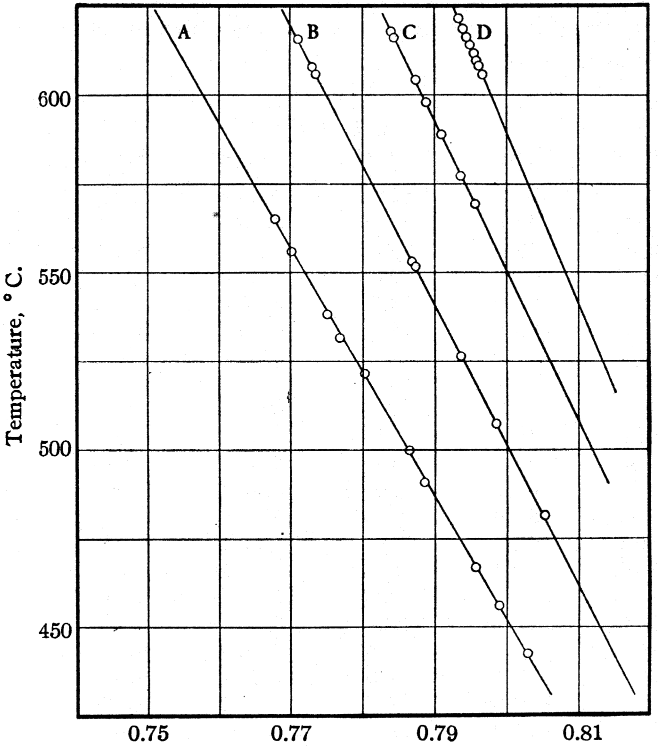

Fig. 1.—Temperature, e. m. f. and composition relations of the cells **Ag/AgBr, NaBr/Br₂.** Mole fraction of silver bromide in A is 1.000, B is 0.7485, C is 0.6045 and D is 0.5130.

TABLE II

DENSITIES OF 0.5 MOLE FRACTION OF NaBr IN AgBr

Temp., °C.	619.3	616.0	615.0	613.2	612.0	609.5	607.4
Density	3.754	3.757	3.758	3.759	3.760	3.762	3.764

The observed values yield the equation for the density of 0.5 mole fraction of sodium bromide in silver bromide, $d^t = 4.311 - 0.0009\ t$. Using the density values for silver bromide obtained by **Lorenz** and **Höchberg**[6]

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[5] Data are not available for calculating the effect of surface tension of the fused solution upon the suspending wire but, because of the fineness of the platinum wire employed, it is believed that such corrections would prove negligible.

[6] **Lorenz** and **Höchberg,** *Z. anorg. allgem. Chem.*, 94, 288 (1916).

and for sodium bromide obtained by Jaeger,[7] we have calculated the molal volumes of silver bromide and sodium bromide at 600° as 34.74 cc. and 42.01 cc., respectively. A 50 mole per cent. solution at this temperature has a molal volume of 38.53 cc., which is 0.15 cc. more than additive.

Discussion of Results

Since our main interest lies in the relation of free energy to composition at constant temperature, we obtained from Fig. 1 plotted on a large scale the values of the e. m. f., E, determined for each solution at the temperatures 550 and 600°, together with their values of dE/dt. These temperature coefficients fall off almost linearly with the mole fraction of silver bromide, N_1. From these values we have obtained by the aid of the usual formulas, values of the entropy, ΔS_1, and partial molal entropy, $\bar{S}_1$, the free energy of formation, ΔF_1, and the partial molal free energy or free energy of dilution, $\bar{F}_1$, the molal heat of formation, ΔH_1, and the heat of dilution, $\bar{H}_1$, the activity, a_1, and the activity coefficient, a_1/N_1.

TABLE III

ENERGY RELATIONS OF SILVER BROMIDE WHEN DILUTED WITH SODIUM BROMIDE

N_1	1 0000	0.7486	0.6045	0.5130
$dE/dT \times 10^6$ (volts/deg.)	−290	− 2	−238	−218
ΔS_1 (cal./deg)	−6.69	−5.91	−5.49	−5.03
$\bar{S}_1$ (cal./deg.)	0.00	0.78	1.20	1.66
550°, E (volt)	.7720	.7877	0.8002	0.8088
550°, ΔF_1 (cal.)	−17810	−18180	−18460	−18660
550°, $\bar{F}_1$ (cal.)	0	−370	−650	−850
550°, ΔH_1 (cal.)	−23320	−23040	−22980	−22800
550°, $\bar{H}_1$ (cal.)	0	280	340	520
550". a_1	1.0000	0.8014	0.6719	0.5952
550°, a_1/N_1	1.000	1.071	1.112	1.160
600°, E (volt)	0.7577	0.7749	0.7883	0.7979
600°, ΔF_1 (cal.)	−17480	−17880	−18190	−18410
600°, $\bar{F}_1$ (cal.)	0	−400	−710	−930
600°, a_1	1.000	0.7956	0.6658	0.5861
600°, a_1/N_1	1.000	1.063	1.101	1.142

These values are given in Table III and Fig. 2; Curve A shows $-\bar{F}_1$ plotted against log $(1/N_1)$ where N_1 is the mole fraction of silver bromide. If we attempt to calculate $-\bar{F}_1$ by assuming the activity to be equal to the mole fraction we find that the simple assumption of complete ionization of both salts or of no ionization yield the same result, namely $a_1 = N_1$. This is evident when it is considered that dilution with sodium bromide would, if both salts were completely ionized, make no change in the proportion of bromide ion, but merely substitute sodium ion for silver ion, thus reducing the activity of the latter and hence of silver bromide in proportion to N_1, the

[7] Jaeger, *Z. anorg. allgem. Chem.*, 101, 16 (1917).

same as for the case of no ionization. Such calculations are represented by curve B, Fig. 2, slightly higher than the observed. There is therefore a positive deviation of the activity from Raoult's law since a_1/N_1 is greater than unity. However, the deviation is not nearly so marked as that found for solutions of lithium bromide and silver bromide.[2]

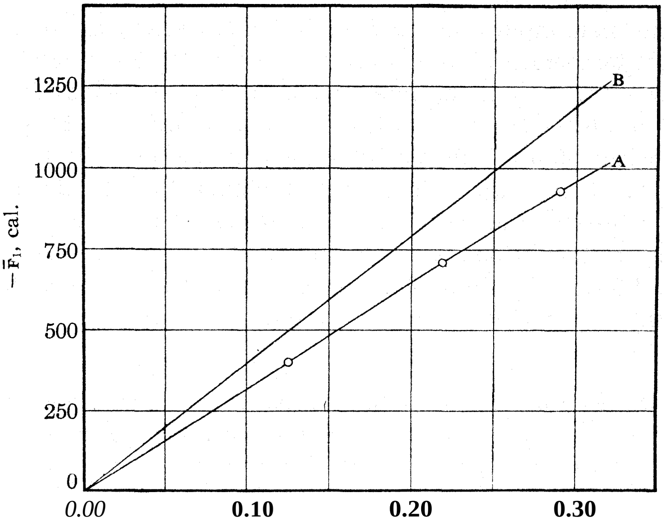

Fig. 2.—Change in free energy of silver bromide at 600° upon dilution with sodium bromide: A, observed; B, calculated.

It is of interest to note that dilution of silver bromide by lithium bromide,[2] which on the basis of complete ionization assumption simply means a substitution of the small lithium ion for the silver ion of more than double its size, lowers the activity of silver bromide far less than a similar dilution by sodium bromide where the substituted silver ion is only about four-thirds the size of the substituting ion. It therefore seems evident that the change in interionic forces due to the substitution of ions of varying size should be considered. This phase of the investigation is being carried further by studying the change in activity of silver bromide upon dilution with potassium bromide and rubidium bromide where the substituting cations are even larger. When data for these systems are at hand we expect to make a more comprehensive study of the whole subject.

Summary

1. E. m. f. measurements have been made of the cell, Ag(s)/AgBr(l), NaBr(l)/Br_2(g) at mole fractions of silver bromide varying from **1.00** to **0.513** between the temperatures **450** and 620°.

2. Calculations have been made of the free energy of dilution, the heat

of dilution, entropy, activity and activity coefficients of these solutions at the temperatures of 550 and 600°.

3. Density determinations of 0.5 mole fraction sodium bromide in silver bromide were made between 600 and 620° and may be expressed by the equation, $d^t = \mathbf{4.311} - 0.0009\,t$.

4. It is pointed out that the positive deviation of the results from Raoult's law seem to indicate that changes in interionic forces upon dilution should be considered.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

DEFORMATION OF ELECTRON SHELLS. III. THE MAGNETIC SUSCEPTIBILITY OF NEODYMIUM NITRATE

BY P. W. SELWOOD[1]

RECEIVED MARCH 4, 1931 PUBLISHED MAY 6, 1931

The object of this work, as pointed out in previous papers,[2] was to investigate the relations existing between the absorption spectra and other properties of certain rare earth salts. It has already been shown that in the case of aqueous solutions of neodymium salts a shift toward the red of the absorption bands with increasing concentration is attended with an increase in the ionic refraction of the neodymium. The purpose of the work here reported was to see whether the magnetic susceptibility of neodymium nitrate suffered a perceptible change as the changes in absorption and refraction were taking place.

Experimental

The magnetic apparatus used resembled the Bauer and Piccard[3] modification of Quinckes' capillary rise method. As shown in Fig. 1 the capillary tube C, which was **1** mm. in internal diameter, was placed between the truncated poles of a Weiss electromagnet. The interspace between the poles was **3** mm. During the course of readings the meniscus was always returned to the same position both while the field was applied and while it was off. It was, therefore, not necessary that the field should be uniform, although an investigation showed that it was uniform over a considerable region. The meniscus was observed by means of the telescope A. The magnet was operated with a current of 5.2 amperes, which was sufficient nearly to saturate the iron pole-pieces as is shown in Fig. 2. This procedure is essential if error is not to be introduced from the hysteresis characteristics of the iron.4 It also reduces the proportionate error from slight deviations in the current through the magnet.

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[1] **National Research Fellow.**

[2] **Selwood, THIS JOURNAL, 52,3112,4308 (1930).**

[3] **Bauer and Piccard, J.** *Phys.,* **1,** 97 **(1920).**

[4] Sève, ***Ann. chim. phys.,*** *27,425* **(1912).**

As the susceptibility of most paramagnetic substances is inversely proportional to the absolute temperature, it was necessary to control the temperature of the solution contained in the magnetic field. This was done by circulating water from a thermostat constant to 0.1° through a brass collar made to fit snugly between the pole-pieces. Windows were provided for illumination and observation of the meniscus,

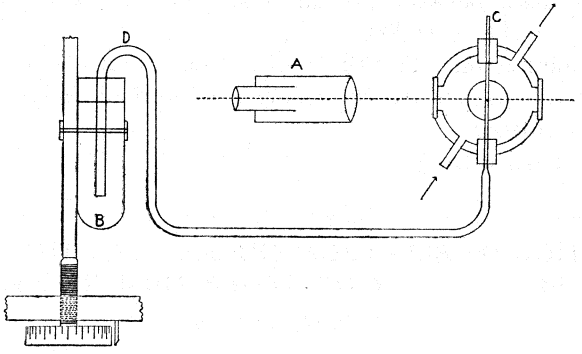

Fig. 1.—Apparatus for measuring magnetic susceptibilities.

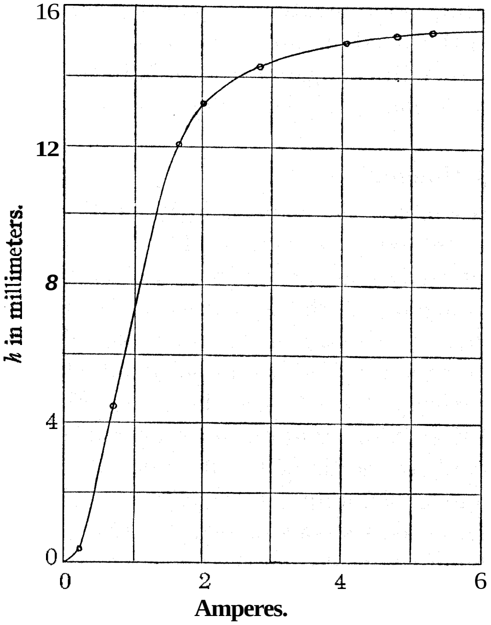

Fig. 2.—Variation of rise of liquid in magnetic field with current through magnet.

The height of the meniscus was controlled by the reservoir B which **was** mounted on the moving frame of a cathetometer. It was possible by this means to duplicate the setting of the meniscus in the absence of the field to **0.01** mm. As the amount of each solution available was not large, it was necessary to reduce the size of the reservoir until the cross section of the tube D was an appreciable fraction of that of the reservoir. This introduced a slight correction to the change in height of the reservoir, owing to immersion of the tube D. The latter had an internal diameter of 2 mm. In the case of the most concentrated solutions *h* was about **30** mm.

As great absolute accuracy for the measurements was not essential, the apparatus was calibrated with redistilled water whose mass susceptibility at 20° was taken as -0.720×10^{-6}.[5] This indicated a field strength of 26,600 gausses with a current of 5.2 amperes. The mass susceptibility of the solutions was then calculated from the relation

$$X_s = \frac{\frac{2hdg}{H^2} + K_0}{d}$$

where h is the true rise of the solution in the reservoir, d is the density of the solution at 20°, g is the gravitational constant, H is the field strength, and K_0 is the volume susceptibility of air, which is given by Brant as 0.0288×10^{-6} at 20°. For diamagnetic substances the above equation is modified to

$$X_s = \frac{\frac{2hd_1g}{H^2} + K_0}{d}$$

where d_1 is the density of the liquid in the reservoir B, which, however, did not differ from d by more than a fraction of 1%.

The apparent susceptibility of the solute was then calculated from the relation

$$X = \frac{X_s + 0.72(1 - p)10^{-6}}{p}$$

where p is the weight fraction of solute present.

The densities and compositions of the solutions were determined as described in previous communications.

The preparation of pure, neutral solutions of rare earth nitrates is a problem which has heretofore given some difficulty. One of the methods used by the author, which consisted of treating the pure oxide with insufficient acid to effect complete solution, has the disadvantage that the resulting excess hydrated oxide is difficult to remove. The other method, which is the prolonged fractional crystallization of the slightly acid salt from distilled water has the disadvantage that it is difficult to remove the last trace of the acid. This is no doubt due to the high solubility of the rare earth nitrates in water.

The method devised for the present work apparently overcomes both these disadvantages. The neodymium oxide, the preparation of which was described elsewhere, was again treated with hydrogen sulfide, and was precipitated repeatedly as oxalate in order to remove all common elements. The oxide was dissolved in a slight excess of redistilled nitric acid and was then heated for half an hour at 250° under reduced pressure (a few mm. of mercury). This resulted not only in the elimination of all excess nitric acid, but in the complete dehydration of the salt, as determined by analysis. The anhydrous salt was very hygroscopic and gave a clear solution in both water and ethyl alcohol, which is not the case with neodymium nitrate which has been heated until decomposition commences at 280–290°. It

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[5] **Brant,** *Phys. Rev,* **17, 678 (1921)**

was found that in the presence of a reducing agent such as alcohol, decomposition of the nitrate took place below 100°. It is believed that this is the first time that anhydrous neodymium nitrate has been prepared. In view of the good solubility of the nitrate in ethyl alcohol, opportunity was taken to measure its magnetic susceptibility in that solvent. The aqueous solutions prepared from the anhydrous salt may be concentrated by slow evaporation without hydrolysis taking place, but if the solution is boiled, a white basic nitrate appears. The solutions so prepared appear to be identical in physical properties with the solutions most carefully prepared by other methods.

Results

The magnetic susceptibilities of the solutions investigated, together with the apparent susceptibility of the anhydrous salt and of the neodymium ion, are given in Table I. The apparent susceptibility of the neodymium suffers a decrease of over 2% in the concentration range 0.3 to 3 molar.

TABLE I

THE MAGNETIC SUSCEPTIBILITY OF NEODYMIUM NITRATE AT 20°

% $Nd(NO_3)_3$ by weight	Moles per liter	$\chi_s \times 10^6$	$\chi_{Nd(NO_3)_3} \times 10^6$	$\chi_{Nd^{+++}} \times 10^6$ per g ion
9.33	0.304	0.764	15.2	4980
18.56	.6574	2.223	15.13	4960
26.63	1.016	3.518	15.19	4980
33.57	1.367	4.587	15.09	4950
39.51	1.709	5.499	15.02	4930
45.05	2.068	6.395	15.08	4940
50.36	2.458	7.163	14.93	4900
51.30	2.524	7.303	14.90	4890
53.99	2.738	7.725	14.92	4890
58.04	3.089	8.267	14.76	4880

The susceptibility of the neodymium ion calculated from the molecular susceptibility in the more dilute solutions agrees with the value 4970 × 10^{-6} found by Decker,[6] who worked with dilute solutions of the nitrate. Zernike and James,[7] who worked with the crystalline sulfate octahydrate, obtained a value of 5109 × 10^{-6}.

In order to find the susceptibility of neodymium nitrate in alcohol solution, it was necessary to measure the susceptibility of ethyl alcohol. The mass susceptibility at 20° was found to be -0.76×10^{-6}. Landolt–Bornstein gives -0.73 for 99% C_2H_5OH to -0.81 for absolute C_2H_5OH.

The susceptibility of a nearly saturated solution of neodymium nitrate in ethyl alcohol, containing 22.57% by weight or 0.6732 mole of $Nd(NO_3)_3$ per liter, was found to be 2.748 × 10^{-6}. This gave an apparent value for the neodymium nitrate of 14.9 × 10^{-6}. In view of the fairly large maxi-

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[6] Decker, Ann. *Physik,* 79,324 (1926).

[7] Zernike and James, THIS JOURNAL, 48,2827 (1926).

mum probable error in determining the susceptibility of the alcohol, this value for the nitrate cannot be said to differ from the value obtained in aqueous solution.

Discussion of Results

The various measurements made by the author have shown that a relation, as predicted by Foex,[8] exists between the absorption spectrum, the refraction and the magnetic susceptibility of the neodymium ion. A concentration shift of the absorption bands toward the red is attended with an increase in refraction and a decrease in magnetic susceptibility. In view of the poor development of magnetochemical theory, and the fact that practically no work has been done on the theoretical investigation of rare earth absorption spectra, it scarcely seems possible to present an interpretation of the author's results in terms of atomic structure. It may not, however, be out of place to offer a few general remarks on the subject.

In general, the effective part of a magnetic ion is capable of independent change of orientation so far as its neighbors can influence it. That is, the magnetic susceptibility is not related to the closeness of association of the positive and negative ions as is, for instance, the dielectric constant. It is reasonable to suppose, however, that the combined influence of neighboring ions in concentrated solutions and especially in crystals would produce a field which would in some way affect the mean susceptibility of the active ion.

Owing to the difficulty of preparing the pure rare earths, it is important that comparisons of the susceptibility of different compounds of the same element should be made by the same investigator using the same materials. Unfortunately, few such measurements are available. St. Meyer,[9] who examined several salts of neodymium, does not give the individual results; but in the table given by Zernike and James[7] it is evident that the susceptibility of neodymium in the oxide has consistently been found to be lower than in the sulfate. That is a result which might be expected if the closeness of atomic binding has anything to do with the magnetic susceptibility.

The theories of Weiss, Kunz and others,[10] in an effort to account for deviations from Curie's law, consider the mutual action of the molecules or ions. These theories yield an expression $X = c/(T - \Theta)$ for the variation of susceptibility with temperature, where Θ is interpreted as a measure of the molecular field, which may be either positive or negative.

Williams'[11] work on neodymium oxide shows that the temperature variation may be expressed by $X = c/(T - \Theta)$ where $\Theta = -44°$. The

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[8] *Foex, Trans. Am. Electrochem. Soc.*, **55**, 97 (1929).

[9] St. Meyer, *Physik. Z.*, *26*, *51* (1925).

[10] *Weiss, J. phys. Radium*, *VI*, *5*, 129 (1924); Kunz, *Phys. Rev.*, *6*, *113* (1915).

[11] Williams, *ibid.*, **12, 158 (1918).**

variation in the susceptibility of neodymium nitrate found here could be accounted for by an increase of ten units (degrees C.) in 8, the molecular field being considered negative. Over the limited temperature range available it would scarcely be possible to detect such a change in 8 directly, with the experimental apparatus described.

In the case of gadolinium sulfate, as is well known, Θ is practically zero, and it might be argued by analogy that, in view of the close chemical relationship between gadolinium and neodymium, the introduction of the molecular field in the case of the latter is artificial; but the author found almost no absorption spectra shift in the case of gadolinium solutions. The explanation is, perhaps, not that the gadolinium sulfate has no molecular field, but that its more stable electron structure is less sensitive to external influence.

The nature of the molecular field remains much in doubt. As stated by Stoner[12] "...the conclusion which may be drawn is that the molecular field cannot be interpreted as being simply either magnetic or electrostatic." However, "...that there are strong forces of some kind, whose effects are similar to those of magnetic fields, is undoubted."

While the work on nitrogen–oxygen mixtures tends to show that the molecular field is a function of the concentration of the magnetic molecule, the situation in such mixtures must be very different from that in the solution of an electrolyte.

Certain small temperature shifts in the absorption spectrum of gadolinium chloride are interpreted by Freed and Spedding[13] as being due to a decrease in difference between the two energy levels involved, under the influence of the electric field of the neighboring negative ions. The same argument applies to the absorption shifts of neodymium previously reported by the author.

Now Fajans[14] interprets an increase of refraction with concentration as resulting from the deformation of the cation owing to the approach of the negative field of the anion. While there is, of course, the possibility that the observed absorption and refraction changes take place by an entirely different mechanism than the magnetic change, still it is natural to try to relate them.

It has already been suggested by Cabrera and Duperier[15] that the molecular field in the case of crystalline paramagnetic substances may be identified with the "deformation" of Fajans. They say, "It is evident that, in general, we can attribute the constant 8 to a deformation of the outer electron layer of the paramagnetic atom, under the action of the

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[12] Stoner, "Magnetism and Atomic Structure," Methuen, London, 1926.

[13] Freed and Spedding, *Phys. Rev.*, 34,945 (1929).

[14] Fajans, *Trans. Faraday Soc.*, 23,357 (1927), et *seq.*

[15] Cabrera and Duperier, *J. phys. Radium,* VI, 6,121 (1925).

other atoms combined chemically with it." There seems no reason, then, why the shift of absorption bands should not be produced by the same mechanism. Some information as to the nature of the molecular field could be gained by measurements on the susceptibility of neodymium salts diluted with the isomorphic **salts** of the diamagnetic rare earth lanthanum.

The author wishes to thank Dr. Charles P. Smyth for his interest and advice in this work. He is also indebted to Dr. B. S. Hopkins, of the University of Illinois, for the use of several hundred grams of pure neodymium oxide.

Summary

The magnetic susceptibility of neodymium nitrate in aqueous solution has been found to decrease with increasing concentration. This behavior is discussed in connection with changes in absorption spectrum and refraction previously reported by the author, and with reference to Fajans' theory of the deformation of electron shells.

PRINCETON, NEW JERSEY

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

OBSERVATIONS ON THE RARE EARTHS. XXXVII. ELECTROLYTIC PREPARATION OF RARE EARTH AMALGAMS. 1. PREPARATION OF AMALGAMS OF LANTHANUM AND NEODYMIUM[1]

BY L. F. AUDRIETH, E. E. JUKKOLA AND R. E. MEINTS, WITH B. S. HOPKINS

RECEIVED MARCH 19, 1931 PUBLISHED MAY 6, 1931

In line with a series of investigations[2] which are being carried out in this Laboratory involving the use of non-aqueous solvents for the electrodeposition of metals, preliminary experiments have been performed in an effort to plate the metals of the rare earth family from solutions of their salts in various organic and inorganic solvents, but with no marked success. That such a suggestion is not new is evident from the researches of Matignon,[3] who prepared anhydrous salts of many of the rare earth elements and investigated their solubilities in various non-aqueous solvents. In connection with these studies he says, "If a solvent could be found in which salts (of the rare earth metals) ionized it would be easy to isolate the metals by simple electrolysis after the manner of Kahlenberg." Matignon had

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[1] This paper was presented before the Division of Physical and Inorganic Chemistry the Indianapolis meeting of the American Chemical Society, April, 1931.

[2] For earlier papers of this series see Yntema and Audrieth, THIS JOURNAL, 52, 2693 (1930); Audrieth and Yntema, J. *Phys. Chem.*, 34, 1903 (1930); Audrieth and Nelson, *Chem. Rev.*, 8,335 *(1931).*

[3] Matignon, Ann. *chim. phys.*, VIII, 8, 267 (1906).

evidently been much impressed by the researches of Kahlenberg,[4] who succeeded in depositing lithium from solutions of the chloride in pyridine. The preparation of the rare earth metals presents a problem of extraordinary scientific interest, in view of the fact that only six of the sixteen elements of this group have ever been obtained in the free form (Yt, Ce, La, Nd, Sm, Eu) and only two in a high state of purity (Ce, La).

Amalgams of many active metals have been prepared by the electrolysis of concentrated aqueous salt solutions using a mercury cathode. In several instances it has been found that amalgams of higher concentration can be prepared very much more readily and with less attendant decomposition by the use of non-aqueous ionizing media. Thus, Hevesy[5] prepared a 30% barium amalgam by the electrolysis of a concentrated solution of the iodide in pyridine using a mercury cathode. Laszczynski[6] prepared concentrated amalgams of potassium and sodium by electrolysis of the corresponding thiocyanates in acetone under similar conditions. Kettenbeil[7] also studied the preparation of amalgams of various elements, but was not able to prepare those "of the rare earth metals by electrolysis of their salt solutions at a mercury cathode." He reported negative results in his attempts to prepare amalgams of cerium, yttrium, didymium, zirconium and thorium electrolytically, using water, pyridine and alcohol as solvents.

However, amalgams of yttrium, cerium and lanthanum have been prepared by thermal methods and their properties studied. The decomposition of cerium amalgam has been suggested as a method for the purification of the metal.[8] In view of these facts a study of the electrolytic preparation of rare earth amalgams was undertaken in the hope that these would lead indirectly to the isolation of metals of the rare earth family which have not, as yet, been obtained in the free state.

The experimental results outlined below prove conclusively that it is possible to prepare rare earth amalgams electrolytically, not only from aqueous solution, but more conveniently by the use of absolute alcoholic solutions. The present paper concerns itself with the amalgams of lanthanum and neodymium,[9] two of the commoner members of the rare earth family. Subsequent papers will deal with the preparation of other amalgams and their decomposition for the preparation of the free metals.

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[4] Kahlenberg, *J. Phys. Chem.*, 3, 602 (1899).

[5] Hevesy, *Z. Elektrochem.*, 16, 672 (1910).

[6] Laszczynski, *ibid.*, 4, 292 (1897).

[7] Kettenbeil, *Z. anorg. Chem.*, 38, 213 (1904).

[8] Kirsch, *Trans. Am. Electrochem. Soc.*, *29*, 57 *(1911)*; *Ind. Eng. Chem.*, 3, 880 (1911).

[9] The authors wish to take this opportunity to acknowledge their indebtedness to Dr. Pierce W. Selwood for his assistance in the preliminary experimental work leading to the preparation of these amalgams.

Experimental

Preparation of Materials.—Anhydrous neodymium chloride was prepared by the dehydration of the hexahydrate in an atmosphere of dry hydrogen chloride in the apparatus designed by Kremers.[10]

Anhydrous lanthanum nitrate can be prepared most advantageously by application of the method employed by Booth[11] in the preparation of anhydrous beryllium nitrate, involving the use of fused ammonium nitrate. In a typical run 20 g. of lanthanum oxide was dissolved slowly in 40 g. of fused ammonium nitrate at a temperature of 170° to yield a clear solution. The temperature was then raised slowly during the course of several hours until most of the ammonium nitrate had been decomposed and the melt had solidified. The material was then ground to a powder and heated for ten hours at a bath temperature of 300° to volatilize completely the remainder of the ammonium nitrate. The resulting product was ignited to the oxide for analysis.

Anal. Subs., 0.3666, 0.3995: La_2O_3, 0.1832, 0.1998. Calcd. for $La(NO_3)_3$: La, 42.77. Found: La, 42.61, 42.65.

The anhydrous nitrate is a white, powdery substance which is extremely hygroscopic. The resulting product is very soluble in water, liquid ammonia, acetone, pyridine and acetonitrile.

Several efforts were made to prepare anhydrous neodymium nitrate by the same method. However, a product was always obtained which contained ammonia and which analyzed for the compound $Nd(NO_3)_3 \cdot NH_4NO_3$. Any attempt to remove the excess of ammonium nitrate by raising the bath temperature above 290" resulted in the formation of the insoluble basic nitrate.

The mono-hydrated halides employed in these experiments were prepared by long continued dehydration of the more highly hydrated salts in *vacuo* at 100°. Their composition was checked by analysis. Dehydration at higher temperatures usually led to the formation of insoluble basic compounds.

Apparatus.—Various types of electrolytic cells were used. The test-tube type (noted as T. T. in the tables) consisted of a large Pyrex test-tube, 200 × 38 mm., to which was sealed a glass-stoppered delivery tube with a small side arm to permit contact with the mercury cathode by means of a platinum wire. A platinum flag was used as the anode and the apparatus fitted with a stirring device. To handle larger quantities of mercury and solution Erlenmeyer flasks of various sizes were used in place of the Pyrex test-tube.

Where aqueous solutions were employed an H-shaped cell was used in order to prevent in so far as possible reaction of the anodic products with

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[10] Kremers, *Ind.* Eng. Chem., 17, 298 (1925).

[11] Booth, THIS JOURNAL, 52, 2581 (1930).

the amalgams. In all cases the electrolytic cells were immersed in running water to keep the solutions at approximately room temperature.

Manipulation.—All solutions were electrolyzed for varying periods of time using a 110 d. c. current. Upon completion of the runs the cathodic materials were separated from the supernatant solutions, washed with either distilled water or absolute alcohol, and then allowed to decompose by contact with air. It was found that hydrochloric acid would not react completely with the amalgams; consequently analyses were carried out by permitting samples to decompose by exposure to the air over a period of ten days, followed by titration with standard acid to determine their rare earth metal content.

Preparation of Neodymium Amalgams.—The results for a number of typical runs are given in Table I. In all experiments involving the use of aqueous solutions an insoluble precipitate of the basic salt was obtained which would settle upon the cathode and render difficult the production of more concentrated amalgams. This did not occur when the anhydrous chloride or the mono-hydrated halides were electrolyzed in alcoholic solution.

Amalgam formation was not observed when the double neodymium ammonium nitrate, $Nd(NO_3)_3 \cdot NH_4NO_3$, was used as the solute. Reduction of the nitrate to the nitrite ion was found to have taken place.

In several experiments a pasty amalgam was obtained, indicating the formation of a Nd–Hg compound only slightly soluble in mercury. This problem is under investigation at the present time.

Neodymium amalgams are readily attacked and decomposed by air with formation of the basic carbonate. Such amalgams also undergo slow reaction with alcohol, acetone and water. They are best preserved in a vacuum or under a saturated alcoholic solution of the electrolyte.

TABLE I
PREPARATION OF NEODYMIUM AMALGAMS

Run	Type of cell	Concn. of soln.	Solvent	Time, hours	Curr. density, amp./sq. cm	Amalgam, per cent. by weight of N
8"	H	15 g. of Nd_2O_3[12] diss. in HCl to 30 cc. of soln.	H_2O	4	0.33	0.2
9[b]	H		H_2O	4	.4	1.75
14[c]	T. T.	6 g. $NdCl_3 \cdot 6H_2O$ in 30 cc.	C_2H_5OH	25	.2	..
6a[d]	T. T.	25 cc. satd. $NdCl_3$ soln.	C_2H_5OH	10	.06	2 1
19a[4]	T. T.	10 g. $NdCl_3$ in 30 cc.	C_2H_5OH	9	.07	1.6
25[f]	T. T.	8 g. $NdBr_3 \cdot H_2O$ in 20 cc.	C_2H_5OH	37	.15	2.92

[a] Poor amalgam, pptn. of basic chloride. [b] Pellet of solid amalgam formed on the surface which was analyzed. Basic salt precipitated. [c] Some amalgam, ppt. of basic chloride. [d] Good amalgam, soln. clear. [e] Pasty amalgam, clear soln. [f] Very good amalgam, clear soln.

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[12] Aqueous chloride solutions prepared by dissolving the oxide in hydrochloric acid.

Much of the mercury may be removed by distillation in *vacuo,* but not completely even at the temperature at which Pyrex glass begins to melt. The product obtained under these conditions is an extremely pyrophoric, black powder which takes fire in air. This material has been decomposed, with the elimination of the remainder of the mercury to give neodymium metal, in a high vacuum furnace using a tungsten boat, which served as the heating element. This same apparatus has even been used for volatilization of the neodymium metal with the deposition of an extremely reactive film of the element.

Lanthanum Amalgams.—Table II gives some of the experimental data covering the preparation of amalgams of lanthanum. These resemble very closely in reactions and properties the corresponding neodymium amalgams. (Table **11.)**

TABLE II

PREPARATION OF LANTHANUM AMALGAMS

Expt.	Type of cell	Composition and concn. of soln	Length of run, hours	Current density, amp./sq. cm.	Atom per cent. of La in amalgam
9a[a]	H	25 g. La_2O_3[12] to give 35 cc. of aqueous chloride soln.	6	0.2–0.1	1.6
1a[b]	T. T.	Satd. soln. of $La(NO_3)_3$ in C_2H_5OH	4	0.3	. .
12[c]	T. T.	Satd. soln. of $LaCl_3 \cdot 7H_2O$ in C_2H_5OH	3	.2	. .
1[d]	T. T.	10 g. La_2O_3[12] to give 25 cc. of aqueous chloride soln.	0.5	.6	Slight
3b[e]	T. T.	9 g. $LaBr_3 \cdot H_2O$ in 20 cc. C_2H_5OH	20	.35	3.1

[a] Formation of much basic salt causing current to decrease gradually, fair amalgam. [b] Reduction of nitrate to nitrite, no amalgam formed. [c] Basic chloride, LaOCl, precipitated; no amalgam. [d] Basic chloride formed, Hg^{++} ions present in electrolyte. [e] Pasty amalgam formed; solution remained clear; no basic salt precipitated.

Summary

Amalgams of neodymium and lanthanum may be prepared by electrolysis of aqueous and alcoholic solutions of various of their salts using a mercury cathode. Electrolysis of the anhydrous halides, or the monohydrated halides, in alcoholic solution gives better results than the use of water as a solvent. These amalgams are extremely reactive and undergo ready decomposition. The free metals may be obtained from them by heating the amalgams in *vacuo.*

URBANA, ILLINOIS

NOTES

Intensive Drying.—One or two papers published in America record failures to obtain results which their authors expected from the drying of liquids.[1]

The explanation appears to be that while expending a great deal of trouble in obtaining the liquids in the pure state, the glass of the apparatus was not sufficiently dried.

As far as can be made out from the published papers, the phosphorus pentoxide was entirely submerged in the liquid. The glass therefore obtained very little drying effect after the apparatus was sealed up. In my original experiments as described[2] a side tube or bulb containing phosphorus pentoxide was always introduced for the sole purpose of drying the glass while the separate drying of the liquid by phosphorus pentoxide was taking place. I have recently pointed out[3] that the deep-seated moisture in glass is very difficult to remove and, in my experience, this removal to the degree necessary for these experiments is only possible by very long exposure to an atmosphere dried by phosphorus pentoxide. It is obvious that the dryness of a system is only the dryness of its wettest part.

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Note on the Reaction between Hydrogen Sulfide and Mercury.— In a recent communication [THIS JOURNAL, 52, 885 (1930)], Lilienfeld and White reported the results of a study of the reaction between hydrogen sulfide and silver, and showed that the metal is attacked by hydrogen sulfide at room temperature only in the presence of oxygen and moisture; the reaction commonly supposed to occur with the production of hydrogen, *viz.*

$$2Ag + H_2S = Ag_2S + H_2$$

was found to be endothermal and not to take place at ordinary temperatures. The following observations, which show qualitatively that the reaction between hydrogen sulfide and mercury is analogous to that of the gas and silver, were noted during the preparation and purification of hydrogen sulfide in an apparatus containing several H_2S/Hg interfaces. Work to be carried out involved the measurement of pressure with a manometer, the mercury of which would be in continuous contact with pure hydrogen sulfide, hence it was necessary to determine whether any reaction took place.

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[1] Lenher and Daniels, Proc. *Nat. Acad. Sci.*, 14, 606 (1928); E. Juanita Greer, THIS JOURNAL, 52, 4191 (1930).

[2] Baker, *J. Chem. Soc.*, 123, 1223 (1923).

[3] Baker, *ibid.*, 1663 (1929).

Hydrogen sulfide, prepared by the action of dilute hydrochloric acid upon "Analytical Reagent" ferrous sulfide *in vacuo*, was passed over powdered ferrous sulfide, dried over phosphorus pentoxide, condensed in liquid air and subjected to fractional distillation. Rejected fractions were discharged at open mercury surfaces, which soon became coated with sulfide. A sample of the pure gas finally obtained was sealed up in contact with pure mercury for three months. No trace of blackening of the surface could be seen, but at the end of this period the introduction of a trace of moist air into the tube caused the mercury surface to be covered with a black film in a few hours.

Ample confirmation of the immunity of mercury from attack by hydrogen sulfide free from air and moisture was evident as the work progressed; the gas could be safely stored in tubes over mercury, and pressure measurements could be carried out without risk of contamination of the meniscus.

In their paper Lilienfeld and White mentioned that phosphorus pentoxide could not be used to dry hydrogen sulfide as it oxidized the gas to sulfur dioxide. To investigate this point the tests employed by these authors were used in an examination of the gas prepared as described. Analyses of samples of the gas showed sulfur dioxide to be absent, while no sulfur residue was left by the evaporation of a carbon disulfide extract of the contents of a phosphorus pentoxide tube through which about 25 liters of gas had passed.

It is probable that the phosphorus pentoxide used by the American workers contained lower oxides of phosphorus, which were responsible for the oxidation of the hydrogen sulfide. The drying agent used in this work was tested according to the method described by Whitaker [J. *Chem. Soc.*, 127, 2219 (1925)], and was found to be free from lower oxides.

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The Construction of a Flexible Glass Diaphragm for a Clicker Gage.—The utility of the glass clicker gage for measuring pressure changes in gas reactions has been emphasized by several investigators, in particular D. F. Smith and W. W. Taylor.[1] The essential part of this gage is the glass diaphragm. It must be strong enough to withstand a considerable pressure difference on the two sides, thin enough to have high sensitivity, and must click audibly at a definite pressure difference. As Smith and Taylor point out, the construction of a good diaphragm is very tedious. The following method is simpler and requires fewer trials to make a satisfactory diaphragm.

[1] Smith and Taylor, THIS JOURNAL, 46, 1393 (1924).

A thin glass bulb is blown at the end of a 3-mm. tube in the usual manner, but just before it becomes rigid it is squeezed lightly by a U-shaped piece of spring brass. This operation forms a banjo-shaped bulb. The flattened sides possess concentric corrugations which give superior clicking characteristics to the diaphragm. Usually only one side clicks well. However, in case there is confusion because both sides click near the same pressure difference, one of them can be heated until the corrugations are destroyed.

CONTRIBUTION NO. 56 FROM THE
EXPERIMENTAL STATION OF
E. I. DU PONT DE NEMOURS AND COMPANY
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RALPH NESTER

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

THE MOLECULAR WEIGHT OF CASEIN. III[1]

BY D. C. CARPENTER

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In the two previous papers of this series, Svedberg, Carpenter and Carpenter[2] have described their experiments dealing with the determination of the molecular weight of casein by use of the ultracentrifuge. Casein prepared either by the method of Hammarsten[3] or the method of Van Slyke and Baker[4] was shown to consist of a mixture of protein molecules of different molecular weights. Furthermore, different specimens prepared by the latter method were shown to consist of different mixtures.

By extracting Hammarsten casein with warm acidified alcohol we have separated a protein which behaved as a monomolecular substance and which had a molecular weight of 375,000. This was found to constitute about 30% of the crude Hammarsten casein. The other chief constituent of crude casein was studied in several samples of Van Slyke and Baker casein and it was shown that the molecular weight of this constituent lay between 75,000 and 100,000.

That the protein of molecular weight between 75,000 and 100,000, the one of 188,000 and the acid-alcohol soluble one of molecular weight 375,000 are separate and distinct species has been shown by the serological studies of Carpenter and Hucker.[5]

This paper deals with the estimation of the molecular weight of the

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[1] Read before the Meeting of the American Chemical Society at Cincinnati, Ohio, on September 9, 1930.

[2] Svedberg, Carpenter and Carpenter, THIS JOURNAL, 52, 241, 701 (1930).

[3] Hammarsten, "Handbuch der biochemischen Arbeitsmethoden," E. Abderhalden, Berlin u. Wien, 1910, Vol. II, p. 384.

[4] Van Slyke and Baker, J. *Biol. Chem.*, 35, 127 (1918).

[5] Carpenter and Hucker, J. Inf. *Diseases*, 47, 435 (1930).

simplest of these proteins, the one which is the chief constituent of crude casein prepared by either of the foregoing methods and which may be fractionated by potassium oxalate. We propose to find the molecular weight of this protein through calculations based upon the sulfur, phosphorus and various amino acid contents of the protein, This idea is not particularly new, as it has been used by Cohn and his co-workers[6] in attempts to calculate the probable molecular weight of several proteins. The method of attack, however, presupposes (a) a monomolecular protein and (b) accurate analytical procedure for the estimation of the desired constituent. The former requisite is most easily fulfilled when we are dealing with a crystallizable protein and is most difficult of fulfilment when we are concerned with the amorphous proteins. The second requirement, of methods which yield the correct amino acid content after hydrolysis of the protein, must take into account the amount of any given amino acid which is destroyed by the hydrolytic process or lost in other ways. Losses by the Fischer ester method have been examined on known mixtures of amino acids by Osborne and Jones[7] and found to range from 20 to 80% for various amino acids.

In determining the molecular weight of a protein from the amino acids which it contains, it is obvious that the larger the individual molecular weight of a given amino acid and the smaller the number of times it occurs in the parent protein, the greater will be the accuracy of the molecular weight estimation. From the older analyses of casein[8] which were based on what we now know to have been a mixture of material, it seems probable that the determination of cystine, tryptophane and histidine will be of most service to us in selecting the molecular weight. Methods for estimating these amino acids have been worked out for use on relatively small quantities of protein and have been reported as satisfactory. As tyrosine can be estimated in the same hydrolysate after removal of the tryptophane, we propose to carry out this determination also, but will bear in mind at the outset that as there is considerable tyrosine in casein, the molecular weight of the parent protein based on the tyrosine content can scarcely have the same degree of certainty as the results of the cystine, tryptophane and histidine analyses.

Part I. Analysis of the Protein

Sulfur.—The various methods proposed for the estimation of sulfur in proteins have been critically examined by Redfield and Huckle.[9] Of these methods the Liebig and Koch, and the Liebig methods gave the maximum recovery of sulfur from a sample of peptone. In brief the Liebig

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[6] Cohn and Hendry, *J. Gen. Physiol.*, *5*, *521* (1923).

[7] Osborne and Jones, *Am. J. Physiol.*, *26*, 305–28 (1910).

[8] Osborne and Guest, *J. Biol. Chem.*, *9*, **333** (1911).

[9] Redfield and Huckle, THIS JOURNAL, 37, 607 (1915).

and Koch method[10] consists of a preliminary digestion of the protein with nitric acid followed by a fusion with potassium hydroxide and potassium nitrate, while the Liebig method is the same except that it omits the preliminary digestion with nitric acid.[11]

Determination of Sulfur.—For the estimation of sulfur in casein we have employed the Liebig and Koch method of oxidation. About one gram of casein was digested in a Kjeldahl flask with *25* cc. of concentrated nitric acid at a brisk boil for two hours. The solution was cooled in running water and ***20*** cc. of a 40% potassium hydroxide solution added slowly to the contents of the flask, which turned deep brown in color. The solution was transferred to a nickel crucible containing 0.5 g. of potassium nitrate and evaporated over an alcohol lamp, the flask being rinsed several times and the rinsings added to the contents of the crucible as the solution volume in the latter was reduced by evaporation. The contents of the crucible were then brought to gentle fusion over an alcohol lamp to complete oxidation of the protein. After cooling, the contents of the crucible were dissolved in water, made acid with hydrochloric acid, evaporated twice to dryness with hydrochloric acid to expel nitric acid, baked to dehydrate silica, dissolved in dilute hydrochloric acid, filtered and the sulfate in the filtrate precipitated in the usual way with barium chloride, filtered, washed, ignited and weighed as barium sulfate. The results of the sulfur analysis are reported in Table I and show that the protein under examination contains 0.785% of sulfur.

Phosphorus.—Hillebrand and Lundell[12] have shown that no volatilization of phosphates occurs when heated with excess sulfuric acid below 150°. Prolonged heating at higher temperatures, however, caused conversion of H_3PO_4 to HPO_2 and $H_4P_2O_7$, which resulted in large phosphorus losses.

Baumann[13] and Martland and Robison[14] appear to be the first workers to recognize the above findings and the significance they had in the phosphorus estimation in phosphorus-containing organic compounds. Both of these workers decomposed organic materials in the presence of concentrated sulfuric acid and emphasized that phosphorus losses occurred when the temperature rose sufficiently for white sulfur trioxide fumes to appear. The former used small amounts of 30% hydrogen peroxide and the latter used nitric acid in the presence of sulfuric acid to carry out the oxidation. Both finally estimated the phosphorus by colorimetric methods.

Determination of Phosphorus.—In our own experiments we have oxidized the protein with sulfuric acid and hydrogen peroxide as recommended by Baumann,[13] adding hydrogen peroxide and heating until no further charring occurred, being careful to so restrict the heating that no sulfur trioxide fumes were lost. The solution was then diluted with water made neutral with ammonia, then acidified with nitric acid and the phosphorus precipitated as phosphomolybdate under the conditions recommended by McCandless and Burton.[15] The yellow precipitate was filtered off, washed with 5%

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[10] Liebig and Koch, *Chem. Zentr.*, **1886**, *894.*

[11] Sherman, "Organic Analysis," The Macmillan Co., New York, **1912**, p. *298.*

[12] Hillebrand and Lundell, THIS **JOURNAL**, 42, *2609 (1920).*

[13] Baumann, *J. Biol. Chem.*, **59**, *667 (1924).*

[14] Martland and Robison, *Biochem. J.*, **18**, *765 (1924).*

[15] McCandless and Burton, *Ind. Eng. Chem.*, **16**, *1267 (1924).*

ammonium nitrate until free from molybdenum, dissolved in ammonia and the solution filtered. The solution was then neutralized to litmus paper by dropwise addition of 1:1 hydrochloric acid, stirring continuotisly, and the phosphorus precipitated in the cold with magnesia mixture, followed after fifteen minutes by the addition of 12 cc. of concentrated ammonia per 100 cc. of solution volume. After standing overnight the precipitate was filtered off, washed with 2.5% ammonia, and finally with a little ammonium nitrate solution to assist in burning the filter paper. The precipitate was dried and heated carefully over a low flame and then ignited to constant weight with strong ignition and weighed as $Mg_2P_2O_7$. Blanks were run on the reagents used in both the sulfur and phosphorus estimations and the results corrected therefor. The results of the phosphorus determinations are given in Table I and show that the protein contains 0.856% of phosphorus

TABLE I

SULFUR AND PHOSPHORUS CONTENT OF CASEIN

Expt	Casein. g	$BaSO_4$ corr., g.	$Mg_2P_2O_7$ corr., g	S %	P, %
1	1 336	0 07640		0 7854	...
2	1 336	07642		7856	..
3	1 336	....	0 04084		0.8519
4	1 336	....	04118	...	8599
Mean				.7855	.8559

Recovery of Cystine.—Hoffman and Gortner[16] have followed the effect of boiling cystine with 20% hydrochloric acid for different lengths of time by the bromate titration of Okuda[17] and found that after boiling periods of twenty-four and forty-eight hours the titratable cystine recovered was 93.99 and 92.52%, respectively, of the initial amount. These authors also record the fact that the recovered cystine was optically inactive and its phosphotungstate was more soluble than that of the original plate cystine used in the experiment, and concluded that an isomeric form of cystine had been produced. Plimmer and Lowndes[18] record that cystine loses 7% of its nitrogen by boiling with acids and that only 40% of the resultant material is precipitated by phosphotungstic acid, whereas about 97% of the original cystine is precipitated by this reagent.

For the purposes of this paper we are not concerned with what products are formed from cystine under the acid treatment but only with the matter of how much cystine escapes this change for a definite period. We have accordingly followed the change during the boiling process by the iodate method of Okuda.[19] This method is applicable for the determination of cystine and cysteine in the presence of all protein cleavage products.

In short the method consists of reducing cystine to cysteine with zinc dust and acid, and oxidizing the cysteine back to cystine with potassium iodate. The reactions involved are

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[16] Hoffman and Gortner, THIS JOURNAL, 44,341 (1922).

[17] Okuda, *J. Col. Agr. Imp. Univ. Tokyo*, 7, No. 1, 69 (1919).

[18] Plimmer and Lowndes, *Biochem. J.*, 21, 247–53 (1927).

[19] Okuda, *J Biochem. (Japan)*, 5, 201, 217 (1925).

$$5KI + KIO_3 + 6HCl = 6I + 6KCl + 3H_2O \qquad (1)$$

$$6HSCH_2CHNH_2COOH + 6I = 3COOHNH_2CHCH_2SSCH_2CHNH_2COOH + 6HI \qquad (2)$$

Okuda recommends a $M/300$ potassium iodate solution for the titration, *1* cc. of which theoretically equals *0.0024* g. of cystine. At *17.5'* Okuda found that 1 cc. corresponded to *0.00215* g. of cystine and the writer has found *0.00226* g. at *18.5'*. Acid concentration and particularly the temperature must be fairly well controlled if concordant results **are** to be obtained. Starch indicator was used to mark the end-point of the titration more clearly.

Experimental

Three hundred and fifty milligrams of cystine four times recrystallized by the method of Folin[20] and dried in *vacuo* at 61°, was weighed out, dissolved in 2% hydrochloric acid and made up to 100 cc.; 10-cc. portions of this standard solution were then placed in Kjeldahl flasks and the calculated amount of concd. hydrochloric acid and distilled water added to make 100 cc. of 20% hydrochloric acid. Test-tube condensers closely fitting the necks of the Kjeldahl flasks were inserted and the entire set of flasks (with the exception of No. 1) were heated by an air-bath to the boiling temperature. At intervals of twenty-four hours one of the series of flasks was removed from the bath, the condensers washed off with a little water, the contents of the flask transferred to a distilling flask and the bulk of the hydrochloric acid removed by distilling in *vacua*. The contents of the flask was then transferred to a 50-cc. volumetric flask and diluted to volume. For determining the acidity of this solution, 1 cc. was removed and titrated with standard sodium hydroxide and the calculated hydrochloric acid or sodium hydroxide required to bring the remainder of the cystine solution to a concentration of 2% hydrochloric acid was added. The cystine was now reduced to cysteine by the addition of 0.5 g. of zinc dust, reacting overnight at room temperature. The solution was filtered and the zinc and filter paper washed with 50 cc. of 2% hydrochloric acid and to the filtrate 5 cc. of 5% potassium iodide solution and an equal volume of 4% hydrochloric acid were added, the temperature adjusted to 18.5° and the titration carried out at once with $M/300$ potassium iodate, using starch as indicator.

The results of these experiments are recorded in Table II. It is to be noted that the recovery of cystine is quantitative in solutions which have not been heated strongly, but that in solutions which have been boiled even for twenty-four hours, considerable

TABLE II

DESTRUCTION OF CYSTINE BY 20% HYDROCHLORIC ACID

No.	Cystine in expt., mg.	Period of boiling, hours	Vol. KIO_3 soln. reqd.,[a] cc.	Cystine recov., mg.	Cystine recov., %
1[b]	35.00	0	15.70	34.94	99.8
2[c]	35.00	0	15.74	35.01	100.0
3	35.00	24	14.42	32.09	91.6
4	35.00	48	13.90	30.93	88.4
5	35.00	72	13.54	30.11	86.1

[a] 1 Cc. of KIO_3 soln. = 2.225 mg. of cystine. [b] Sample 1 not boiled with 20% hydrochloric acid and not vacuum distilled. [c] Samples 2, 3, 4 and 5 with varying periods of boiling; vacuum distilled.

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[20] Folin, J. *Bwl. Chem.*, 8, 9 (1910).

cystine has been lost. The rate of loss appears to be greatest during the first twenty-four hours but additional boiling produces additional losses. These results parallel those obtained by Hoffman and Gortner[16] but the losses in cystine are somewhat greater in magnitude than they record.

That cystine analyses on proteins must be corrected for the losses incurred during the period of boiling with 20% hydrochloric acid is evident. That the same amount of destruction of cystine would occur in the hydrolysis of a protein or in a solution where other amino acids are present, from the foregoing data we are unable to say. This matter will be taken up later in this paper.

Recovery of Cystine.—It is entirely possible that what has often been reported in the literature as cystine in proteins, existed in the protein not as cystine, but in the reduced form as cysteine. It is almost useless to try to distinguish between cystine and cysteine quantitatively when both occur together, without the presence of an invert gaseous phase during the entire period of hydrolysis of the protein. Cysteine is very easily oxidized to cystine by oxygen of the air, particularly if the solution is warm, and strong reducing agents are required to carry out the reduction of cystine to cysteine.[21]

Experimental Part

A solution of purified cystine in hydrochloric acid was reduced overnight with tin,[21] treated with hydrogen sulfide to remove tin, filtered in an atmosphere of hydrogen, and hydrogen sulfide removed from the filtrate by the rapid passage of hydrogen gas through the solution; 10-cc. samples of this solution (39.00 mg. of cysteine) were pipetted into Kjeldahl flasks and the calculated amounts of concd. hydrochloric acid and water were added to make 100 cc. of 20% hydrochloric acid. Test-tube condensers were lowered into the necks of the flasks and the flasks heated in an air-bath at the boiling temperature in the same way as the cystine experiments just described. Number 1 was made up to volume in a 100-cc. volumetric flask with 2% hydrochloric acid and was not boiled or distilled in *vacuo*. Numbers 2, 3, 4 and 5 were boiled for various intervals, transferred to distilling flasks and the bulk of the hydrochloric acid distilled off in *vacuo*, the residue transferred to 50-cc. volumetric flasks and made up to volume; 1-cc. samples of these were titrated with standard sodium hydroxide and the calculated amount of hydrochloric acid or sodium hydroxide added to the remainder of the solution to bring the hydrochloric

TABLE III

DESTRUCTION OF CYSTEINE BY 20% HYDROCHLORIC ACID

No	Cysteine in expt., mg.	Period of boiling, hours	Vol. KIO_3 soln. reqd.,[a] cc.	Cysteine recov., mg.	Cysteine recov., %
1[b]	39.00	0	17.64	39.00	100
2[c]	39.00	0.5	15.98	35.33	90.6
3	39.00	24	15.34	33.90	87.0
4	39.00	48	15.40	34.05	87.3
5	39.00	72	15.36	33.98	87.1

[a] 1 Cc. of KIO_3 soln. = 2.211 mg. of cysteine. [b] Sample 1 not boiled with 20% hydrochloric acid and not vacuum distilled. [c] Samples 2, 3, 4 and 5 with varying periods of boiling; vacuum distilled.

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[21] Andrews, J. Biol. Chem., 69, 209–217 (1926).

acid concentration to *2%*. Each of these solutions was then reduced with *0.5* g. of powdered zinc overnight at room temperature, the solutions filtered and the zinc residue and paper washed with 50 cc. of *2%* hydrochloric acid; then 5 cc. each of 5% potassium iodide and *4%* hydrochloric acid solutions were added and the solutions titrated with $M/300$ potassium iodate without delay in the presence of starch indicator. The results of these experiments are given in Table III, and show that considerable cysteine is lost even by a short period of boiling with 20% hydrochloric acid. No further loss seems to occur after twenty-four hours.

Recovery of Cystine and Cysteine in Protein Hydrolysis.—While the foregoing data show that considerable cystine or cysteine is lost during a heating with 20% hydrochloric acid, they do not necessarily represent the losses encountered in the presence of other amino acids, especially in the presence of the quantities of the latter present in the native protein under investigation. We have, therefore, determined the recovery of known amounts of cystine and cysteine when added to gelatin and also to casein when hydrolyzed with 20% hydrochloric acid for seventy-two hours, following the same procedure for handling the hydrolysate and estimating cystine and cysteine as outlined before. These data are given in Tables IV and V and show that in both gelatin and casein there is considerably less cystine or cysteine recovered when the boiling with 20% hydrochloric acid is done under conditions approximating those of the actual protein hydrolysis. There is, therefore, no "sparing action" on the decomposition of the cystine or cysteine through the presence of other amino acids. The

TABLE IV

RECOVERY OF ADDED CYSTINE AND CYSTEINE FROM HYDROLYSIS OF GELATIN BY 20% HYDROCHLORIC ACID FOR SEVENTY-TWO HOURS

Expt.	Gelatin, g.	Added cystine, mg.	Added cysteine, mg.	Vol. KIO_3 soln. reqd.,[a] cc.	Cystine or cysteine recov., mg.	Cystine recov., %	Cysteine recov., %
1	*1.000*	*0*	*0*	*0.00*			
2	*1.000*	*4.00*	*0*	*12.49*	*2.54*	*63.5*	
3	*1.000*	*0*	*4.00*	*14.03*	*2.82*		*70.5*

[a] By actual standardization *1* cc. of KIO_3 soln. = *0.2033* mg. of cystine and *0.201* mg. of cysteine.

TABLE V

RECOVERY OF ADDED CYSTINE FROM HYDROLYSIS OF CASEIN BY 20% HYDROCHLORIC ACID FOR SEVENTY-TWO HOURS

Expt.	Casein hydrolyzed, g.	Added cystine, mg.	Vol. KIO_3 soln. reqd.,[a] cc.	Cystine recov., mg.	Cystine recov.. %
1	*1.068*	*0*	*14.66*	*3.32*	
2	*1.068*	*0*	*14.60*	*3.30*	
3	*1.068*	*0*	*14.71*	*3.33*	
4	*1.068*	*4.00*	*25.87*	*6.85*	*63.2*
5	*1.068*	*4.00*	*26.00*	*5.87*	*63.9*
Mean					*63.5*

[a] By actual standardization 1 cc. of KIO_3 soln. = *0.226* mg. of cystine

above data show that of added amounts of cystine only about 63% is reclaimed under the conditions of hydrolysis stated, with either protein. In the case of cysteine about 70% is recovered when gelatin is hydrolyzed. That account must be taken of these losses before an accurate estimation of the cystine or cysteine in a protein can be made is entirely obvious.

Cystine Content of Casein.—In Table VI are recorded data of four separate casein hydrolyses in which the cystine has been determined as outlined before. In calculating the actual cystine content of the protein we have assumed that the added amino acid behaves the same in the hydrolysis process as the original amino acid contained in the protein and for cystine we have used the recovery factor as obtained from Tables IV and V. These data show that the cystine content of casein is close to 0.488%. Calculated as cysteine this is 0.44%, but as will be shown later in this paper, it is probable that there is no cysteine in casein, it being there in the oxidized form as cystine.

TABLE VI

CYSTINE CONTENT OF CASEIN

Expt.	Casein hydrolyzed, g	Vol KIO_3 soln reqd, cc (a)	Cystine, mg.	Corr cystine, mg (b)	Cystine. %
1	1 336	18 41	4 16	6 55	0 490
2	1 336	18 25	4 12	6 49	485
3	1 068	14 60	3 30	5 20	487
4	1 068	14 71	3 33	5 24	490
Mean					488
Calculated as cysteine					440

(a) 1 Cc. of KIO_3 soln. equals 0.226 mg. of cystine at 18.5°. (b) Using recovery factor of 63.5% for cystine and 70.5% for cysteine.

Tryptophane and Tyrosine.—In the hydrolysis of protein to be used for tryptophane analyses we are limited to alkaline reagents and to splitting by enzymes. Even with these, appreciable amounts of the tryptophane are converted into indole.[22] The majority of methods for the estimation of tryptophane are colorimetric and in practically all of these the presence of indole or its derivatives so alters the color of the solution to be compared that anything but a rough match is impossible. For instance the method of Folin and Ciocalteu[23] gives excellent results on pure tryptophane solutions but is of little use on hydrolysates, due to the red color developed by indole derivatives on the phenol reagent. Kraus[24] finds that the indole products may be removed quantitatively by shaking out with toluene and meets with considerable success in using the vanillin–hydrochloric reaction in estimating tryptophane after an enzymatic hydrolysis of the protein.

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[22] Herzfeld, *Biochem. Z.*, 56, 82 (1913).

[23] Folin and Ciocalteu, *J. Biol. Chem.*, 73, 627 (1927).

[24] Kraus, *ibid.*, 63, 157 (1925); 80, 543 (1928).

Homer[25] hydrolyzes the protein with barium hydroxide and after the customary separating by mercuric sulfate, brominates the tryptophane with nascent bromine and titrates the excess bromine as iodine with sodium thiosulfate.

Experimental

The method which we have adopted and used in this work is essentially the hydrolysis method of Folin and Ciocalteu[23] using sodium hydroxide, followed by Homer's method of bromination[25] at a low temperature.

One gram of protein was introduced into a new clean 250-cc. Kjeldahl flask, 2 cc. of butyl alcohol added to prevent foaming, and also a short spiral of silver wire and 4 g. of sodium hydroxide (as a 20% soln.). A test-tube condenser was placed in the neck of the flask, the flask mounted over a hot air-bath and boiled for twenty-four hours. At the end of the boiling period the condenser was removed, washed off with 10 cc. of water, and the boiling continued for ten minutes to remove the alcohol; the flask was then removed from the bath and while still hot 10 cc. of 14 N sulfuric acid added dropwise from a pipet, shaking well to precipitate silica; 5 cc. more of 14 N sulfuric acid was added, the flask cooled, the contents rinsed into a 100-cc. volumetric flask and diluted to 100 cc. The flask was well shaken and the solution filtered through a dry filter. The filtration is slow and the funnel should be covered with a watch glass to prevent evaporation.

To ascertain whether tryptophane was removed from a solution containing freshly precipitated silica we have conducted the experiments given in Table VII, adding various amounts of sodium silicate to change the amount of silica present. After silica removal these solutions were compared by the colorimetric method of Folin and Ciocalteu using

TABLE VII

RECOVERY OF TRYPTOPHANE

No.	Tryptophane in expt., mg.	SiO_2, g.	Mean height compared color. mm. (a)	Tryptophane recov., mg.	Tryptophane recov., %
1	8.70	0	29.15	8.70	100
2	8.70	0.445	30.00	8.45	97.1
3	8.70	0.890	30.05	8.43	96.9
4	8.70	1.335	30.00	8.45	97.1
Mean					97.1

(a) Color standard contained 0.60 mg. of tyrosine (0.676 mg. of tryptophane) per 100 cc.; height compared, 30 mm.

TABLE VIII

RECOVERY OF TYROSINE

No.	Tyrosine in expt., mg.	SiO_2, g.	Mean height compared color, mm. (a)	Tyrosine recov., mg.	Tyrosine recov., %
1	60.0	0	26.88	58.05	96.8
2	60.0	0.445	26.70	58.5	97.5
3	60.0	0.890	27.03	57.7	96.2
4	60.0	1.335	26.14	59.8	99.7
Mean					97.5

(a) Color standard contained 5.00 mg. of tyrosine per 100 cc.; height compared, 25 mm.

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[25] Homer, J. *Biol.* Chem., 22, 369 (1915).

carefully prepared tyrosine as the color standard. As there was no indole in these solutions the color comparison was entirely satisfactory. Approximately 97% of the total tryptophane content appeared in the filtrate no matter how much silica was present as adsorbent. This seems to indicate that whatever loss of tryptophane occurs is due to adsorption by the filter paper rather than by silica. About the same recovery is shown for tyrosine in the experiments reported in Table VIII. In subsequent experiments the first 10 cc. of filtrate from the removal of silica was discarded, the remainder of the filtrate reserved for analysis and stored in the dark at 0°.

For the analysis of the hydrolysate, 8 cc. of hydrolysate was transferred to a 15-cc. centrifuge tube and 4 cc. of 15% mercuric sulfate in 6 N sulfuric acid added. The mixture was allowed to stand overnight in the ice box and then centrifuged for five minutes. The liquid was decanted into a 100-cc. volumetric flask, draining well and rinsing the tube edge with 0.1 N sulfuric acid. The sediment in the centrifuge tube was washed with 10 cc. of 1.5% mercuric sulfate in $2N$ sulfuric acid, stirring with a fine glass rod. The tube was centrifuged again and the liquid decanted as before into the 100-cc. flask, draining arid washing again as before. The sediment in the centrifuge tube was reserved for the tryptophane determination.

Tyrosine.—Tyrosine in the mother liquid was determined as recommended by Folin and Ciocalteu, except that we have found that diluting the red-orange solution after development of the color was best done with N sulfuric acid instead of with water. If the dilution to standard volume is made with water, an opacity develops within a few moments that renders color comparisons inaccurate. No trouble has been experienced when N sulfuric acid has been used as the diluent.

Tryptophane.—The sediment in the centrifuge tube was suspended in 10 cc. of N hydrochloric acid, warmed on the steam-bath, decomposed with hydrogen sulfide and centrifuged. The solution containing the tryptophane was then decanted into a beaker and the precipitated mercuric sulfide washed twice with 0.1 N hydrochloric acid, which after centrifuging was added to the main tryptophane solution. The solution was heated over the steam-bath until freed from hydrogen sulfide and treated with phosphotungstic acid solution to remove polypeptides, avoiding an excess. The solution was placed in the ice box overnight and the slight precipitate of polypeptides filtered off. The excess phosphotungstic acid was removed by barium hydroxide and the excess barium removed by sulfuric acid, avoiding an excess of the latter. The solution was filtered into a stoppered Erlenmeyer flask and cooled to 0°.

For the bromination of the tryptophane, 0.5 cc. of concd. hydrochloric acid, 5 cc. of 10% potassium bromide and 10 cc. of 0.01 N potassium bromate were added to the solution and the flask placed at 0° overnight (eighteen hours) for the reaction to complete itself. The excess bromine in the reaction flask was estimated by adding 5 cc. of 10% potassium iodide and titrating the liberated iodine with 0.01 N sodium thiosulfate solution, adding 1 cc. of starch solution as indicator.

The potassium bromate and sodium thiosulfate solutions are, of course, standardized against each other and the potassium bromate in turn against purified tryptophane in known amounts. Conducting the bromination under the conditions we have used, 1 cc. of 0.01 N potassium bromate will brominate 0.2296 mg. of tryptophane. This is practically identical with the value 0.2304 mg. found by Homer[25] for the bromination at 17" after six to eight hours, each tryptophane molecule requiring 8.86 moles of nascent bromine.

Recovery of Tryptophane and Tyrosine from Casein Hydrolysates and the Tryptophane and Tyrosine Contents of Casein.—In Tables IX and X are recorded our results on the tryptophane and tyrosine content of

casein and the percentage recovered of known amounts of each amino acid added before hydrolysis of the protein. The data show that 81.3% of the added tryptophane and 99.4% of the added tyrosine were reclaimed quantitatively under the conditions of hydrolysis. The correct contents of tryptophane and tyrosine in the simplest casein are therefore 1.237 and 5.55%, respectively.

TABLE IX

TRYPTOPHANE CONTENT OF CASEIN

Expt.	Casein, g.	Added tryptophane, mg.	Added tyrosine, mg.	$N/100$ $KBrO_3$ soln. reqd., cc.[a]	Tryptophane found, mg.	Tryptophane recov., %	Tryptophane in casein %
1	0.948	0.00	0.00	41.60	9.55		1.235
2	0.948	8.70	0.00	72.55	16.60	81.3	
3	0.948	0.00	60.00	41.50	9.52		1.239
Mean							1.237

[a] Standardization of $N/100$ potassium bromate solution against weighed amounts of pure tryptophane gave 1 cc. of $N/100$ $KBrO_3 = 0.2295$ mg. of tryptophane.

TABLE X

TYROSINE CONTENT OF CASEIN

Expt.	Casein, mg.	Added tryptophane, mg.	Added tyrosine, mg.	Mean heights in mm. of column compared		Tyrosine found, mg.	Tyrosine recov., %	Tyrosine in casein, %
				Stand.[a]	Unknown			
1	94.8	0.00	0.00	30.00	34.23	5.205		5.52
2	94.8	0.87	0.00	30.00	34.56	5.255		5.58
3	94.8	0.00	6.00	25.00	26.84	11.160	99.4	
Mean								5.55

[a] Standard for Expts. 1 and 2 contained 6.00 mg. of tyrosine per 100 cc. Standard for Expt. 3 contained 12.00 mg. of tyrosine per 100 cc.

Homer[25] has shown that the bromination of indoleacetic and indolepropionic acid takes very nearly the same amount of bromine as required by tryptophane and hence the presence of these substances would not interfere materially in the above determination, as each of them no doubt originally occurred in the protein as tryptophane. Indole and skatole, however, require only about two-thirds as much bromine as tryptophane in the bromination reaction. Homer believes that as the solubility of both of these substances is very low, very little error will be introduced into the final titration by their presence. At any rate the tendency would be to give a calculated tryptophane content slightly too low and a calculated molecular weight of the protein too high on this account.

Our data show that the presence of added tryptophane and tyrosine has no influence on the recovery of each other from the hydrolysate.

Histidine.—For the determination of the basic amino acids in proteins, Vickery and Leavenworth[26] have worked out a reliable method. The

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[26] Vickery and Leavenworth, *J. Biol. Chem.*, 76, 707 (1928).

method is, however, only applicable to large quantities of protein. As we have not had sufficient material for carrying out their method, we have used the method described by Hanke[27] and Koessler and Hanke[28] in our work, as the latter is a colorimetric method in which only small amounts of protein are required. The method in brief after separation of histidine and arginine from the hydrolysate consists in coupling histidine with *p*-diazobenzenesulfonic acid in the presence of sodium carbonate to form a reddish-orange color. The principal drawback to the determination is the fleeting character of the color developed, which usually makes more than one reading on a given trial impossible. Hanke states that no other substances likely to be present except histamine and tyramine affect the color to be compared, and that these would not be expected to be present except in putrescent decomposition. The reader is referred to Hanke's paper[27] for details of the method. We have used Hanke's method throughout with no changes, except that we have hydrolyzed the casein with sodium hydroxide in the same way as in the foregoing tryptophane determinations. In fact we have used the identical hydrolysate solutions which were prepared for the tryptophane and tyrosine determinations.

Through lack of a larger supply of the pure casein species under examination, we have been unable as yet to carry out experiments to ascertain the recovery of known added amounts of histidine from casein digests under the conditions of the alkaline hydrolysis used, and we will report the histidine content as we have found it, without reference to any possible corrections for histidine destroyed during the hydrolysis.

Histidine Content of Casein.—In Table XI are recorded data of three separate casein hydrolyses, in which the histidine has been determined as

TABLE XI

HISTIDINE CONTENT OP CASEIN

Expt.	1	2	3
Casein hydrolyzed, g.	0.948	0.948	0.948
Tryptophane added, mg.	None	8.70	None
Tyrosine added, mg.	None	None	60.00
Casein in color soln. compd., mg.	1.896	1.896	1.896
Standard color (a) depth (mm.) matched against 20 mm. depth of unknown	18.10	18.20	18.20
	18.15	18.20	18.30
	18.35	18.40	18.30
	18.40	18.10	....
Mean	18.25	18.225	18.26
Histidine found, mg.	0.0337	0.0336	0.0337
Histidine, %	1.777	1.774	1.778

[a] 21.67 mm. standard color = 0.04 mg. of histidine.

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[27] Hanke, *J. Biol. Chem.*, 66, 475 (1925).

[28] Koessler and Hanke, *ibid.*, 66, 505 (1925).

given above. Assuming that no histidine has been lost during the hydrolysis, the histidine content appears to be 1.776%. As the same amount of histidine was recovered from hydrolyzing casein to which known amounts of tryptophane and tyrosine had been purposely added, it appears that either these amino acids interfere to a like degree or else not at all, in the recovery and determination of histidine.

Part II. Estimation of the Molecular Weight.—It is obvious that provided we have a pure protein and have made no mistakes in the analyses for the various constituents, each constituent will occur in the molecular weight of the protein a whole number of times its own molecular (or atomic) weight. In the instance at hand we may also be guided by the centrifuging results of Svedberg, Carpenter and Carpenter,[2] who showed that the molecular species in question had a molecular weight between 75,000 and 100,000.

Calculated from the Sulfur and Phosphorus Content.—On the basis of 0.7855% sulfur in the protein we calculate that the minimal molecular weight possible for the protein is 4081.4 and from the value 0.8559% for phosphorus, that the corresponding value is 3626.5. The smallest number which will contain each of these numbers a whole number of times (least common multiple) is obviously

Sulfur.............................. 4081.4 × 8 = 32,651.2
Phosphorus......................... 3626.5 × 9 = 32,598.5

with a mean value for the least common multiple (S_8P_9) of 32,624.8. The actual molecular weight of the protein is some whole multiple of this last number. The values possible are

1×	2×	3×	4×
32,625	65,250	97,875	130,500

Out of these values the only one which satisfies the centrifuging results is the number 97,875, which shows that the least common multiple number is multiplied by 3 and that S_{24} and P_{27} represent the respective proportions of these elements in the protein. Calculating the molecular weight directly from the content of each of these elements separately, we obtain

From sulfur determination (S_{24}), molecular weight = 97,954
From phosphorous determination (P_{27}), molecular weight = 97,796

Calculated from Cystine Content.—From the cystine value 0.488% we calculate that the minimum molecular weight of the protein is 49,234. The molecular weight is some whole multiple of this number

1×	2×	3×
49,234	98,468	147,702

from which 98,468 is selected as the *only* value possible to reconcile with the centrifuging results. This result agrees well with that calculated from the sulfur and phosphorus analyses.

Assuming that the cystine occurs as cysteine in the amount 0.44%, we calculate that the minimum molecular weight must be 27,536 and the possible molecular weight

1×	2×	3×	4×
27,536	55,072	82,608	110,144

The value 82,608 is the only possibility from this series and this is impossible to reconcile with the values obtained from the sulfur and phosphorus analyses. In other words the assumption that cysteine occurs in the protein instead of cystine does not appear to be in accord with the facts.

Calculated from Tryptophane Content.—From the tryptophane content of 1.23% we calculate the minimum molecular weight of the protein to be 16,498. The molecular weight is, of course, a whole number multiple of this minimum number

1×	2×	3×	4×	5×	6×
16,498	32,996	49,494	65,992	82,490	98,988

Of this series the values 82,490 and 98,988 both satisfy the centrifuging results, but only the latter, 98,988, is in harmony with the sulfur and phosphorus results. It is concluded, therefore, that the latter is the only possible choice.

Calculated from Tyrosine Content.—As there is so large a quantity of tyrosine present in casein, 5.55%, we cannot estimate the molecular weight of the protein with any certainty, for the minimal molecular weight is calculated to be 3266. Thirty times this value, however, gives a possible molecular weight of 97,980, which is in harmony with all the results we have obtained thus far with this protein.

Calculated from Histidine Content.—Assuming that the histidine figure, 1.776%, requires no correction, we calculate that the minimal molecular weight is 8953. The only possible multiples of this value that are in harmony with the centrifuging results are the multiples 9, 10 and 11, giving molecular weight values, respectively, of 80,577, 89,530 and 98,480. As the latter value 98,480 is in harmony with our results with other constituents, it is considered to be the best choice of the three values.

Table XII

Summary of Results and Calculation of Molecular Weight

	Found, %	Minimum mol. wt.	Multiple	Probable mol. wt. of casein
Sulfur	0.7855	4,081	24	97,954
Phosphorus	0.8559	3,626	27	97,796
Cystine	0.488	49,234	2	98,468
Tryptophane	1.237	16,498	6	98,988
Tyrosine	5.55	3,266	30	97,980
Histidine	1.776	8,953	11	98,480
			Mean	98,279

Results and Conclusions

We have summarized our analytical results and calculations of the molecular weight of the simplest casein species in Table XII and conclude that the value 98,000 for the molecular weight agrees best with all our different analyses and also with our previous results with the ultracentrifuge.

Summary

1. The protein contained in crude casein, which has been shown to have a molecular weight between 75,000 and 100,000 by the ultracentrifuge, has been subjected to analysis.
2. The sulfur, phosphorus, cystine, tryptophane, tyrosine and histidine contents have been found to be 0.785, 0.856, 0.488, 1.237, 5.55 and 1.776%, respectively.
3. The most probable value for the molecular weight of this protein, consistent between the above analyses and the results obtained with the ultracentrifuge, was shown to be 98,000.

GENEVA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF ZOOLOGY, UNIVERSITY OF CALIFORNIA]

THE ABSORPTION SPECTRA OF ORTHO-CHLOROPHENOL INDOPHENOL AND OF ORTHO-CRESOL INDOPHENOL

BY MATILDA MOLDENHAUER BROOKS

RECEIVED OCTOBER 29, 1930 PUBLISHED MAY 6, 1931

Spectrophotometric determinations of the absorption spectra of *o*-chlorophenol indophenol and of o-cresol indophenol[1] between wave lengths of 480 and 680 mμ are presented in this paper. Two samples of each dye were used: a very pure sample[2] obtained from Dr. W. Mansfield Clark, to whom the writer is indebted for its presentation, and a commercial sample from the LaMotte Chemical Products Co.

The dyes were dissolved in various buffer solutions in concentrations of 0.00005, 0.0001 and 0.0002 M. These concentration values were based upon the assumption that the samples used consisted of the designated dyestuffs exclusively. Since in the case of one sample, this was apparently not true, the actual concentrations in this case were probably lower than

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[1] Cohen, Gibbs and Clark, *Public Health Rpts.*, **39,** 381 (1924).

[2] Dr. Clark writes: "Each of the dyes was sufficiently free from components of an oxidation–reduction system other than the dye system to permit fairly accurate characterizations of the oxidation–reduction potential of the true dye system, but no claim is made that the material consists of dye alone. Indeed, it was found preferable to salt-out the sodium salts of the indophenols rather than to attempt methods of purification which were found to produce appreciable decomposition of the dye with the introduction of other oxidation–reduction systems. In consequence, many of the preparations in this group of dyes contain large quantities of sodium chloride."

those given. At ***PH*** 8.0, Sorensen's phosphate buffers were used; at PH's 8.6 and 9.6, Clark's boric acid buffers in the concentrations indicated. These buffers differ in salt concentration but neither adding sodium chloride nor changing the concentration of the buffer produced any change in the absorption curve.

The analyses were made with a 1928 model Bausch and Lomb spectrophotometer.

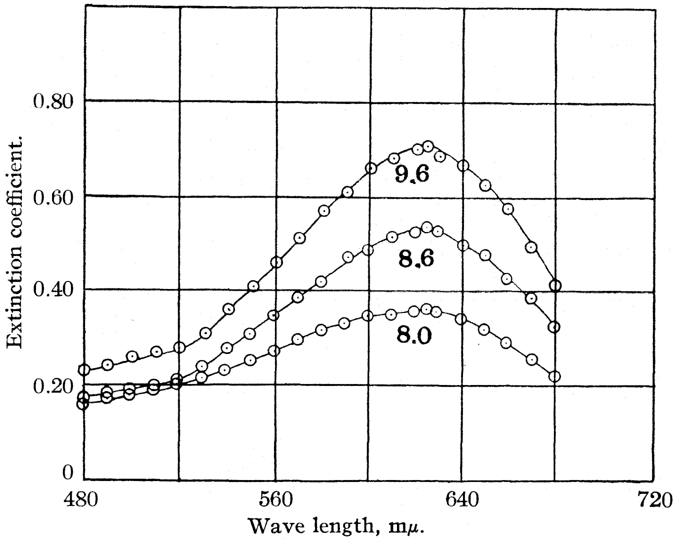

Fig. 1.—*o*-Chlorophenol indophenol: 0.0001 *M;* Clark's sample.

Figures 1 and 2 represent the absorption curves of Clark's sample and of the commercial sample of o-chlorophenol indophenol, respectively. The letters on the curves refer to ***P**H* of the solution. In both cases the absorption maximum is at 625 mμ. Since the two samples give extinction coefficients that are almost identical, they would appear to have essentially the same purity with respect to dye content. Since this dye is almost completely dissociated at PH 9.6 (*pK*, 7.0) the absorption curve at that PH is that of the blue ion. The curves at PH 8.0 and 8.6, which represent predominantly also the blue ion, differ from that *at* PH 9.6 only in the height of the peak, decreasing as the PH decreases. In Fig. 2 9.6 (2) represents a concentration of 0.0002 M or twice that of the remaining curves of both figures. The height of the maximum in this case is about twice that of the corresponding curve at half the concentration, as demanded by the Lambert–Beers Law.

Figures *3* and 4 are absorption curves of *o*-cresol indophenol, based upon Clark's and the commercial sample, respectively. Since the *pK* in this case is at 8.4, the dye at 9.6 is about 95% dissociated, and the absorption maximum of the blue ion is at 610 mp. As the *P*H and the concentration of the dye decrease, there is a decrease in the height of the peak. In these curves the symbol (1) represents a M concentration of 0.00005; (2), 0.0001 M and (3), 0.0002 M.

At *P*H 8.0 the red acid dye predominates and the absorption maximum shifts to 500 mμ with a slight secondary maximum at 610, indicating the presence of some of the blue ion (28%).

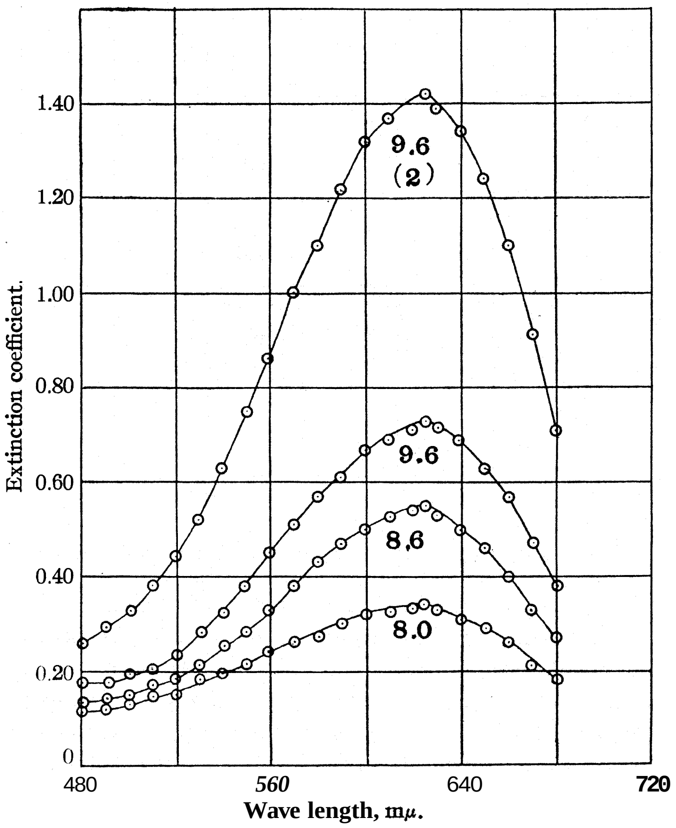

Fig. 2.—*o*-Chlorophenol indophenol: 0.0001 M; 0.0002 M; commercial sample.

These curves show the rise in the absorption maximum with increase in *P*H and in concentration of the dye solution. Alkalinities higher than *P*H 9.6 have no further effect.

Corresponding to rather rough colorimetric studies indicating that the color of the commercial sample was about 50% of that of Clark's sample, it will be seen that the extinction coefficients of the commercial sample at the wave length of maximum absorption at all *P*H values are between 51 and

54% of those for Clark's sample. It therefore appears that uncolored impurities are present in the commercial sample of o-cresol indophenol to the extent of about 47.5% by weight.

When the depth of the absorbing layer was increased to 2 or 3 cm. (as compared with 1 cm. used in the figures), the absorption curves coincided with those observed when a 1 cm. layer of dye solution of twice or three times the concentration was used. Lambert and Beer's Law is therefore valid over this range of concentrations.

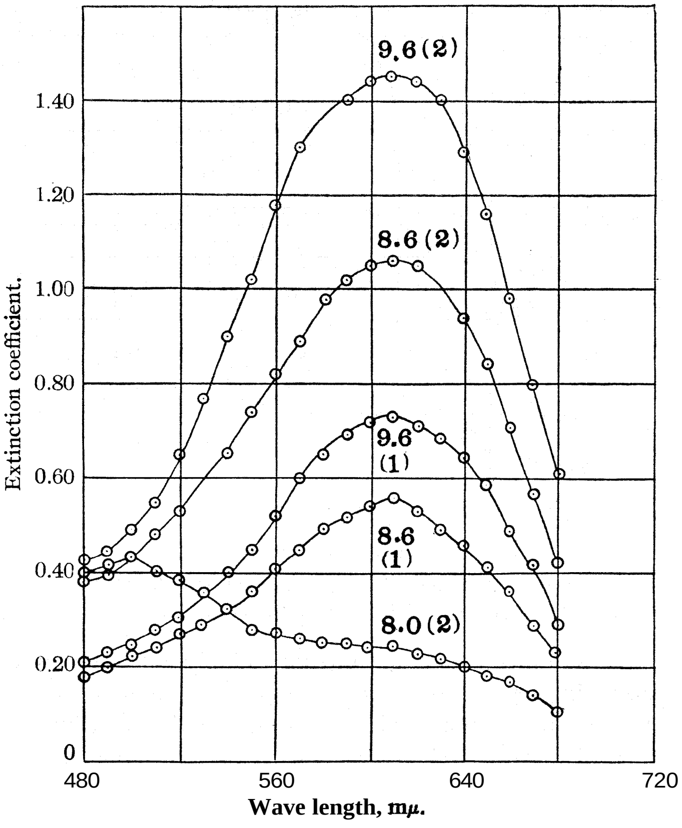

Fig. 3.—o-Cresol indophenol: (1), 0.00005 *M;* (2), 0.0011 M; Clark's sample.

The writer wishes to thank the Board of Research of the University of California for purchasing the spectrophotometer with which these readings were made.

Summary

1. Spectrophotometric studies of o-chlorophenol indophenol and of o-cresol indophenol have been made using two samples of each dye; one a

commercial sample and the other a very pure one obtained from Dr. W. Mansfield Clark.

2. The absorption maximum of o-chlorophenol indophenol at *P*H's 8.0 to 9.6 is at 625 mp. At these PH values the blue ion predominates. The absorption maximum of the dissociated form of o-cresol indophenol is at **610** mμ and that of the red acid form is at **500** mp.

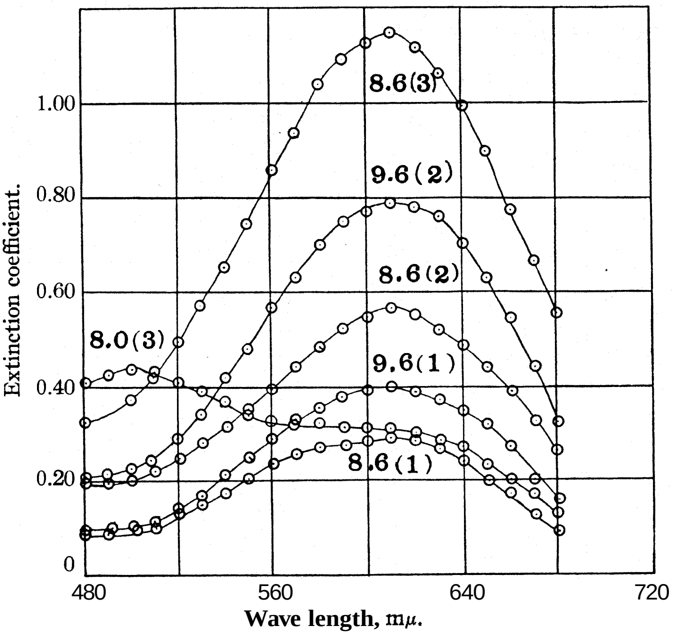

Fig. 4.—o-Cresol indophenol: (1). 0.00005 *M;* (2). 0.0001 M; (3), 0.0002 *M;* **commercial sample.**

3. The two samples of o-chlorophenol indophenol are about of equal purity, whereas in the case of o-cresol indophenol the commercial sample appears to be only between 51 and 54% as pure as that of Clark.

4. The height of the maxima varies with PH and concentration of the dye.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

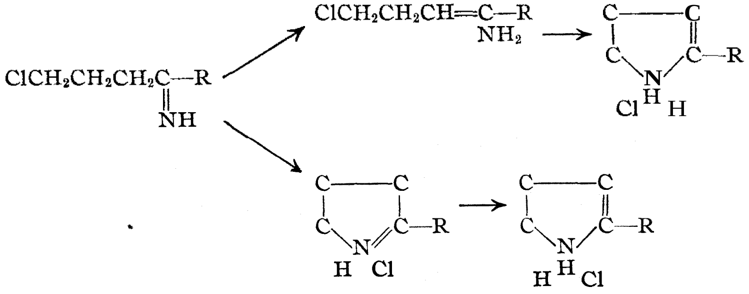
A GENERAL METHOD OF SYNTHESIS FOR ALPHA-SUBSTITUTED PYRROLINES AND PYRROLIDINES

BY LYMAN C. CRAIG, HELEN BULBROOK AND R. M. HIXON

RECEIVED DECEMBER 1, 1930 PUBLISHED MAY 6, 1931

In extending the series of pyrrole and pyrrolidine compounds for the contemplated study of insecticidal action and physical properties[1] several α-substituted pyrrolidine derivatives were desired. The methods of synthesis reported in the literature[2] are, in general, difficult and inadequate for the preparation of larger amounts of these compounds. Cloke[3] described a rearrangement of y-chloropropylketimines to pyrroline derivatives and proposed this as a convenient synthesis of a-substituted pyrrolines. His work was devoted chiefly to a study of the mechanism of the reaction, the yields of pyrroline compounds formed being particularly disappointing for the preparation of the aliphatic substituted pyrrolines. If satisfactory yields of a-substituted pyrroline derivatives could be obtained by this reaction, reduction would offer a convenient method of synthesis for α-substituted pyrrolidine derivatives. The reaction has been studied for this particular purpose.

If we accept the mechanism given by Cloke for the formation of the a-substituted pyrrolines as indicated by either one or both of the equations



then it would seem possible that ring closure could be effected by raising the temperature of the reaction mixture containing the addition product of the y-chlorobutyronitrile without going through the steps of forming the ketimine itself. The reaction would then go according to either or both of the equations

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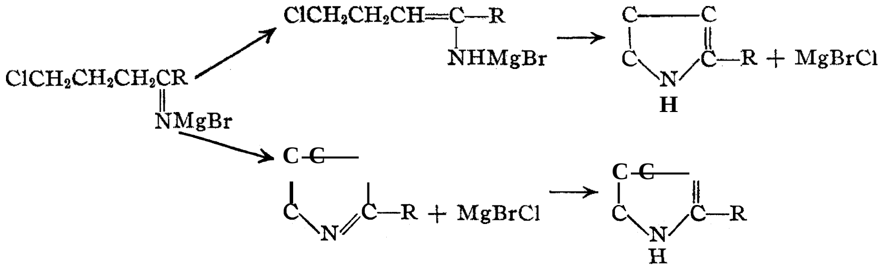
[1] **Craig and Hixon,** THIS JOURNAL, 52, 804 (1930).

[2] **Fenner and Tafel, Ber.,** 31, 906 (1898) ; Hielscher, ***ibid.,*** 31, **277** (1898) ; **Braun, ibid., 43,** 2864 (1910); **Gabriel and Colman,** ***ibid.,*** **41,** 517 (1908); **Miiller and Wachs,** *Monatsh.,* 53, **420** (1929).

[3] **Cloke,** THIS JOURNAL, 51,1174 (1929).



Accordingly an experiment was performed in which the ether was removed from the phenylmagnesium bromide–nitrile addition product and dry xylene added, keeping the volume constant. When the temperature approached that of boiling xylene, the mixture suddenly reacted to give a viscous semi-crystalline material which was probably a mixture of MgClBr and a-phenylpyrroline-N-magnesium bromide, the latter compound being formed by reaction of the a-substituted pyrroline with the excess phenylmagnesium bromide. This method of ring closure gives much better yields than are obtained by passing through the ketimines since there is partial hydrolysis of the ketimine to the corresponding ketone. The procedure is also shorter as the pyrroline can easily be recovered from the mixture by either steam distillation or extraction with ether, according to solubility in water. The yields of a-phenyl, a-ethyl and a-benzylpyrroline are, respectively, 55, 46 and 13% of the theoretical. The order of reactivity of the Grignard compounds from which they are derived is the reverse of this.

Since the yield of the pyrroline compound as obtained by the ketimine reaction is reduced through unavoidable hydrolysis to the ketone, it seemed probable that this loss could be eliminated by reducing the ketimine acetate of the substituted γ-chloropropylketimine to the corresponding amine. These compounds on heating split out hydrochloric acid to give a-substituted pyrrolidines. a-Phenylpyrrolidine was prepared by this method but the yield was not as high as that obtained by passing through α-phenylpyrroline as an intermediate. No attempt was made to extend the method of synthesis to the a-alkylpyrrolidines.

Aliphatic a-substituted pyrrolidines can be obtained easily by catalytic reduction[4] of a-substituted pyrrolines. With aromatic a-substituted pyrrolines, reduction of the benzene ring also takes place. Catalytic reduction of a-phenylpyrroline gave a mixture of reduction products that could not be separated. The literature is conflicting regarding chemical reduction of a-phenylpyrroline. Gabriel and Colman[2] obtained a quantitative reduction to a-phenylpyrrolidine using tin and concentrated hydrochloric acid, while LaForge[6] was not able to reduce a-phenylpyrroline. In this Laboratory the results of Gabriel and Colman were confirmed.

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[4] Wibaut, Rec. trav. *chim.*, 49, 237 (1930).

[5] LaForge, This Journal, 50, 2471 (1928).

Experimental

α-Phenylpyrroline.—A solution of phenylmagnesium bromide was prepared using 150 cc. of anhydrous ether, 8.6 g. of magnesium and 56 g. of bromobenzene. To this 15 g. of γ-chlorobutyronitrile in an equal volume of ether was added. The Grignard addition product precipitated when most of the nitrile had been added. The mixture was refluxed for two hours; the reflux condenser was then reversed and the ether allowed to distil off, keeping the volume constant by addition of xylene dried over sodium. When the ether had practically all distilled over, the mixture suddenly reacted to give a solid semi-crystalline mass. The mixture was then treated with a solution of ammonium chloride and the xylene layer removed. The aqueous layer was extracted once with ether and the ether extract added to the xylene solution. The a-phenylpyrrolidine was extracted from the organic solvents with a small volume of hydrochloric acid, the hydrochloric acid layer washed once with ether to remove xylene and heated to remove the ether. It was then treated with excess strong caustic solution, the oily layer dried over solid potassium hydroxide and distilled, 11 g. coming over at 120–130° under 18 mm. The yield was 55% of the theoretical. Several grams of a high-boiling residue was left. The picrate melted at 198° as reported by Gabriel and Colman.[2] The identity of this compound was further proved by reduction to a-pheaylpyrrolidine.

Reduction of α-Phenylpyrroline.—α-Phenylpyrroline was reduced with tin and hydrochloric acid according to the method of Gabriel and Colman.[2] The reduction product showed a constant boiling point of 120" under 20 mm. and gave a picratc that melted at 148° as previously reported. Catalytic reduction using absolute alcohol acidified with hydrochloric acid as a solvent did not go quantitatively but gave an indefinite mixture from which a picrate melting at 148° was isolated.

α-Phenyl-N-methylpyrrolidine.—In attempting to prepare the a-phenyl-N-methyipyrrolidine by methylation of a-phenylpyrrolidine according to the directions of LaForge,[5] it was found that large quantities of the quaternary derivative were formed and purification by the Hinsburg secondary–tertiary amine separation gave a few drops only of a tertiary amine when 5 g. of starting material was used. A picrate prepared from the tertiary amine melted at 196°. This tertiary amine in ether solution reacted with benzoyl chloride, which indicated ring rupture in analogy to nicotine. Purification of a-phenyl-N-methylpyrrolidine is for this reason difficult and analysis is not sufficiently sensitive to show the absence of large amounts of a-phenylpyrrolidine in the a-phenyl-N-methylpyrrolidine fraction.

Reduction of Phenyl-γ-chloropropyl Ketimine.—The phenylmagnesium bromide addition product of γ-chlorobutyronitrile was prepared as in the synthesis of α-phenylpyrroline using the same quantities throughout. Glacial acetic acid was then slowly added until all the Grignard reagent was destroyed, the ether decanted and the residue dissolved in as little glacial acetic acid as possible. After adding 0.3 g. of platinum oxide–platinum black catalyst the solution was shaken in an atmosphere of hydrogen. In two hours reduction was complete and the catalyst was filtered off. Most of the acetic acid was removed by distillation using a water-bath and reduced pressure. The residue was then made strongly alkaline and steam distilled. Recovery of the base by making the distillate strongly acid with hydrochloric acid, evaporating to a small volume, treating with excess of strong caustic and drying over solid potassium hydroxide gave 5 g. of base boiling at 120" under 20 mm. pressure. A picrate melted at 148° as reported by Gabriel and Colman[2] for a-phenylpyrrolidine and a mixed melting point confirmed its identity. It is interesting to note that in this case the benzene ring was not reduced.

α-Ethylpyrroline.—A Grignard reagent was prepared using 8.6 g. of magnesium. 38 g. of ethyl bromide and 150 cc. of anhydrous ether. To this was added 15 g. of γ-chlorobutyronitrile in an equal volume of ether. The mixture was refluxed for two hours, then the ether removed by distillation, replacing it as a solvent with anhydrous xylene. After the mixture had reacted it was treated with **50** cc. of water and the xylene decanted. The residue was treated with caustic solution and steam distilled. After adding **15** cc. of concentrated hydrochloric acid to the distillate it was shaken in a separatory funnel with the xylene layer. The acid layer was washed once with ether and concentrated to a volume of approximately **50** cc. It was then treated with strong caustic, the oily layer drawn off and dried over solid potassium hydroxide. The oil, amounting to 11 cc., was distilled, **6.5** g. of distillate coming over under a temperature of 140". The yield was 46% of the theoretical. It gave a picrate melting at 87° when crystallized from absolute alcohol. The gold chloride could be crystallized from water strongly acidified with hydrochloric acid and melted at **122".** A sample for analysis was dried in a vacuum desiccator at room temperature. a-Ethylpyrroline was first prepared by Dennstedt[6] but the only derivative reported was the chloroplatinate.

Anal. Calcd. for $C_6H_{11}NHAuCl_4$: Au, **45.20.** Found: Au, **45.25, 45.30.**

As a further confirmation of the identity of this compound it was reduced catalytically with Adams and Shriner platinum oxide platinum black catalyst to a-ethyl' pyrrolidine. The reduction was quantitative. A picrate of a-ethylpyrrolidine melted at 85° as reported by Muller and Wacks.[2] A sample of the free oil with a constant boiling point was obtained by recrystallizing the picrate and regenerating; **12** g. of distillate and **28** g. of picric acid were added to **300** cc. of absolute alcohol. The alcohol was heated to effect solution and slowly cooled to the temperature of ice water; **24** g. of crystalline picrate, **melting at 85–86°,** was filtered off. The whole was treated with **50** cc. of water containing **15** cc. of concentrated hydrochloric acid, heated to boiling, cooled, then filtered and the picric acid washed with a small volume of water. The filtrate was then treated with strong caustic, the oil separating dried over solid potassium hydroxide and distilled. It distilled entirely at 125–126° and weighed **5.5** g. It was a colorless oil with a foul musty odor and did not color on standing. It is interesting to note that Hielscher[2] reports that he was not able to distil pure a-methylpyrroline or α-methyl-N-methylpyrroline without decomposition. There was no sign of decomposition during the distillation of pure a-ethylpyrroline.

In the literature" it is reported that a-methylpyrroline and compounds of like structure exist in water solution in a state of equilibrium, a molecule of a-substituted pyrroline reacting with one of water to form y-aminopropyl substituted ketones. Pure a-ethylpyrroline dissolved in a small volume of water did not react with either phenylhydrazine or phenylsemicarbazide in the cold. However, upon warming in a small volume of water for one hour on the water-bath equivalent quantities of α-ethylpyrroline and phenylsemicarbazide hydrochloride, a white solid insoluble in water and alcohol and melting at 244° was formed.

α-Benzylpyrroline.—A Grignard reagent was prepared using **8.6** g. of magnesium, **45** g. of benzyl chloride and **220 cc.** of anhydrous ether; **15** g. of y-chlorobutyronitrile was slowly added and the mixture refluxed for two hours. The ether was then removed by distillation, replacing it as solvent by xylene. As was the case with the other two derivatives prepared there was no sudden separation of solid material. When all of the ether had volatilized, the mixture was heated for one-half hour and the α-benzylpyrroline recovered in the same manner as was a-phenylpyrroline; **3** g. of distillate boiling at 126–128° under 15 mm. pressure was obtained. The yield was 13% of the theoretical. It was a colorless oil which rapidly colored in air, and was soluble in all organic

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[6] Dennstedt, German Patent **137,086,** ***Chem. Centr.,*** **I,** ***73,*** **338 (1902).**

[7] Lipp and Widnmann, **Ann., 409,** 79 **(1915).**

solvents and insoluble in water. A picrate crystallized from alcohol melted at 89°. A gold chloride crystallized from an alcohol–water mixture, strongly acidified with hydrochloric acid, melted with decomposition at 125°. A sample was dried in a vacuum desiccator at room temperature and immediately analyzed as it showed some signs of decomposition. The following analyses were run on the gold chloride and free base, respectively.

Anal. Calcd. for $C_{11}H_{13}NHAuCl_4$: Au, **39.50.** Found: Au, **39.45, 39.43.** Calcd. for $C_{11}H_{13}N$: C, **82.80;** H, **8.23.** Found: C, **82.70;** H, 8.61.

A reference to this compound could not be found in the literature.

Summary

A study has been made of the synthesis reported by Cloke for the preparation of α-substituted pyrrolines from y-chlorobutyronitrile. The yields have been increased and the procedure shortened by elimination of magnesium chlorobromide from the addition product of the Grignard reagent with y-chlorobutyronitrile, closing the ring without passing through the intermediate ketimine.

α-Ethylpyrroline has been obtained pure for the first time and its boiling point reported.

The work of Gabriel and Colman on the reduction of a-phenylpyrroline with tin and hydrochloric acid has been confirmed. The catalytic reduction of this compound yields an indefinite mixture.

γ-Chloropropylphenyl ketimine acetate has been reduced catalytically to 1-phenyl-1-amino-4-chlorobutane although the latter compound was not isolated due to the ease with which it splits out hydrochloric acid to form α-phenylpyrrolidine.

α-Benzylpyrroline has been synthesized for the first time and suitable derivatives of it are reported.

AMES, IOWA

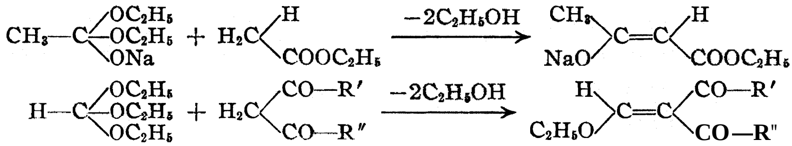
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

CONDENSATION OF ORTHO ESTERS WITH ACETOACETIC ESTER AND MALONIC ESTER[1]

BY PETER P. T. SAH

RECEIVED DECEMBER 19, 1930 PUBLISHED MAY 6, 1931

The condensation of ortho-formic ester with compounds containing a reactive methylene group between two carbonyl groups, such as acetoacetic ester, malonic ester, acetylacetone, etc., was a classical piece of work of Claisen,[2] who compared the analogy of this type of condensation to the formation of acetoacetic ester



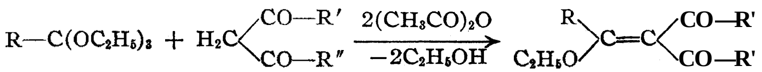
$$\mathrm{CH_3{-}C(OC_2H_5)_2(ONa) + H_2C(H)(COOC_2H_5) \xrightarrow{-2C_2H_5OH} (CH_3)(NaO)C{=}C(H)(COOC_2H_5)}$$

$$\mathrm{H{-}C(OC_2H_5)_3 + H_2C(CO{-}R')(CO{-}R'') \xrightarrow{-2C_2H_5OH} (H)(C_2H_5O)C{=}C(CO{-}R')(CO{-}R'')}$$

where R′ and R" are alkyl, aryl or alkoxy groups.

The condensation products, esters of hydroxymethylene acids, formed very stable inorganic salts. The unstable acids were also isolated by Claisen and found to be exceedingly strong acids. They may be considered as derivatives of formic acid in which the carbonyl oxygen is replaced by a carbon atom attached to two negative groups.

By using triethyl ortho-acetate[3] and triethyl orthobenzoate[4] in place of triethyl ortho-formate in the above condensation, we have been able to isolate the methyl and the phenyl derivatives of ethoxymethylene esters and identify them through their copper salts. The condensation is, therefore, a general reaction for the class of ortho esters. The mechanism of the reaction may be expressed according to the following general equation, where R represents an alkyl or an aryl group



$$\mathrm{R{-}C(OC_2H_5)_3 + H_2C(CO{-}R')(CO{-}R'') \xrightarrow[-2C_2H_5OH]{2(CH_3CO)_2O} (R)(C_2H_5O)C{=}C(CO{-}R')(CO{-}R')}$$

Experimental

General Procedure for the Condensation.[5]—All the reagents used were freshly distilled and the apparatus kept absolutely anhydrous. One

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[1] This paper was constructed from a part of a thesis, presented by Peter P. T. Sah to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June 21, 1926. The investigation was carried out under the direction of Professor Richard Fischer.

[2] Claisen, *Ber.*, 26, 2731 (1893); Ann., 295, 311 (1897); *ibid.*, 297, 1–98 (1897).

[3] Geuther, *Z. Chemie*, 128 (1871); Reitter and Hess, *Ber.*, 40, 3020 (1907); Sah, THIS JOURNAL, 50, 516 (1928).

[4] Limpricht, *Ann.*, 135, 87 (1865); Tschitschibabin, *Ber.*, 38, 563 (1905).

[5] Wheeler and Johns, *Am. Chem. J.*, 40, 237–238 (1908).

mole of ortho ester, one mole of acetoacetic ester or malonic ester and two moles of acetic anhydride (freshly distilled over sodium, b. p. 137°) were mixed and refluxed vigorously for four hours on an oil-bath with or without the addition of fused zinc chloride to catalyze the condensation. The resulting ethyl acetate and acetic acid were removed by distillation at atmospheric pressure till the thermometer, which was immersed in the solution, registered 120°. The mixture was then again refluxed for an hour and some more ethyl acetate was distilled out.[6] The residue was then fractionated under a reduced pressure of 3 mm. produced by an oil pump. A small amount of acetic acid and acetic anhydride distilled over first, then the unreacted esters and finally the condensation product. The yield of the ethoxymethylene esters thus obtained varied exceedingly, depending upon the following factors: (1) purity of the reagents used, (2) time of reaction, (3) stability of the ortho ester used, (4) stability of the condensation product and (5) the presence of catalysts. With this procedure, Claisen's experiments could be easily repeated with a yield of 50–60% under the best condition.

Description of the Condensation Products

Ethyl **methyl-ethoxymethylene-acetoacetate**, from triethyl ortho-acetate (b. p. 144–146°) and ethyl acetoacetate, was a yellowish-white glycol-thick liquid, boiling unsteadily between 108 to 123° at 3 mm. The low yield of the product, the color, and the unsteadiness of its boiling point were undoubtedly due to partial decomposition during distillation. On standing, the compound deepened in color; yield, about 8 g. from 162 g. of triethyl ortho-acetate used. The addition of fused zinc chloride during the condensation produced no favorable effect upon the yield.

Diethyl **methyl-ethoxymethylene-malonate,** from triethyl ortho-acetate and diethyl malonate, was a glycol-thick liquid distilling unsteadily from 123 to 128° at 3 mm. The reddish-brown color due to partial decomposition could not be removed by redistillation; yield, about 5 g. from 162 g. of triethyl ortho-acetate used. The greater part of the ortho ester was decomposed by acetic anhydride to 3 moles of ethyl acetate.[6] Addition of fused zinc chloride produced no favorable effect upon the yield.

Ethyl **phenyl-ethoxymethylene-acetoacetate**, from triethyl ortho-benzoate[7] and ethyl acetoacetate, was a glycol-thick liquid, boiling very steadily at 185–186° at 3 mm. without any decomposition; d_4^{25} 1.0949; n_D^{25} 1.5512. Freshly distilled, the liquid was practically colorless. It may be kept in a well-stoppered bottle for months without any noticeable change; yield, over 40 g. from 124 g. of triethyl orthobenzoate used. Addition of fused zinc chloride increased the yield slightly.

Diethyl **phenyl-ethoxymethylene-malonate,** from triethyl ortho-benzoate and diethyl malonate, was a stable, colorless, glycol-thick liquid, boiling very constantly at 188–190° at 3 mm. without any decomposition; d_4^{25} 1.0738; n_D^{25} 1.4928; yield, over

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[6] The enormous amount of ethyl acetate formed during the condensation was undoubtedly due to the side reaction between acetic anhydride and ortho ester as mentioned by Sawitsch, *Jahrsb. über die Fortschritte der Chemie,* 391 (1860).

[7] This was prepared by adding an alcoholic solution of sodium ethoxide to benzotrichloride: b. p. 240° at atm. pressure; 128–130° at 3 mm.; n_D^{25}, 1.4938; d_4^{25}, 1.0325. Compare with Röse, Ann., 205, 250 (1880).

25 g. from 75 g. of triethyl ortho-benzoate used. Addition of fused zinc chloride increased the yield considerably.

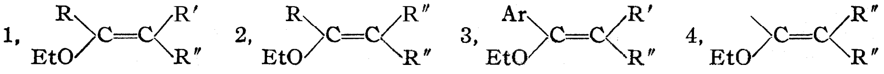
All these condensation products were insoluble in water, but very soluble in ether, ethyl alcohol, ethyl acetate, glacial acetic acid, acetone, benzene, chloroform and carbon tetrachloride. Warm water decomposed them to their corresponding constituents. the double bond being very sensitive to hydrolysis.[2]

TABLE I

ANALYSES OF THE CONDENSATION PRODUCTS

No.	Formula	Carbon, % Calcd.	Carbon, % Found			Hydrogen, % Calcd.	Hydrogen, % Found		
1	$C_{10}H_{16}O_4$	59.96	58.79	59.01	59.22	8.06	7.59	7.49	7.51
2	$C_{11}H_{18}O_5$	57.36	56.48	56.64	56.50	7.88	7.10	7.08	7.09
3	$C_{15}H_{18}O_4$	68.66	69.02	68.51	68.39	6.92	6.96	7.01	6.90
4	$C_{16}H_{20}O_5$	65.72	65.85	65.78	65.87	6.90	6.92	6.87	6.95

Structures:



R, CH_3; Ar, C_6H_5; R′, CH_3CO; R″, $COOC_2H_5$.

Copper Salts of the Condensation Products.—These were easily obtained by shaking the ester with a cold saturated solution of copper acetate. They were quite stable and served to characterize these new condensation products. The copper salts of the methyl homologs had the same solubility as those of the hydroxymethylene acids described by Claisen.2 They were insoluble in cold concentrated copper acetate solution, soluble in ethyl alcohol, isoamyl alcohol, acetone and hot benzene, from which they reprecipitated on cooling. With pyridine they formed a beautiful violet solution, which distinguished them from copper acetoacetate and copper malonate. Warm water hydrolyzed them to copper oxide. Both are greenish-blue in color.

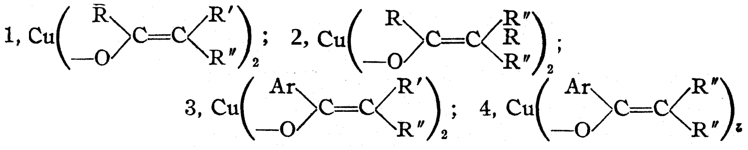
The copper salts of the phenyl analogs, light blue in color, were very insoluble in the ordinary solvents. Warm water hydrolyzed them to copper oxide and their corresponding constituents, the odor of which, especially ethyl benzoate, could be easily identified. They gave no violet color with pyridine.

TABLE II

ANALYSES OF THE COPPER SALTS[8]

No.	Formula	Subs., mg.		$Na_2S_2O_3$, $N/100$, cc.		Copper, % Calcd.	Copper, % Found	
1	$C_{16}H_{22}O_8Cu$	20.62	22.71	5.10	5.65	15.67	15.72	15.82
2	$C_{18}H_{26}O_{10}Cu$	25.03	20.02	5.35	4.35	13.65	13.59	13.81
3	$C_{26}H_{26}O_8Cu$	31.50	33.86	5.86	6.38	12.00	11.83	11.98
4	$C_{28}H_{30}O_{10}Cu$	33.33	30.06	5.73	5.15	10.78	10.93	10.89

Structures:



R, CH_3; Ar, C_6H_5; R', CH_3CO; R'', $COOC_2H_5$.

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[8] Abderhalden and Schnitzler, Z. *physiol. Chem.*, 163, 95 (1926).

Summary

1. Triethyl ortho-acetate condensed only with difficulty with either ethyl acetoacetate or diethyl malonate in the presence of acetic anhydride, forming the methyl homologs of ethoxymethylene esters. They were unstable liquids, decomposing partially on distillation. They formed, however, characteristic copper salts which could be purified and identified.

2. Triethyl ortho-benzoate condensed easily with either ethyl acetoacetate or diethyl malonate, forming very stable phenyl analogs of ethoxymethylene esters with definite physical properties. Their copper salts were also made and analyzed.

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STUDIES IN THE 3-NITROPHTHALIC ACID SERIES

BY H. W. UNDERWOOD, JR., AND R. L. WAKEMAN[1]

RECEIVED DECEMBER 29, 1930 PUBLISHED MAY 6, 1931

I. Phenol-3-nitrophthalein and Resorcinol-3-nitrophthalein.—This paper gives an account of the preparation of phenol-3-nitrophthalein and resorcinol-3-nitrophthalein and a comparison of the properties of these compounds with those of phenolphthalein and fluorescein. In previous contributions[2] dealing with derivatives of phthalic and diphenic acids, it was pointed out that the groups in diphenic anhydride give the sodium salt of phenoldiphenein a light yellow instead of a red color and that an alkaline solution of resorcinoldiphenein does not show fluorescence.

Discussion of Experiments

All of the temperatures given are uncorrected.

Phenol-3-nitrophthalein.—Fifteen grams of 3-nitrophthalic anhydride, 16.1 g. of phenol (calcd. amt. × 1.1) and 3 g. of concd. sulfuric acid (*d* 1.84) were placed in a loosely stoppered Erlenmeyer flask and heated in an oil-bath which was rapidly raised to 170°, maintained at this temperature for about two and one-half hours and then at 215–220" for three hours longer. After the reaction product had cooled, it was powdered and added to about 600 cc. of water in a beaker. The mixture was boiled for four hours to remove the excess of phenol; the water lost by evaporation was replaced from time to time. The insoluble solid was collected on a filter, transferred to a beaker and stirred with three 60-cc. portions of 3.5% sodium hydroxide solution. Acidification of the combined, filtered alkaline liquids yielded a dark colored precipitate. This material was collected on a filter, dried for forty-eight hours at room temperature and then ground with six 100-cc. portions of ether in a mortar. The ether

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[1] Some of the experimental results described in this paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by R. L. Wakeman in partial fulfilment of the requirements for the degree of Bachelor of Science.

[2] Underwood and Kochmann, THIS JOURNAL, 45,3071 (1923); 46,2069 (1924).

extract was filtered, and the solvent was removed by distillation on a water-bath. Phenol-3-nitrophthalein was obtained in the form of long yellow needles, m. p. 20P 205°, by crystallization from acetone, with the use of decolorizing carbon. The crystals weighed 0.6 g. (2.1% yield). The compound dissolves in sodium hydroxide solution with the development of a violet color. A very dilute solution of the sodium salt of phenol-3-nitrophthalein becomes practically colorless upon the addition of a large excess of concd. sodium hydroxide solution. Apparently the nitro group in 3-nitrophthalic anhydride gives a violet instead of a red color to the sodium salt of the phenol condensation product.

Anal. Calcd. for $C_{20}H_{13}O_6N$: C, 66.10; H, 3.61; N, 3.86. Found: C, 65.91, 65.73; H, 3.80, 3.85; N, 4.01, 4.12.

Resorcinol-3-nitrophthalein.—An intimate mixture of 5 g. of 3-nitrophthalic anhydride and 6.3 g. of resorcinol (calcd. amt. X 1.1) was placed in a large test-tube, and heated at 195–200° for one and one-fourth hours. After the melt had cooled, it was powdered and boiled with 150 cc. of water for half an hour. The solid reaction product was collected on a filter, and then stirred with two 60-cc. portions of 2% sodium hydroxide solution. The filtered alkaline solution was acidified with 6 N sulfuric acid and shaken with three 80-cc. portions and one 40-cc. portion of ether. The ether extract was filtered, and the solvent was removed by distillation on a water-bath. The solid residue was extracted with 40 cc. of boiling alcohol, and water was added to the hot filtered solution, with stirring, until it became turbid. The mixture was heated to its boiling point and then allowed to cool slowly to room temperature. The precipitated resorcinol-3-nitrophthalein was collected on a filter, dried in the air and for a short time at 105°. Another lot of resorcinol-3-nitrophthalein was obtained by concentrating the filtrate to approximately one-half its volume. The product was dissolved in a small amount of boiling alcohol, precipitated by the addition of water, collected on a filter and dried at 105°. The yield of resorcinol-3-nitrophthalein, m. p. 260°, was 1.7 g. (17.4%). The product formed red crystalline granules, which dissolved in sodium hydroxide solution with the development of a brownish-yellow color. A dilute alkaline solution of resorcinol-3-nitrophthalein exhibited a green fluorescence, but not nearly to the same extent as a solution of fluorescein.

Anal. Calcd. for $C_{20}H_{11}O_7N$: C, 63.65; H, 2.94; N, 3.71. Found: C, 63.54, 63.30; H, 3.20, 3.11; N, 3.95, 3.88.

II. Reactions of Derivatives of 3-Nitrophthalic Acid with Acetic Anhydride.—Investigations dealing with the removal of alcohol, water and ammonia from derivatives of phthalic and diphenic acids have been previously described. It was noted that monomethyl diphenate and mono-ethyl diphenate, as well as the dimethyl and diethyl esters of diphenic and phthalic acids, remain unchanged when heated with acetic anhydride, but monomethyl and mono-ethyl phthalates yield phthalic anhydride. Under similar conditions diphenamic acid is dehydrated in two different ways, giving diphenimide and 2-cyanobiphenyl-2'-carboxylic acid; the diamide of diphenic acid is transformed into 2,2'-dicyanobiphenyl, through the loss of two molecules of water. Phthalamic acid is converted into phthalimide and phthalic anhydride by treatment with acetic anhydride, and phthalamide gives *o*-cyanobenzamide and phthalimide.[3]

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[3] Underwood and Clough, THIS JOURNAL, 51, 583 (1929); Underwood and Barker, *ibid.*, 52, 4082 (1930).

Discussion of Experiments

The methyl esters and the amides of 3-nitrophthalic acid have been previously prepared. We used dry hydrogen chloride instead of concd. sulfuric acid as a catalyst in the synthesis of dimethyl 3-nitrophthalate. The procedures given in the literature for the preparation of 3-nitrophthalimide and 3-nitrophthalic acid monoamide (1) involve the dehydration of mono-ammonium 3-nitrophthalate by heat alone and the treatment of 3-nitrophthalimide with barium hydroxide solution, respectively.[4] We found that it was advantageous to employ a mixture of the mono-ammonium salt and anhydrous zinc chloride and to use sodium hydroxide instead of barium hydroxide; typical experiments are described below.

Monomethyl 3-Nitrophthalates.—Five grams of each ester was heated with 5 g. of glacial acetic acid and 8 g. of acetic anhydride for six hours at 145°. Practically all of the liquid was then removed by distillation, and the residue was cooled in ice. The product was crystallized from a small amount of glacial acetic acid. 3-Nitrophthalic acid methyl ester (1) was recovered unchanged. Two grams of 3-nitrophthalic anhydride was obtained from the 3-nitrophthalic acid methyl ester (2).

Dimethyl 3-Nitrophthalate.—After a mixture of 5 g. of dimethyl 3-nitrophthalate, 5 g. of glacial acetic acid and 8 g. of acetic anhydride had been refluxed for six hours at 145°, the liquid was removed by distillation, and the residue was cooled in ice. Practically all of the ester was recovered unchanged.

3-Nitrophthalimide.—A solution of the mono-ammonium salt of 3-nitrophthalic acid, prepared by the addition of the acid to the calculated amount of concd. ammonium hydroxide, was evaporated practically to dryness. The product was collected on a filter and dried. An intimate mixture of 15 g. of powdered mono-ammonium 3-nitrophthalate and 5 g. of powdered anhydrous zinc chloride was placed in a large test-tube and heated at 225–230° for four and one-half hours. The melt was allowed to cool, transferred to a mortar, reduced to a powder and extracted with four 15-cc. portions of boiling acetone. The filtered acetone solution was refluxed with 0.3 g. of decolorizing carbon for several minutes and filtered; this treatment was repeated. About two-thirds of the solvent was removed by distillation on a water-bath, and the residue was cooled in ice. The 3-nitrophthalimide was collected on a filter and dried for half an hour at 100°. The yield of 3-nitrophthalimide, m. p. 214–215°, was 5.05 g. (40%).

3-Nitrophthalamic Acids.—Five grams of 3-nitrophthalic acid monoamide (2) was refluxed with 5 g. of glacial acetic acid and 8 g. of acetic anhydride for six hours at 145°. The crystals deposited when the solution was cooled in ice were collected on a filter and recrystallized from alcohol. Two and one-tenth grams of 3-nitrophthalimide was obtained.

When 10 g. of 3-nitrophthalimide was heated with 25 cc. of 10% sodium hydroxide solution (calcd. amt. × 1.34) and 35 cc. of water for an hour at 80–85°, most of the solid gradually dissolved. 3-Nitrophthalic acid monoamide (1) was precipitated by acidification of the hot filtered solution with concd. hydrochloric acid. After the reaction mixture had been cooled in ice, the solid was collected on a filter, washed with 20 cc. of water and dried in a vacuum desiccator over anhydrous calcium chloride. The yield of 3-nitrophthalic acid monoamide (1) was 7.5 g. (68.6%). The product softened at 144–146°, solidified as the temperature was raised and remelted at 214–215°.

A solution of 5 g. of the monoamide in 5 g. of glacial acetic acid and 8 g. of acetic anhydride was refluxed for six hours at 145°, and then allowed to stand for twelve hours. The solid which formed was collected on a filter. The filtrate was diluted

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[4] Bogert and Boroschek, THIS JOURNAL, 23, 740 (1901).

with 40 cc. of ether and filtered again. The reaction product, which weighed 2.9 g. after crystallization from a small amount of a mixture of equal volumes of alcohol and acetone, was identified as 3-nitrophthalimide.

3-Nitrophthalamide.—By use of the procedure described above, we obtained 2.1 g. of 3-nitrophthalimide by heating 5 g. of 3-nitrophthalamide with 5 g. of glacial acetic acid and 8 g. of acetic anhydride for six hours at 145°. A small amount of impure acetamide was secured by fractionation of the distillate.

Summary

Phenol-3-nitrophthalein and resorcinol-3-nitrophthalein are formed by the condensation of 3-nitrophthalic anhydride with phenol and resorcinol respectively. Phenol-3-nitrophthalein dissolves in sodium hydroxide solution with the development of a violet color. A dilute alkaline solution of resorcinol-3-nitrophthalein exhibits a green fluorescence, but not nearly to the same extent as a solution of fluorescein.

When 3-nitrophthalic acid monomethyl ester (1) and dimethyl 3-nitrophthalate are heated with acetic anhydride, each ester remains unchanged. Under similar conditions 3-nitrophthalic acid monomethyl ester (2) yields 3-nitrophthalic anhydride. The isomeric 3-nitrophthalamic acids and 3-nitrophthalamide are converted into 3-nitrophthalimide by treatment with acetic anhydride.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NOTRE DAME UNIVERSITY]

A NEW MODIFICATION OF THE REFORMATSKY REACTION

BY J. A. NIEUWLAND AND S. FLORENTINE DALY

RECEIVED JANUARY 19, 1931 PUBLISHED MAY 6, 1931

Reformatsky published a new method for making β-hydroxy acids from ketones or aldehydes by condensing them with α-iodo esters in the presence of zinc.[1] Later, he and his associates and others[2] published records of reactions in which bromo acid esters had been substituted for iodo esters. Reformatsky also made the statement that chloro esters react with ketones in a manner analogous to bromo and iodo esters but do not react with aldehydes.[3]

Although β-hydroxy acids have been made from chloro esters by the use of sodamide,[4] with an aldehyde or ketone, there is no record in the literature to show that it has been done with zinc as a condensing agent.

We have found that chloro esters do not condense with ketones or aldehydes in the presence of zinc alone, but that the reaction can be effected

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[1] Reformatsky, *J. Russ. Phys-Chem. Soc.*, 22, 44 (1890).

[2] Reformatsky, *J. prakt. Chem.*, 54, 469 (1896); Reformatsky and Plesconossoff, *Ber.*, 28, 2838 (1895); Lindenbaum, *ibid.*, 50, 1272 (1917).

[3] Reformatsky, ibid., 28, 2842–2847 (1895); *J. Chem. Soc.*, 70, 126 (1896).

[4] Feyerabend, *Ber.*, 38, 697 (1905).

by the addition of copper powder to the reaction mixture. The following is typical of the procedure used and is a modification of the method of Lindenbaum and others.[2,5]

A mixture of *35* g. of acetophenone, 38 g. of chloroacetic ester and *35* g. of benzene with 18 g. of zinc and 3 g. of copper is refluxed and heated with a small flame until the most vigorous reaction subsides. When the reaction mixture is shaken frequently the unused zinc does not cake.

After cooling, the mixture is decomposed with 20% solution of ice-cold sulfuric acid, which is added slowly until all the solid matter in the reaction mixture has dissolved. The oily layer is separated and the water layer extracted several times with ether. The ether extract and oil are combined and allowed to remain overnight on anhydrous sodium sulfate. The liquid is decanted and after the ether and benzene have been removed on a water-bath it is fractionated under diminished pressure.

The ester is saponified with 25% alcoholic sodium hydroxide, and refluxed for two hours. The alcohol is then distilled off on a water-bath, the solid salt dissolved in a small quantity of water and the acid precipitated with concentrated hydrochloric acid. In most cases an oil as well as a white precipitate of acid forms in the water solution. When the oil does not disappear on standing or by reprecipitating the acid from sodium carbonate solution, it is removed by drying the crystals of the acid between filter papers or on a porous plate.

Among the condensations accomplished in this way are those of the esters of chloroacetic acid, phenylchloroacetic acid and chlorobutyric acid, respectively, with benzaldehyde, benzophenone, propiophenone, *p*-methoxyacetophenone, *p*-tolyl methyl ketone, acetophenone, ethyl acetoacetate and acetone. These reactions were carried out under varied conditions. The results are indicated in the following table.

Percentage yield is calculated from the original quantity of aldehyde or ketone used

	Product formed	In benzene	In xylene	**Without** solvent
1[a]	Cinnamic acid	35% acid	10% acid	22% acid
2"	2,2-Diphenylhydracrylic acid	30% acid	47% acid	52% acid
3	2-Ethylcinnamic acid		33% acid	
4"	p-Methoxy-2-methylcinnamic acid	52% ester	48% ester	
5	*p*-Tolyl-2-methylacrylic acid	13% ester		No ester
6	2-Methylcinnamic acid	40% ester	10 5% ester	No ester
7	2-Hydroxy-2-methylglutaric acid	27% ester		
8	1-Ethyl-2-methyl-2-hydroxymethylbutyrate	33% ester		No ester
9	I-Phenylcinnamic acid	18% ester		No ester
10"	1-Phenyl-2,2-hydroxy-*p*-methoxyphenylbutyric acid	27% ester		No ester

[a] Some of the original ketone may be recovered.

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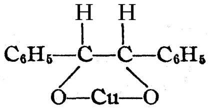
[5] Rupe and Busolt, *Ber.,* 40, 4537 (1907).

The acids and esters synthesized were identified by their physical constants recorded in the literature, with the exception of 1-phenyl-2,2-hydroxy-*p*-methoxy-phenylbutyric acid. This compound is not described in the literature. From analysis and the Zeisel reaction its formula is CH_3-$C(OH)C_6H_4OCH_3CHC_6H_4COOH$.

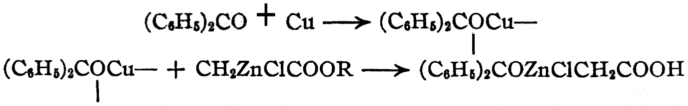
The methyl ester is a colorless liquid, boiling at 113–115° at 20 mm. A yield of about 64% is obtained when calculation is based on the amount of unused ketone recovered. Although the methyl ester has a constant boiling point, the saponification product from it is a mixture of white crystalline solid and oil. This oil is probably one or more of the possible isomers of the acid, since on standing it solidifies to a white crystalline solid. The crystals, white leaflets, dried on filter paper to remove traces of oil, melt at 75°. They dissolve readily in alcohol, ether, benzene and hot water and to some extent in cold water.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71; H, 6.71; O, 21.23. Found: C, 72.8; H, 6.8; O, 20.4. Zeisel reaction for methyl group in methyl ester: Calcd.: OMe, 20.6; equivalent. 300.016. Found: 19.82.

The effect produced by copper powder in β-hydroxy acid synthesis is probably due to the formation of *a* copper–ketone compound such as has been described by Bernoulli and Schaaf.[6] Two moles of benzaldehyde is combined with copper. The formula assigned by them to the compound is



Since such compounds as this, once formed, do not, as a rule, break up readily, it seems more reasonable to attribute the accelerating effect to some copper-containing radical in solution. In that case a reaction such as the following might be offered as a plausible explanation



$$(C_6H_5)_2CO + Cu \longrightarrow (C_6H_5)_2COCu\text{—}$$

$$(C_6H_5)_2COCu\text{—} + CH_2ZnClCOOR \longrightarrow (C_6H_5)_2COZnClCH_2COOH$$

According to Bernoulli and Schaaf,[6] the copper–aldehyde compounds do not form with pure aldehyde or ketone, but only in the presence of a solvent. The rate of formation is dependent on the fluidity of the solvent and the temperature of the solution. These compounds form most readily in benzene as a solvent. Their presence is detected by the green, green-blue or green-yellow color of refluxed solutions of copper powder and an aldehyde or ketone dissolved in benzene or in a chloro ester. These solutions, freed from all unused copper powder, effect β-hydroxy syntheses. A synthesis is also accomplished when dry copper oxide is substituted for copper powder,

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[6] Bernoulli and Schaaf, *Helv. Chim. Acta,* 5, 721–731 (1922); Fritz Schaaf, *Z. anorg. allgem. Chem.,* 126, 237–253 (1923).

but no synthesis takes place with anhydrous copper sulfate as a catalyst. Zinc bronze also fails to promote synthesis.

All efforts to form and use the zinc–chloro ester compound, CH_2ZnCl-COOH, assumed by Reformatsky,[2] instead of zinc metal and a chloro ester, were unsuccessful.

Cadmium powder alone, as well as cadmium powder with copper powder as condensing agents, fails to promote a β-hydroxy acid synthesis.

In general, then, the reaction is most satisfactory in a medium of benzene (Table). This is not because the copper–aldehyde or copper–ketone compound forms most readily in benzene; the same reaction occurs in some cases (Table) with no solvent other than a chloro ester added to the ketone or aldehyde. The fact leads to the conclusion that the primary function of the additional solvent is the regulation of the temperature of the reaction mixture.

The importance of benzene as a temperature regulator can be seen in its use with phenylchloroacetic ester. If the temperature in these reactions be high, diphenylsuccinic ester is formed. High temperature also destroys some ketones, as methoxyacetophenone, so that a low boiling point solvent must be present to prevent decomposition. In small quantities of benzene (equivalent molar quantities of ketone and solvent), *p*-methoxyacetophenone condenses with chloroacetic ester to a β-hydroxy acid ester, but decomposes with an equivalent quantity of benzene with phenylchloroacetic ester. If, however, enough benzene is used to keep the boiling point of the mixture between 98 and 100°, synthesis takes place.

The length of time for the reaction has a notable effect on the yield of β-hydroxy acid ester. When the calculation is based on the amount of zinc dissolved, the theoretical yield of β-hydroxy acid ester is never obtained. If the percentage yield be calculated from the amount of aldehyde or ketone used, which is found by deducting the amount of unused aldehyde or ketone recovered, fairly high percentage yields are obtained. If the reaction runs long enough to use the theoretical amount of zinc, a viscous residue with high boiling point results, no ketone can be recovered, and the percentage yield of β-hydroxy acid ester is low.

The effects of temperature and reaction time on these reactions are illustrated by the results obtained from successive runs of acetophenone with chloroacetic ester, in various solvents and during periods of time extending from thirty minutes to eight hours. With benzene as a solvent, a one-hour run gave 42% ester and an eight hour gave 38% ester; with xylene as a solvent the yield for a one-hour run was 28% ester and for an eight-hour run, 10.5% ester; without a solvent, the corresponding yields were, respectively, 14% ester and no ester.

High temperature as well as prolonged heating tends to increase the quantity of viscous material formed. For example, when xylene is used as a solvent, the reaction product forms a char-cake with zinc in the bottom of the flask. With benzene as a solvent, even on prolonged heating, the reaction products continue to dissolve in the solvent.

There is evidence then of reactions subsequent to the formation of P-hydroxy esters and runs of brief periods and minimum reaction temperatures are the most satisfactory. So that, in general, the most satisfactory yields are obtained when the reaction time is limited to the period of most vigorous reaction and when an optimum reaction temperature is secured. Benzene is the best solvent, since it brings the temperature into the necessary range; it also keeps free metal surface available since the reaction products are soluble in it; it obviates the formation of char-cake.

Summary

1. A β-hydroxy synthesis is obtained from a-chloro esters and aldehydes or ketones and zinc, through the action of copper metal or cupric oxide.
2. The catalytic action of copper is accounted for by the formation of an intermediate between copper and the aldehyde or ketone present, which then reacts with the zinc–chloro ester compound of the chloro esters and accelerates the synthesis.
3. Benzene is the best solvent, since it brings the temperature into the necessary range. It also keeps free metal surface available since the products are soluble in it.

Limited reaction time increases yields.

NOTRE DAME, INDIANA

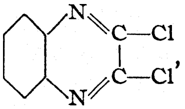
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

CYCLIC AMMONO KETONES[1] AND ACID CHLORIDES OF THE QUINOXALINE SERIES

BY R. A. OGG, JR., AND F. W. BERGSTROM

RECEIVED JANUARY 30, 1931 PUBLISHED MAY 6, 1931

In a previous communication[1a] quinoxaline was shown to be formally an ammono glyoxal, and experimental evidence was presented in confirmation of this view. In the present article it is desired to consider a number of derivatives of quinoxaline from the standpoint of the ammonia system, and to give the results of the experimental work supporting the analogies advanced.

2,3-Dichloroquinoxaline.—From its structural formula, 

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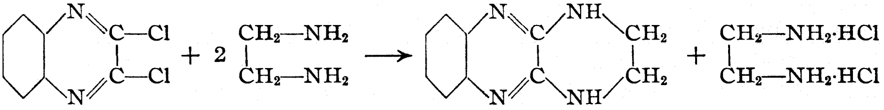
[1] The strict ammonia analogues of the aquo ketones are unknown. Because of the third valence of the nitrogen, all ammono ketones are acetals at the same time. Strain, THIS JOURNAL, 49, 1559 (1927).

[1a] Ogg and Bergstrom, *ibid.*, 53,245 (1931).

this compound is seen to be a substituted ammono oxalyl chloride,[2] and hence should show properties analogous to those of acid chlorides. The method of preparation is in accord with this view. 2,3-Dichloroquinoxaline is prepared[3] by the action of phosphorus pentachloride on 2,3-dihydroxyquinoxaline, which was shown in the previous communication to be an ester of a mixed aquoammono oxalic acid. This reaction is analogous to the formation of oxalyl chloride from oxalic acid and phosphorus pentachloride.

As an acid chloride, 2,3-dichloroquinoxaline should react with primary and secondary amines, *i. e.*, ammono alcohols, eliminating hydrogen chloride and producing ammono esters. This is actually the case, Hinsberg and Schwantes[4] having carried out such reactions with various aromatic diamines and with ethylamine. In the present work, a similar reaction has been obtained with ethylenediamine, resulting in a new cyclic ammono ester, o-phenylene ethylene oxamidine. It should be mentioned that the reactivity of 2,3-dichloroquinoxaline is much less than that of aquo acid chlorides.



2,3-Dichloroquinoxaline.—2,3-Dihydroxyquinoxaline was prepared by the method of Meyer and Seelinger,[5] and converted into 2,3-dichloroquinoxaline by heating with two equivalents of phosphorus pentachloride at 180°, according to the procedure of Hinsberg and Pollak.[3]

o-Phenylene Ethylene **Oxamidine.**—Two grams of 2,3-dichloroquinoxaline and 2 *g.* (three equivalents) of ethylenediamine were sealed in a tube and heated for two hours at 150°. The tube was then opened and the contents were washed with water. The residue was treated with dilute hydrochloric acid, and the solution, after filtration, was rendered alkaline with ammonia. The white precipitate was recrystallized from alcohol in the form of colorless leaves, sparingly soluble in alcohol, insoluble in water, but soluble in acids. Alcoholic solutions showed a faint fluorescence. The melting point was above 350°. The compound was halogen free.

Anal. Subs., 0.0977: 0.09537 *N* HCl (Kjeldahl), 21.90 cc. Calcd. for $C_{10}H_{10}N_4$: N, 30.09. Found: N, 29.94.

The reaction of an acyl chloride with a Grignard reagent gives as the first product a ketone and magnesium halide. 2,3-Dichloroquinoxaline, as an ammono di-acid chloride (-ester), has been found to react with two equivalents of alkyl magnesium halide, yielding the corresponding ammono diketone (-diacetal), *i.* e., 2,3-dialkylquinoxaline.

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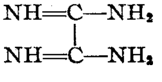
[2] It is an o-phenylene ester and acid chloride of ammono oxalic acid,

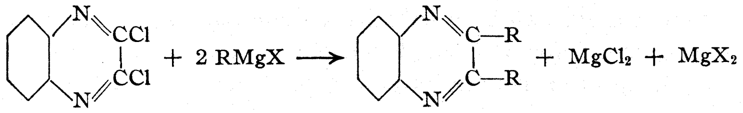


$$\begin{array}{l} NH{=}C{-}NH_2 \\ \quad\;\; | \\ NH{=}C{-}NH_2 \end{array}$$

[3] Hinsberg and Pollak, *Ber.*, 29, 784 (1896).

[4] Hinsberg and Schwantes, *ibid.*, 36, 4048 (1903).

[5] Meyer and Seelinger, *ibid.*, 29,2641 (1896).



This reaction constitutes a new method of synthesis of such compounds, and was used to prepare 2,3-dimethylquinoxaline and the hitherto unknown 2,3-di-*n*-propylquinoxaline. The latter substance was found to be identical with that prepared by another method (*vide infra*).

The reaction of a considerable excess over two equivalents of methylmagnesium iodide with 2,3-dichloroquinoxaline yielded only a small quantity of 2,3-dimethylquinoxaline and a considerable amount of a red tarry substance, possibly a reduction product of the 2,3-dimethylquinoxaline. It was hoped that 2,2,3,3-tetramethyl-1,2,3,4-tetrahydroquinoxaline might be formed in this reaction.

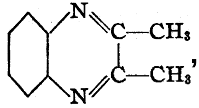
One remarkable fact noted was that 2,3-dichloroquinoxaline did not react at all with phenylmagnesium bromide, even on prolonged refluxing of the ether solution.

2,3-Dimethylquinoxaline.—Three grams of solid 2.3-dichloroquinoxaline was added to an ethereal solution of methylmagnesium iodide (2.1 equivalents). A very vigorous reaction ensued, the 2,3-dichloroquinoxaline dissolving to give a brilliant red solution. After an hour of refluxing, the mixture was decomposed by addition of liquid ammonia, which was then evaporated. The residue was extracted with ether. The red ether solution was steam distilled, the ether first coming over, then a small quantity of unidentified solid, and finally the main product, an oil which readily solidified as fine white needles. This was purified by repeated steam distillation. The substance possessed the peppermint-like odor and the same melting point (106° corr.) as pure 2,3-dimethylquinoxaline, prepared by the method of Gabriel and Sonn.[6] A mixture of equal quantities of the two melted sharply at 106° (corr.), proving their identity; yield of 2,3-dimethylquinoxaline, 60%.

2,3-Di-*n*-propylquinoxaline.—Five grams of 2,3-dichloroquinoxaline was added to an ethereal solution of *n*-propylmagnesium iodide (2.1 equivalents). A vigorous reaction took place, the solution turning deep brown in color. After two hours, the mixture was treated with ammonia as above, and then extracted with ether. Evaporation of the ether left a dark, mushy residue which was extracted with dilute hydrochloric acid. The acid solution was decolorized with charcoal and then made alkaline with ammonia, whereupon an oil separated. The solution was heated to boiling and filtered with suction, the oil passing through the paper and leaving a slight solid residue. After cooling, the solidified oil was filtered off and pressed on a porous plate. It was dissolved in acetone and reprecipitated by careful addition of water, appearing as white cubical crystals, melting at 42.9° (corr.); yield of 2,3-di-*n*-propylquinoxaline, 30% of the theoretical.

Anal. Subs., 0.0547: 0,09537 N HCl (Kjeldahl), 5.40 cc. Calcd. for $C_{14}H_{18}N_2$: N, 13.08. Found: N, 13.19.

2,3-Dimethylquinoxaline.—It is readily seen from the structure of this compound,



, that it contains two ammono carbonyl groups,

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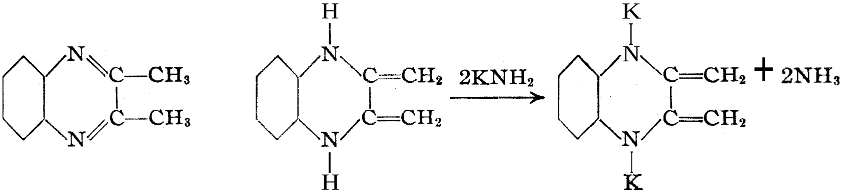
[6] Gabriel and Sonn, *Ber.*, 40, 4850 (1907).

>C=N—, and is to be regarded as a substituted ammono 1,2-diketone, a substituted ammono diacetyl.' The methods of synthesis are in agreement with the analogy. 2,3-Dimethylquinoxaline was prepared by Gabriel and Sonn[6] by the action of o-phenylenediamine on diacetyl, a reaction which is to be interpreted as the ammonolysis of diacetyl by a substituted ammonia. In this investigation, 2,3-dimethylquinoxaline was synthesized by the action of methylmagnesium iodide on 2,3-dichloroquinoxaline, just as, hypothetically, oxalyl chloride and methylmagnesium iodide should yield diacetyl.[8] Furthermore, 2,3-dimethylquinoxaline behaves as an ammono diketone on reduction, yielding the corresponding ammono di secondary alcohol, *i. e.*, I, 2,3,4-tetrahydro-2,3-dimethylquinoxaline.[9] In addition, 2,3-dimethylquinoxaline yields with benzaldehyde a dibenzal derivative, a type of reaction characteristic of ketones[10] that contain an acetyl group.

Since diacetyl readily adds Grignard reagents[1'''] and hydrocyanic acid,[11b] similar reactions were attempted with 2,3-dimethylquinoxaline, but without result. Hydrogen cyanide had no effect, while ethereal methylmagnesium iodide caused slow conversion to a red tar not further investigated.

A typical property of ketones having a hydrogen atom on the a-carbon atom is the formation of salts of the enol form through the agency of alkali metals, alcoholates or alkali metal amides. Furthermore, such salts react with alkyl halides, yielding usually metal halide and an a-alkyl derivative of the ketone.[12] In the present investigation, it has been found that the ammono diketone, 2,3-dimethylquinoxaline, behaves in an analogous fashion. Thus it has been found to react with potassium amide in liquid ammonia, giving a well-crystallized dipotassium salt of the ammono dienol modification.



Mills and Smith, J. *Chem. Soc.*, *121*, 2724 (1922), have suggested the strong resemblance between the CH_3—C=N— group of heterocyclic bases and the carbonyl group of the aquo ketones containing a methyl group.

[8] Actually, oxalyl chloride decomposes so readily into phosgene and carbon monoxide that it does not give this reaction.

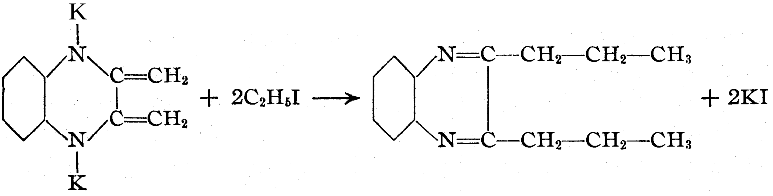
[9] Gibson, *J. Chem. Soc.*, 342 (1927).

[10] Bennet and Willis, *ibid.*, 1960 (1928).

[11] (a) Zelinsky, *Ber.*, **35**, 2138 (1902); (b) Fittig, Daimler and Keller, *Ann.*, 249, 208 (1888).

[12] Haller, *Bull. soc. chim.*, *31*, 1073 (1922), and other articles.

This salt on hydrolysis yielded unchanged 2,3-dimethylquinoxaline and potassium hydroxide. Furthermore, the salt reacted readily with two equivalents of ethyl iodide, producing potassium iodide and 2,3-di-*n*-propylquinoxaline, found to be identical with that described earlier in this paper. This reaction is seen to be analogous to that undergone by the salts of aquo ketones.[13]



It should be noted that the structure of this new compound has been definitely proved from its synthesis by two entirely different methods.

The above reaction should proceed equally well with other alkyl halides and constitutes a new method for the synthesis of 2,3-dialkylquinoxalines. It is also apparently the first synthesis of this type to be carried out with an ammono diketone.

2,3-Dimethylquinoxaline.—This was prepared by the method of Gabriel and Sonn[6,14] from o-phenylenediamine and diacetyl monoxime, and was purified by steam distillation. The white crystals of the hydrate readily effloresced, and when anhydrous melted at 106° (corr.).

Dipotassium Salt of 2,3-Dimethylquinoxaline.—This was prepared in an ammonia tube, using the technique described by Franklin.[15] One gram of anhydrous 2,3-dimethylquinoxaline was treated with two equivalents of potassium amide in liquid ammonia. The 2.3-dimethylquinoxaline (which was only slightly soluble in pure ammonia) dissolved rapidly to give a clear deep red solution. On cooling in a bath of liquid ammonia, an abundant precipitate of long greenish-yellow crystals formed. These were washed by decantation and recrystallized four times. The final washings were of the same red color as the initial, showing this to be the color of the dissolved salt. The leg containing the salt was evacuated for analysis at 60°. The sample was dissolved in dilute hydrochloric acid and one quarter of the solution was used for each analysis; weight of salt, 1.0280 g.

Anal. Subs., 0.2570: 0.09537 N HCl (Kjeldahl), 23.30 cc. Subs., 0.2570: K_2SO_4, 0.1914. Calcd. for $C_{10}H_8N_2K_2$: N, 11.95; K, 33.37. Found: N, 12.12; K, 33.42.

Qualitative investigation of the products of hydrolysis showed them to be potassium hydroxide and 2,3-dimethylquinoxaline.

2,3-Di-*n*-propylquinoxaline.—One gram of 2,3-dimethylquinoxaline was converted

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[13] The alkylation of quinaldine, which is to be regarded as a substituted ammono ketone, has likewise been carried out by the action of alkyl halides on alkali salts of the ammono-enol modification of quinaldine. Bergstrom, Science, 72, 402 (1930); Ziegler and Zeiser, *Ann.*, 485, 178 (1931). As to a possible mechanism of alkylations of this type, see Decker, Helv. *Chim. Acta*, 13, 666 (1930).

[14] Henderson, J. Chem. *Soc.*, 466 (1929).

[15] Franklin, THIS JOURNAL, 27, 831 (1905); 29, 1694 (1907); 35, 1460 (1913); *J. Phys.* Chem., 15, 510 (1911); 16, 694 (1912).

into the dipotassium salt by treatment (in an ammonia tube) with two equivalents of potassium amide in liquid ammonia. After evaporation of the ammonia, the tube was evacuated at 50°. A slight excess over two equivalents of ethyl iodide (2 g.) in 10 cc. of absolute ether was sucked into the evacuated tube. A very vigorous reaction ensued, the greenish-yellow crystals being replaced by a fine white precipitate of potassium iodide The tube was finally warmed for a few minutes at 100°, and then cooled and opened. The contents were washed out with water. The ether layer was separated and evaporated, leaving a brown partially crystalline mass. By suction on a filter some dark oil was removed, leaving cubical crystals. These were pressed on a porous plate, and then dissolved in dilute hydrochloric acid. The solution was decolorized with charcoal and neutralized with ammonia. The precipitate was filtered off (after cooling), again pressed on a plate, and finally precipitated from acetone solution by addition of water. So obtained, the product consisted of colorless cubical crystals, m. p. 42.9° (corr.), very soluble in organic solvents, insoluble in water, soluble in dilute acids. It was slightly volatile with steam.

Anal. Subs., 0.1449, 0.1508; CO_2, 0.4166, 0.4329; H_2O, 0.1125, 0.1149. Subs., 0.1023, 0.1020; 0.09537 N HCl, 9.99 cc., 9.92 cc. (Kjeldahl). Calcd. for $C_{14}H_{18}N_2$: C, 78.47; H, 8.46; N, 13.07. Found: C, 78.39, 78.30; H, 8.69, 8.53; N, 13 05, 12.99.

The above substance was identical in all respects with the 2,3-di-*n*-propylquinoxaline prepared (*vide supra*) from 2,3-dichloroquinoxaline and n-propylmagnesium iodide. A mixture of the two gave exactly the same melting point as either constituent: yield by the above reaction, 70% of the theoretical.

The small amount of oily by-product mentioned above decolorized a carbon tetrachloride solution of bromine (a reaction not given by 2,3-di-*n*-propylquinoxaline). It is suggested that this substance may have been the di-N-ethyl derivative of the ammono dienol of 2,3-dimethylquinoxaline.

2,3-Diphenylquinoxaline.—In accord with previous analogies, 2,3-diphenylquinoxaline is to be regarded as a substituted ammono aromatic diketone, a substituted ammono benzil. In agreement with this view, it is synthesized[r6] by the action of o-phenylenediamine on benzil, an ammonolysis of the type before described. Just as benzil on partial reduction yields benzoin, which can be reoxidized to benzil, so 2,3-diphenylquinoxaline gives on gentle reduction 1,2-dihydro-2,3-diphenylquinoxaline,[16] an ammono benzoin, which may also be prepared from benzoin and *o*-phenylenediamine.[17] Upon oxidation, the compound yields 2,3-diphenylquinoxaline.

On strong reduction benzil gives the optically isomeric di-secondary alcohols hydrobenzoin and isohydrobenzoin, while 2,3-diphenylquinoxaline yields the corresponding ammono di-secondary alcohols, racemic and internally compensated 1,2,3,4-tetrahydro-2,3-diphenylquinoxalines.[18]

Since benzil adds hydrocyanic acid and Grignard reagents, similar reactions were attempted with 2,3-diphenylquinoxaline, but as in the case of 2,3-dimethylquinoxaline, unsuccessfully.

The most remarkable of the reactions of benzil is the well-known rearrangement in the presence of a base to a salt of benzilic acid.

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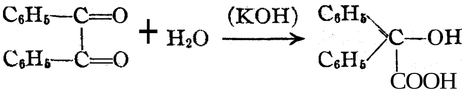
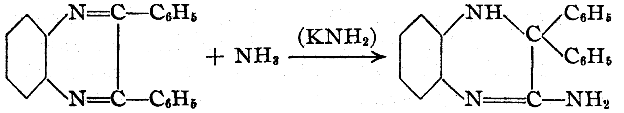
[16] Hinsberg and Konig, Ber., 27, 2181 (1894).

[17] O. Fischer, *ibid.*, 24, 719 (1891).

[18] Bennett and Gibson, *J. Chem. Soc.*, 123,1570 (1923).



It has been found that 2,3-diphenylquinoxaline probably undergoes an analogous rearrangement in the presence of the ammono base potassium amide in liquid ammonia, producing what appears to be the hitherto unknown 1,2-dihydro-2,2-diphenyl-3-aminoquinoxaline, which is to be regarded as a substituted ammono benzilic acid.



Although we were unable to prove this structure by direct synthesis, it is the most probable. If this is the structure, the reaction is the first example of the benzilic acid rearrangement in the ammonia system.

2,3-Diphenylquinoxaline.—This was prepared by the method of Hinsberg and König[18] from benzil and o-phenylenediamine.

1,2-Dihydro-2,2-diphenyl-3-aminoquinoxaline.—When 2,3-diphenylquinoxaline, which was practically insoluble in liquid ammonia, was treated with two equivalents of potassium amide in that solvent it dissolved, giving a deep violet solution, but underwent no further change, or at best only a very slow one. (It is worth noting that benzil dissolves in cold alcoholic potassium hydroxide to give a deep violet solution.) Heating was therefore employed to accelerate the reaction: 1.2 g. of potassium was converted catalytically into amide in a straight tube containing liquid ammonia; 2.2 g. of diphenylquinoxaline was then added and the tube sealed off, enclosing about 20 cc. of liquid ammonia. The sealed tube was heated in the steel bomb described by Blair[19] for ten hours at 130–140°. The solution was then still colored but contained a precipitate. After evaporation of the ammonia, the residue was treated with water, and the resulting brown solid was washed and dried. It was extracted twice with hot benzene (to remove 2.3-diphenylquinoxaline). The residue was dissolved in alcohol and decolorized with charcoal. By concentrating and cooling the solution, the product was obtained as colorless rhombohedra, fairly soluble in alcohol, insoluble in water and benzene. The substance melted without decomposition at 287° (corr.) and could be sublimed in beautiful colorless flakes. It was basic, giving a crystalline hydrochloride with alcoholic or aqueous hydrochloric acid. It dissolved in concentrated sulfuric acid without color.

Anal. Subs., 0.1417, 0.1491: CO_2, 0.4178, 0.4389; H_2O, 0.0686, 0.0733. Subs., 0.0706, 0.1032: 0.09537 N HCl (Kjeldahl), 7.48, 10.90 cc. Calcd. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.41, 80.28: H, 5.42, 5.50; N, 14.16, 14.11.

Thus the substance is seen to have the correct composition for the expected 1,2-dihydro-2,2-diphenyl-3-aminoquinoxaline. This is the most probable structure for the new compound, in view of its stability and high melting point. Oddly enough, the substance did not react with nitrous acid. Also, it was unaffected by heating with alcoholic hydrochloric acid at 150°. It is realized that in view of these facts some doubt may be cast upon the structure assigned, and attempts will be made to prove this structure by direct syntheses. The yield was 30% but much of the diphenylquinoxaline was recovered unchanged.

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[19] Blair, THIS JOURNAL, 48, 87 (1926).

Summary

2,3-Dichloroquinoxaline, 2,3-dimethylquinoxaline and 2,3-diphenylquinoxaline have been shown to be substitution products, respectively, of an ammono oxalyl chloride, an ammono diacetyl and an ammono benzil, and experimental evidence confirming this view has been presented.

Two new methods for the synthesis of 2,3-dialkylquinoxalines have been developed.

The alkylation of an ammono diketone by converting it into a salt of the ammono dienol modification and treating this with an alkyl halide has been carried out for the first time.

Evidence of a benzilic acid rearrangement of an ammono benzil has been found.

The following new compounds have been prepared: o-phenylene ethylene oxamidine, 2,3-di-*n*-propylquinoxaline, the &potassium salt of 2,3-dimethylquinoxaline dienol, 1,2-dihydro-2,2-diphenyl-3-aminoquinoxaline (structure not definitely proven).

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

SOME RELATIONSHIPS OF THE RATIO OF REACTANTS TO THE EXTENT OF CONVERSION OF BENZALDEHYDE AND FURFURALDEHYDE TO THEIR ACETALS

BY HOMER ADKINS, JOSEPH SEMB AND LESTER M. BOLANDER

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Most of the measurements which have been made in this Laboratory upon the relationship of the structure of aldehydes and alcohols to the extent of the acetal reaction have been made upon mixtures resulting from the reaction of approximately eleven moles of alcohol with one mole of aldehyde.[1] This ratio of reactants was originally selected in order to preserve the homogeneity of the reaction mixtures, and has been used in other cases in order to obtain a direct comparison of the extent of conversion of various pairs of reactants. More recently it has seemed desirable to ascertain to what extent, if at all, the calculated equilibrium constants for this reaction are dependent upon the ratio of reactants. Such a study has now been made for certain of the acetals of benzaldehyde and furfuraldehyde.

The Reaction of **Benzaldehyde with** Alcohols.—Test-tubes (1 X 15 cm.) so marked as to make it easy to measure into them approximately the desired volume of alcohol and benzaldehyde, were drawn out preparatory to

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[1] Adkins, Adams, Hartung, Street and Broderick, THIS JOURNAL, 47, 1358 (1925); 49,2517 (1927); 50,162 (1928); 50,178 (1928).

sealing, placed in an oven at 115° overnight, cooled in a desiccator and weighed. Approximately the desired quantity of ethanol and 0.00045 g. of hydrogen chloride in ethanol were added and the tube again weighed. Approximately the desired amount of benzaldehyde was added and the tube sealed off and weighed. The tube was then placed in a thermostat and held at 25° for approximately four days. The tubes were opened and samples varying from 0.9 to 5.0 ml., depending upon the concentration of the benzaldehyde, were removed by means of a pipet for analysis.

The Determination of **Benzaldehyde.**—The sulfite method[2] is not satisfactory in the analyses for benzaldehyde because of the indefiniteness of the end-point. The hydrogen peroxide method was found to be much more satisfactory if the method of Adams[3] was modified as in the following procedure. Thirty ml. of 3% hydrogen peroxide, prepared by diluting "superoxol," was added to 20 ml. of 0.34 N sodium hydroxide previously heated in a 250-ml. Erlenmeyer flask to 40°. The sample to be analyzed, and which contained approximately 0.35 g. of benzaldehyde, was added and followed by 5 ml. of ethanol. The reaction mixture was kept with occasional shaking in a thermostat at 40° for thirty-five minutes, after which 10 ml. more of the hydrogen peroxide solution was added and the flask again placed in the thermostat. After a total of fifty minutes in the thermostat the reaction mixture was titrated with standard acid. Blanks containing all the reagents noted above except the sample from the acetal reaction mixture were subjected to the same treatment as in the analyses and a correction made for the acidity so developed. The effect of varying the size of the sample, the quality of the hydrogen peroxide, and the temperature and time for oxidation were investigated and the above procedure was found to be quite accurate and the most satisfactory, The reliability of the method is indicated by the fact that in five successive analyses a sample of benzaldehyde showed a purity of 98.6, 99.2, 97.6, 97.4 and 99.0%.

The Reaction of **Furfural with** Alcohols.—The desired amounts of furfural and ethanol containing hydrogen chloride were weighed into a flask so that they were in the desired ratio and the total volume was 25 ml. The reaction mixture contained 0.0001 g. of hydrogen chloride. The reaction of furfural and ethanol is complete within a few hours but in these experiments the mixtures were allowed to stand for at least twenty-four hours before an analysis was made.

The Determination of **Furfural.**—The sulfite method was used for the analysis and the procedure was essentially the same as that previously described.[4] The equation on which this analysis is based is

$$C_5H_4O_2 + Na_2SO_3 + H_2O = C_5H_4O_2NaHSO_3 + NaOH$$

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[2] Seyewetz and Bardin, J. *Soc. Chem. Ind.*, 25,202 (1906).

[3] Adams and Adkins, THIS JOURNAL, 47,362 (1925).

[4] Adkins and Broderick, *ibid.*, 50,184 (1928).

In the case of certain aldehydes the amount of aldehyde may be calculated on the basis of a titration with a solution of an acid which has been standardized by one of the methods commonly used in acidimetry. However, this is not a justifiable procedure for all aldehydes at various concentrations and it is far more accurate to standardize the acid against the aldehyde, under the conditions in which the acid is to be used in analysis. In this case samples containing from 0.10 to 0.25 g. of furfural with and without the addition of alcohol and furfural acetal were added to 40 ml. of a 10% sodium sulfite solution and the solution titrated with acid having a normality of 0.215 N as standardized against a solution of sodium hydroxide. In seven determinations 1 ml. of the acid was equivalent to 0.0231 * 1 g. of furfural. The normality of the acid against furfural was thus 0.241. This relationship between the normality of an acid against alkali and against furfural is not fixed but varies somewhat with the operator, because the end-point in the furfural titration is rather indefinite and is determined by a color comparison. This makes it necessary for each operator to standardize his acid solution against furfural.

Preparation of **Furfural Acetal.**—This acetal has been prepared by the reaction of the aldehyde with orthoformic ester as described by Claisen.[5] The preparation of the acetal by the less costly method involving the reaction of furfural with alcohol has apparently hitherto not been successful because of the sensitivity of the aldehyde toward hydrogen chloride, and because of its low equilibrium point in the acetal reaction. A practical method for carrying out this preparation has been developed after a rather extended study. A reaction mixture containing 96 g. (1 mole) of furfural, 276 g. (6 moles) of dry ethanol and 0.0012 g. of anhydrous hydrogen chloride was allowed to stand for one day. Ten ml. of water containing 1 g. of sodium carbonate was then added and the mixture subjected to fractionation through a Widmer column 30 cm. in length. The fractionation was carried out slowly so that the distillate was not more than 2 ml. per minute. After removal of the alcohol the liquid was filtered, transferred to a 250-ml. flask and fractionated through the Widmer column under a pressure of 16 to 19 mm. A yield of 24% of the theoretical amount, *i.* e., 41 g. of acetal of b. p. 77–79' (16 mm.) and 184–185° (740 mm.) was obtained on the average. Claisen reported the boiling point of the acetal as 189–191°, while Scheibler, Sotschek and Friese[6] reported 180–184°. If the amount of alcohol in proportion to the furfural was much less than that recommended above or if the concentration of catalyst was much greater the yields of acetal were materially reduced. The acetal may also be obtained from the reaction mixture by pouring it into a liter of water containing 1 g. of sodium carbonate. The water-insoluble layer was

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[5] Claisen, Ber., 40, 3907 (1907).

[6] Scheibler, Sotschek and Friese, *ibid.*, 57B, 1444 (1924).

then placed over anhydrous sodium sulfate, while another liter of water was added to the aqueous layer in order to throw out more of the acetal. The combined water-insoluble layers after drying were then fractionated. The yield of acetal so obtained was usually about 2 g. less than by the first process in which the alcohol was removed by distillation.

Ratio of Reactants and Extent of Acetal Reaction.—There are recorded in Table I the percentage conversions of benzaldehyde and furfuraldehyde to their acetals in their reaction with various alcohols at various concentrations. The average deviation from the mean in these determinations is indicated in column two of the table after the sign for plus or minus. The number of reaction mixtures which were analyzed is indicated by the figures in parentheses in column two of the table. The value for the equilibrium constant given in column three of the table was calculated on the basis of the concentrations at equilibrium expressed as mole fractions.

TABLE I

RATIO OP REACTANTS AND EXTENT OF ACETAL REACTION

Moles of alcohol per mole of aldehyde	Conversion of aldehyde to acetal, %	*K*
	Ethanol and Benzaldehyde	
2.08	25.1±1.1 (8)	0.091
3.90	34.110.8 (6)	.079
5.87	41.9±2.0 (6)	.089
7.80	48.6±1.8 (7)	.082
9.96	53.0±1.1 (8)	.081
	n-Butanol and Benzaldehyde	
2.02	24.8±1.5 (7)	.091
4.17	36.0±1.9 (6)	.082
6.13	44.0±2.2 (6)	.084
8.01	48.9±1.3 (7)	.080
9.90	52.7±0.7 (6)	.080
	Propanol-2 and Benzaldehyde	
1.85	6.7±1.1 (5)	.0045
5.86	11.1±0.8 (3)	.0030
10.41	18.7±0.5 (2)	.0047
	Ethanol and Furfuraldehyde	
2.02	17.1±0.5 (2)	.036
6.06	32.6±0.5 (2)	.036
6.21	32.9±0.3 (2)	.035
9.80	39.8±0.7 (2)	.034
11.08	43.7±0.6 (2)	.039
	Methanol and Furfuraldehyde	
4.40	39.5±0.5 (2)	.098

In addition to these determinations upon the synthesis of acetals a reaction mixture was made containing 0.3 mole of furfural acetal, 0.181 mole of water, **3.335** moles of ethanol and **0.0001** g. of hydrogen chloride. After equilibrium had been established the concentrations of the reactants were **0.193** mole of acetal, **3.549** moles of ethanol, **0.074** mole of water and 0.107 mole of furfuraldehyde. The equilibrium constant is thus **0.041.** The analysis of another equilibrium mixture resulting from the hydrolysis of furfuraldehyde acetal indicated the value of K to be **0.039.**

The percentage conversion of benzaldehyde to the acetals in its reaction with ethanol and propanol-2, and for the reaction of furfuraldehyde with ethanol and methanol, have been determined previously for reaction mixtures which contained **1** mole of aldehyde to **11** moles of the alcohol.[7] The values for the equilibrium constants calculated from Adams' data on the basis of the concentrations at equilibrium expressed as mole fractions are as follows: benzaldehyde with ethanol, 0.024, with propanol-2, **0.0030;** furfuraldehyde with methanol, **0.113,** with ethanol, **0.029.** It may be seen from a comparison of these values with those given in Table I that there is a fair agreement between the values of K now reported and those calculated from Adams' data except for the reaction of benzaldehyde and ethanol. It is believed that this discrepancy is due to his procedure for the oxidation of benzaldehyde, which has been proved in this investigation to give inaccurate results.

The values for the equilibrium constant recorded in Table I indicate that there is very little if any change in the constant when the moles of alcohol per mole of aldehyde is increased from **2** to **10.** It is possible that there is a small decrease in the value of the constant with increasing concentrations of alcohol. Such a change in the calculated equilibrium constant is not surprising if it is considered that the acetal reaction is not the only reaction which may modify the concentration of the components of the system under study.

$$\mathrm{RCHO + R'OH = RCH(OH)OR'} \qquad \text{(I)}$$

$$\mathrm{RCH(OH)OR' + R'OH = RCH(OR')_2 + H_2O} \qquad \text{(II)}$$

$$\mathrm{RCHO + H_2O = RCH(OH)_2} \qquad \text{(III)}$$

It was previously shown[8] that the formation of acetals probably proceeds through Reactions I and II. Some of the water formed according to Equation II would add to the aldehyde as in Equation III. Thus as the extent of the acetal reaction increased with increase in the ratio of alcohol to aldehyde, there would also occur an increase in Reaction III which would decrease the actual concentration of aldehyde (or hemiacetal) and thus the increase in the conversion of aldehyde to acetal would not be as great as would be calculated. On the basis of this argument such an effect would become even more marked with those aldehydes which show much higher percentage conversion. It is hoped that the effect of the ratio of reactants

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[7] Adkins and Adams, This journal, 47, 1370 (1925).

[8] Adkins and Broderick, *ibid.*, 50, 499 (1928).

upon the equilibrium constant may be extended to the study of aldehydes which show much higher percentage conversion than do those referred to in this paper.

Summary

For the first time a method for the preparation of furfural acetal from the aldehyde and ethanol has been described.

The effect of the ratio of reactants upon the extent of the reaction of benzaldehyde with ethanol, butanol and propanol-2 and of furfural with ethanol has been determined when the ratio of aldehyde to alcohol is varied from 1 to 2 to 1 to 10. The equilibrium constant for the first two of these reactions was found to be identical for the two alcohols but to decrease slightly with increase in ratio of alcohol to aldehyde.[9] The equilibrium constant for the reaction of benzaldehyde with propanol-2 and of furfuraldehyde with ethanol appeared to be independent of the concentration of reactants. The equilibrium constant for the reaction of furfuraldehyde and methanol has been redetermined.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

RESIN STUDIES. I. THE PREPARATION AND AUTOXIDATION OF PRECIPITATED LEAD ROSINATE

BY W. A. LA LANDE, JR.

RECEIVED FEBRUARY 3, 1931 PUBLISHED MAY 6. 1931

I. Preparation of Precipitated Lead Rosinate

Introduction.—In attempting to study quantitatively the absorption of oxygen by lead rosinate it was obviously important to begin with a material of known and reproducible composition, preferably a normal salt, which had not been exposed to oxidation. Lead rosinate was made by several of the methods proposed in the literature for the preparation of rosinates and abietates[1] and was found objectionable for two reasons. (1) The rosinate responded positively to the starch–iodide test for peroxides immediately after the preparation was completed. (2) The composition (usually complex) of the precipitates obtained according to the

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[9] The equilibrium constants for the reactions of butanol and ethanol with benzaldehyde are the same only when they are calculated upon the basis of concentrations expressed as mole fractions. They are not identical if the calculation is made upon the basis of concentrations expressed as moles per liter as was done in previous papers in this series.

[1] Pardeller, *Seifensieder-Ztg.*, 1256 (1909); Ellingson, THIS JOURNAL, 36, 325 (1914); Bontoux, *Rev. chim. ind.*, *28*, 157 (1919); Steele, THIS JOURNAL, 44, 1332 (1922); Dupont, Desalbres and Bernette, Bull. *soc. chim.*, 39, 488 (1926); Uzac, *ibid.*, 37, 1194 (1925); Uzac, *Chimie* et *industrie*, *14*, 186 (1925).

given directions was not reproducible within a reasonable range. All of the products contained an appreciable quantity of alkali.

In order to provide a suitable material, a study was made of the factors governing the composition of the precipitate formed on adding a solution of a lead salt to a sodium rosinate solution.

Discussion.—From preliminary experiments it was evident that with the ordinary methods of preparation, oxidation of the rosinate began in the early stages of the procedure. Oxidation and absorption of carbon dioxide progressed during the saponification of the rosin and the precipitate was exposed to air during washing, filtration and drying. As a result, in spite of ordinary precautions and reasonably rapid manipulation, the precipitate always responded positively to tests for oxidation. In order to obtain a product uncontaminated by oxidation it was necessary to carry out all steps in the preparation of lead rosinate in the absence of oxygen. Accordingly, the apparatus illustrated in Fig. 1 was devised.

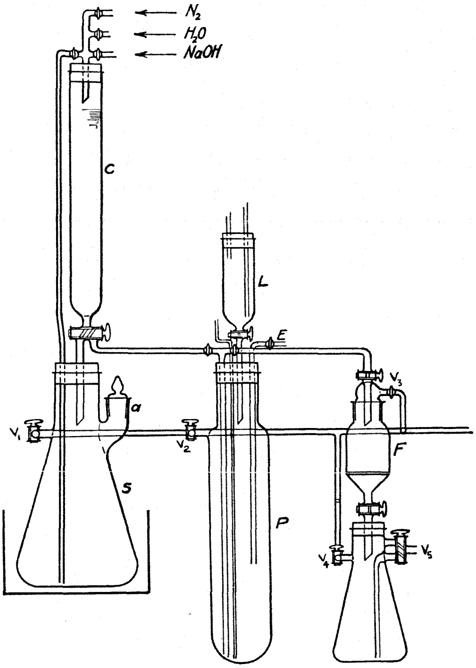

Fig. 1.

The problem presented by the second objection mentioned above was met by investigating several hitherto apparently neglected factors in the preparation of lead rosinate. It was possible to obtain precipitates of reproducible and nearly theoretical composition only by using very dilute solutions of lead acetate and sodium rosinate. Two per cent. solutions of the reactants were found most practical for the precipitation. With more concentrated solutions the precipitate formed was lumpy, bulky and heterogeneous, difficult to wash and purify, and altogether unsuitable for the purpose for which it was intended. The composition of the precipitate was also found to vary with the rate of addition of the lead acetate solution to the sodium rosinate, and with the time and rate of agitation of the reaction mixture. When lead acetate is added dropwise to sodium rosinate solution, several reactions can take place simultaneously. As the solutions mix, an insoluble rosinate tends to be precipitated. Due to its gelatinous, bulky structure the precipitate immediately occludes some of the rosinate solution and some of the lead acetate solution. This precipitate is of indefinite composition and is further reacted upon by the excess rosinate solution. The composite precipitate at first contains an excess of abietic acid. By agitation with a large excess of lead salt the abietic acid content of the precipitate is transposed to lead abietate. This transposition is a slow one and accounts for the results obtained by varying the time of agitation, i. e., the lead content of the precipitate is increased to a maximum, corresponding to lead abietate, by agitating the acid salt with the excess lead solution. If the lead solution is added slowly the composite precipitate is subsequently very much more slowly (never completely) transposed to the normal salt. In one experiment where the lead solution was added over a period of forty minutes, the precipitate contained only 22% of lead. The best results were obtained by adding the lead solution over a period of four to five minutes. Vigorous and prolonged agitation was absolutely essential during all stages of the preparation. Room temperature was most satisfactory for the preparation of the rosinate. Both lead nitrate and lead acetate were used as precipitants. Previous investigators have usually employed the acetate. No difference in composition of the rosinate dependent on the use of nitrate or acetate was observed.

Experimental

Materials.—Hercules "I" wood rosin of recent manufacture was used in all the experiments: Sap. no., 172.1; acid no., 161.1. Samples in the form of rather large lumps were taken from the interior of a large piece of the rosin and quickly weighed and transferred to the apparatus.

The water used for the preparation of solutions and for the washing of the precipitate was purified by redistilling ordinary distilled water from an alkaline suspension of manganous hydroxide.

Carbonate-free sodium hydroxide was made according to the directions of Küster.[2] The solution was stored in a ceresine lined bottle fitted with the lines and stopcocks necessary for transferring the solution to the various parts of the apparatus, $N = 0.5670$.

Tank nitrogen was bubbled through alkaline pyrogallol solution to remove the gross amounts of oxygen. The remaining traces of oxygen were removed by passing the gas over glowing copper. Tank oxygen was dried by passing the gas through concentrated sulfuric acid, ascarite and calcium chloride.

The organic solvents were dried over sodium and redistilled. The other reagents used in the work were "Baker's Analyzed" brand.

All parts of the apparatus were thoroughly purged with nitrogen before being used.

Seventy-five grams of rosin was charged into the saponifying flask F through "a" (Fig. 1). The equivalent amount of sodium hydroxide and enough water to make a 5% solution were then added through C Four hundred cc. of this solution was displaced into P, the precipitating vessel, by nitrogen pressure. After diluting the solution until it contained 1.64% of rosin, 1.37 times the equivalent of lead acetate (17.26 g.) in 800 cc. of water was added through L. The reaction mixture was vigorously agitated

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[2] Küster, *Z. anorg. Chem.*, 13, 134 (1897).

for one hour after the addition of the lead solution, and for five minutes after each subsequent addition of wash water. The washing was considered complete when the decantate failed to give a coloration with sodium sulfide solution. The precipitate was displaced onto the filter F[3] by nitrogen pressure on V_1 and suction on V_5. It was possible to obtain in this way a thick, firm cake of the precipitate. The stopcocks on the filter were then closed and the product kept thus until needed. The precipitate was dried by shaking a portion of it onto a clock glass and quickly transferring it to a phosphorus pentoxide desiccator which was immediately evacuated. The total time of exposure to the air at this point did not exceed twenty seconds. A one-gram sample of the rosinate did not oxidize a starch–iodide solution. After exposing another sample to the air for a few minutes the product liberated iodine from the iodide. Solutions of the rosinate in various organic solvents were perfectly clear—an indication of the absence of any free inorganic compound. After 200 days in an evacuated tube the rosinate had become slightly darker in color. On heating a sample of the rosinate in a capillary tube in a sulfuric acid bath, no visible change occurred until the temperature rose to 70°, then a progressive darkening and shrinking began. There was no definite melting point, but the sample shrunk to small, clear, dark amber globules (140–150°) and then spread around the wall of the tube in a viscous film This film became almost black and quite opaque at 160–170°, due in part to a separation of metallic lead, and in part to decomposition of the acid.

Analysis of Lead Rosinate.—The metal content of a rosinate or abietate is a reliable index of its purity. In this investigation the ordinary methods of determination were abandoned in favor of the following procedure.

A weighed sample of the rosinate (0.5 g.) was dissolved in 20 cc. of hot 50% alcoholic 2 *N* sodium hydroxide. Twice the calculated amount of 50% alcoholic 2 *N* sodium sulfide was added and after boiling gently for ten minutes the mixture was filtered. The precipitate was first washed with dilute alcoholic sodium hydroxide solution, then with hot water saturated with hydrogen sulfide, and finally dissolved in boilig 1:3 nitric acid. The lead was precipitated electrolytically as lead dioxide. The deposit was dried at 220–230°.

Anal. Subs., 0.4502, 0.5648: PbO_2, 0.1252, 0.1575. Calcd. for this rosinate: Pb, 24.13.[4] Found: Pb, 24.18, 24.02.

These results were checked against those obtained by decomposing samples with concentrated sulfuric acid and a little nitric acid in a Kjeldahl flask. The lead was weighed as sulfate or chromate.

Anal. Subs., (1) 0.9650, (2) 0.7940, (3) 0.6475, (4) 0.6952: $PbSO_4$: (1) 0.3389, (2) 0.2791; $PbCrO_4$: (3) 0.2444, (4) 0.2492. Found: Pb, 24.00, 24.03, 24.20, 24.25.

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[3] This piece of apparatus was made from a Jena glass, tall form Büchner funnel with a sealed-in fritted glass filter plate. The glassblower worked the open end into a bottle neck and fitted it with a ground-in stopper bearing the two stopcocks. Precipitates can be dried very conveniently in inert atmospheres in this type of filter by closing the stopcocks, transferring the apparatus to the oven and connecting the stem of the funnel to the source of the gas.

[4] Calculated from the saponification no., the rosin used contained 92.90% of abietic acid, or 1 g. of rosin = 0.929 g. of abietic acid. This is equivalent to 0.318 g. of Pb. Since the unsaponifiables are co-precipitated, the precipitate will contain 0.318 g. of Pb + 0.929 g. of abietic acid + 0.071 g. of unsaponifiable, or 1.318 g. for each 1 g. of rosin originally present, provided the normal salt forms. The calculated lead content is therefore 24.13%. By the same reasoning the precipitate of rosinate contains 94.7% of normal lead abietate.

The alkali content of the rosinate was determined by Steele's method.[5] One drop of 0.05 N hydrochloric acid discharged the faint pink color produced in the aqueous extract of the ash by phenolphthalein. The amount of alkali in the sample was therefore negligible.

2. The Autoxidation of Precipitated Lead Rosinate

Introduction.—Maly was probably the first to notice that rosin and abietic acid increase in weight on exposure to the air.[6] Subsequently identified as a process of autoxidation, this phenomenon has been the subject of considerable study, both in the solid acid and in solutions of the acid.[7] On the other hand, little work has been done on the obviously related subject of the autoxidation of metallic rosinates and abietates. To supply some necessary data for an investigation still in progress, the course and extent of the reaction

$$\underset{\substack{\text{solid}\\\text{(as rosinate)}}}{Pb(C_{20}H_{29}O_2)_2} + O_2 \longrightarrow$$

was studied. A solution of the rosinate offers the best means of obtaining rapid and complete absorption of oxygen, but the method does not permit of the obtaining or manipulation of indisputably unchanged intermediate products. Another objection arises from the fact that the degree of absorption is somewhat affected by the solvent used. In the type of system studied in this paper, the reaction proceeds at a conveniently slow rate and the reversibility of the reaction can be directly and easily studied by submitting the reaction mixture to various changes of temperature and pressure. Lead rosinate rather than pure lead abietate was used because results obtained with it had the same significance as those obtained by using pure lead abietate. It was, therefore, unnecessary to execute the much more laborious preparation of the latter compound.

Several methods were tried for following the course of the progressive absorption of oxygen by lead rosinate. Manometric technique was found to be unsatisfactory; the results obtained were not reproducible and the final values were misleading. Frequent shaking of the sample did not improve the results. Since some of the products of the autoxidation of the rosinate liberate iodine from potassium iodide, it appeared possible to follow the course of the oxidation by an iodimetrie method. This procedure required too much material and was abandoned. The gravimetric method outlined below was finally adopted as the most practical from the standpoints of convenience, accuracy and economy.

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[5] Steele, THIS JOURNAL, 44, 1332 (1922).

[6] Maly, *Ann.*, 161, 115 (1872).

[7] Fahrion, *Z. angew. Chem.*, 13, 1197 (1901); Fahrion, *ibid.*, 20, 356 (1907); Klason and Kohler, *J. prakt. Chem.*, 63, 337 (1906); Knecht and Hibbert, *J. Soc. Dyers Colourists*, 25, 148 (1919); Dupont and Dubourg, *Bull. inst. pin*, 52, 205 (1928); Dupont and Lévy, *Compt. rend.*, 189, 763 (1929).

Experimental.—The lead rosinate used in all the experiments was prepared by the method outlined in the first part of this paper. All of the samples were taken at the same time from the same batch of material.

Samples of the rosinate of equal weight (0.4840 g.), in the form of fine powder, were weighed into glass-stoppered weighing bottles. 40 mm. in diameter and 50 mm. in height. The average thickness of the layer of rosinate was 2 mm. Each of the samples thus prepared was used immediately. The stopper of the weighing bottle was removed and the bottle was placed in the vessel shown in Fig. 2. The piece of apparatus was then transferred to the oven or thermostat, and dry preheated oxygen or nitrogen (as the experiment required) passed through at the rate of 300 cc. per hour. This rate provided a slowly but constantly changing atmosphere of the gas, without danger of loss through agitation of the powder. No attempt was made to obtain a fine temperature control, but all of the given temperatures were the same throughout a given run with a maximum variation of ±1°. Each sample was heated for a timed interval, then allowed to cool in oxygen or nitrogen, and finally weighed after six hours in the desiccator. Before each subsequent exposure to the gas the powder was mixed by rotating the stoppered weighing bottle. In the experiment carried out under pressure the weighing bottle was placed in an Emerson bomb, the pressure raised to the required amount, and the bomb then transferred to the oven.

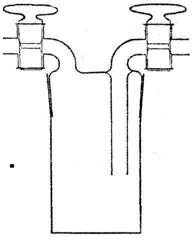

Fig. 2.

Experimental Results.—All the results recorded are average values obtained from at least two experiments conducted under precisely the same conditions.

In Table I showing the increase in weight of lead rosinate in pure dry oxygen at various temperatures, the final value in each sub-table represents the time and percentage increase in weight at which the system came to equilibrium. All runs were continued for at least one hundred hours after this point was reached in order to eliminate the possibility of a false or transient equilibrium. In each sub-table (except 125°) the data between the last result and the one immediately above it have been omitted

TABLE I

INCREASE IN WEIGHT OF LEAD ROSINATE IN OXYGEN AT VARIOUS TEMPERATURES AND AT 28° UNDER 60 ATMOSPHERES' PRESSURE

28°. Sample, 0 4836 g			65° Sample, 0 4835 g		
Total hours	Total increase, g.	Increase in weight, %	Total hours	Total increase, g.	Increase in weight. %
14	0 0003	0.00	1	0 0001	0 021
32	.0013	.26	8	.0056	1.15
47	0028	.58	26	.0104	2.13
68	0055	1.14	40	.0128	2.65
90	.0105	2 18	71	.0146	3.02
118	.0150	3.10	95	.0155	3.20
150	.0184	3 80	114	0162	3.35
184	.0200	4.14	156	.0173	3.57
232	.0214	4.12	204	.0182	3.76
294	.0231	4.78	252	.0186	3.84
911	.0306	0.33	398	0196	4.05

Table I *(Concluded)*

100°. Sample, 0.4840 g.

Total hours	Total increase, g.	Increase in weight, %
3	0.0031	0.64
9	.0051	1.04
22	.0069	1.44
49	.0077	1.60
75	.0080	1.66
100	.0083	1.72
129	.0085	1.76
177	.0089	1.84
218	.0091	1.88
258	.0092	1.90

28°, 60 atm. Sample, 0.4021 g.

Total hours	Total increase, g.	Increase in weight, %
34	0.0066	1.63
93	.0149	3.71
141	.0201	4.77
189	.0235	5.63
240	.0253	6.33
307	.0266	6.62
362	.0282	7.01
410	.0297	7.38
460	.0298	7.42
508	.0307	7.63

125°. Sample = 0.4838 g.

Total hours	Total increase, g.	Increase in weight, %
11	0.0002	0.041
37	.0008	.165
60	.0010	.206
84	.0016	.328
108	.0019	.391
132	.0026	.532

for space reasons. These omitted values when plotted all fall on a curve gently sloping to the maximum or final value. The calculation of the percentage increase in weight is based on the original weight of the sample. The results are plotted in Fig. 3 for the first two hundred hours.

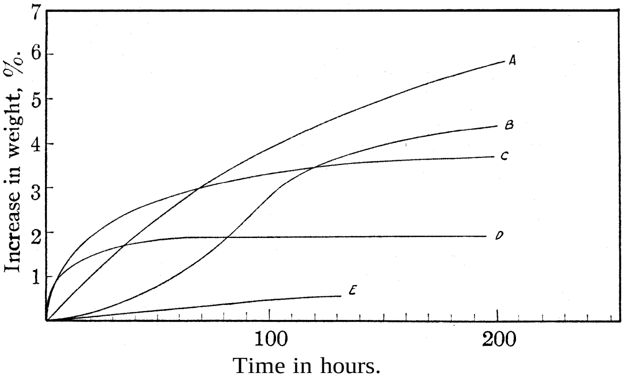

Fig. 3.—Course of the increase in weight of lead rosinate in oxygen at various temperatures and at 28° and 60 atmospheres: A, 28° at 60 atm.; B, 28°; C, 65°; D, 100"; E, 125°.

In Table II the results obtained for maximum absorption at the various temperatures are summarized. For comparison and correction, the results obtained by heating the rosinate in nitrogen at the various temperatures are included (Col. 2). These values represent a loss in weight, *i.* e., the rosinate is appreciably volatile at 100 and 125°. The values for the apparent oxygen absorption at 100 and 125° (Col. 3) have been corrected, in'order to take into account the loss in weight of the rosinate when heated to these temperatures in an inert atmosphere. The corrected values are shown in the fourth column and represent the actual oxygen absorption. The molar equivalent of oxygen absorbed is calculated from the weight of oxygen absorbable by a rosinate containing 94.70% of normal lead abietate.

TABLE II

ABSORPTION DATA

T, °C.	Change in weight, % a, in N_2	 b, in O_2	a + b Oxygen absorbed, %	Molar equiv. of O_2 absorbed
28 (60 atm.)	−0.00	7.63	7.63	2.04
28	− .00	6.33	6.33	1.59
65	− .00	4.03	4.05	1.08
100	− .31	1.89	2.20	0.55
125	−1.52	0.53	2.05	.51

The relation of the apparent oxygen absorption (Table II, Col. 3) to the actual oxygen absorption (Table II, Col. 4) is shown graphically in Fig. 4.

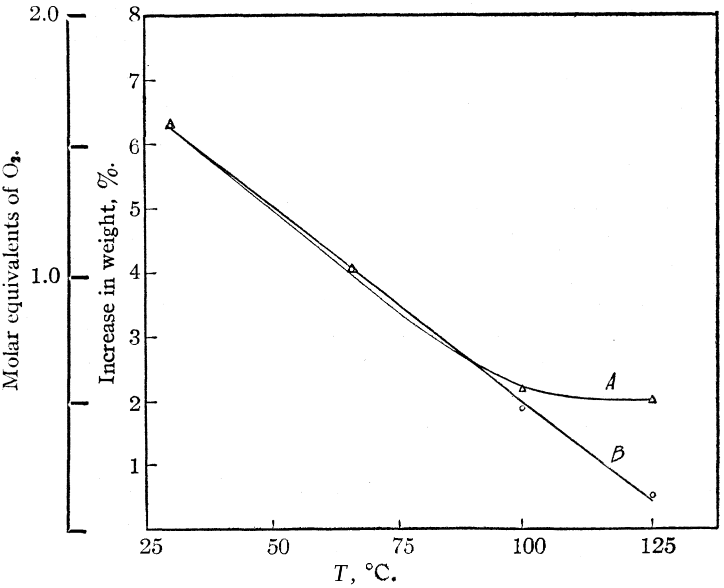

Fig. 4.—Maximum oxygen absorbed at various temperatures by lead rosinate: A, *actual* O_2 absorbed; B, apparent O_2 absorbed.

The results obtained after heating several of the oxidized samples in nitrogen to constant weight are reproduced in Table III. All the values determined for 100° are corrected for the slight volatility of the rosinate itself at that temperature (see Table II, Col. 2).

TABLE III

EXPERIMENTAL DATA

Oxygen originally absorbed at	28° (60 atm.)	28°		65°
Loss on heating in N_2 to constant weight at	100°	65°	100°	100°
As % O_2 (of total absorbed)	57.0	17.6	48.7	47.0
As molar equivalent of Or	1.14	0.28	0.77	0.51
Molar equivalent of O_2 remaining	0.86	1.31	.82	.57

Discussion of Results.—The results recorded in Tables I and II show that the rate and degree of oxygen absorption by lead rosinate depend, for a given pressure, on the temperature. Dupont and Lévy[8] worked at only one temperature (60°) and it must, therefore, be assumed that this temperature was designedly or fortuitously selected since their final results indicated a sharp end-point when one mole of oxygen had been absorbed. The curve B (Fig. 3) is the familiar S-shaped curve characteristic of autocatalytic processes. The amount of oxygen absorbed at equilibrium corresponded to three atoms of oxygen. This does not necessarily indicate the formation of a compound $Pb(Ab)_2 \cdot 3O$. It is a great deal more probable that the reaction mixture at this point was a combination of all the possible reaction products, with the final product present in largest amount. The mixture slowly liberated iodine from aqueous iodide, quickly from acidified iodide. The product obtained when the experiment was repeated at the same temperature but under sixty atmospheres' pressure also liberated iodine from aqueous and acidified iodide. The results in this experiment are in good agreement with those obtained by Dupont and Lévy for abietic acid, *i. e.*, each abietate group absorbed one mole of oxygen at equilibrium.

In curves C, D and E there is again an indication that the amount of oxygen absorbed corresponded to one or two atomic equivalents of oxygen. It is more possible however, that the reaction product was a mixture. All of these oxidation products liberated iodine from aqueous iodide (very slowly) and from acidified iodide (more rapidly).

If the degree of oxygen absorption at constant pressure decreases with rising temperature, a reversibility of the initial reaction is indicated. The dissociation of the end-product (or equilibrium product) in the autoxidation of the rosinate evidently proceeds progressively as the temperature is raised. There is an indication that this dissociation is never complete, and that a maximum dissociation is reached when one atomic equivalent of oxygen remains fixed by the rosinate (Fig. 4). The amount of oxygen absorbed in each case is thus an index of the stability (and the concentration) of the end-product at a given temperature, for a constant pressure. This reasoning was applied in an experiment, the results of which are recorded in Table III. If the end-product in the autoxidation of the rosinate at *a* given temperature and pressure was placed in an atmosphere

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[8] Dupont and Lévy, *Compt. rend.*, 189, 763 (1929).

of lower oxygen pressure, it slowly lost weight. If, however, the temperature was raised at the lower pressure, the loss in weight occurred quickly. In the experiment, in order to increase the effect, the temperature was raised about 30° and the partial pressure of the oxygen was decreased to zero (100% nitrogen). All the oxidized samples which were treated thus still liberated iodine from iodide although the reaction was much slower compared with the action of the rosinate on the iodide before this treatment. The gas evolved from the oxidized samples was passed over anhydrous copper sulfate and bubbled through barium hydroxide and palladous chloride solutions. There was no indication of the color or turbidity which water, carbon dioxide and carbon monoxide would have produced with these reagents. The gas evolved from two half-gram samples of the oxidized rosinate was passed through the heated, packed tube of a combustion furnace. The effluent gas was received in barium hydroxide solution. No turbidity was observed. The author thus feels justified in assuming that the gas evolved from the oxidized rosinate was pure oxygen. The rosinates again absorbed oxygen when exposed to the gas, but very slowly, an effect undoubtedly due to the change in surface produced by a slight sintering of the powder at the higher temperatures. It was believed before the experiment was tried that the relative amount of oxygen lost and the actual amount remaining fixed would be the same in each case. This would have proved decisively that a stable oxygen compound was formed during the autoxidation. The data obtained (Table III) were not in sufficiently good agreement to be interpreted as substantiating this belief. It is possible that such a compound was formed, but in an amount depending on the conditions of the particular experiment. Hence the amount of oxygen remaining fixed would vary. Another explanation of the apparent non-existence of a relationship among the values obtained for the amount of oxygen remaining fixed at zero oxygen pressure is the possibility of an immeasurably slow but positive dissociation of the more stable oxygen compounds formed during the autoxidation. In other words, these values would approach each other if the conditions were maintained for a sufficiently long time.

According to Dupont and Lévy the autoxidation of abietic acid is accomplished through the agency of an intermediate oxide HAbO, and a peroxide $HAbO \cdot O_2$, the final product being $HAbO_2$. Unfortunately, the action of this final product on an iodide solution was not investigated. If the autoxidation of lead rosinate proceeds by a similar mechanism, two moles of oxygen should be absorbed by one mole of lead abietate. Actually, this result was obtained in only one instance (Table 11), *i. e.*, under the most extreme conditions tried, and the product readily oxidized iodide. This would indicate that the end-product itself is capable of acting as an oxidizer, or that the product obtained under the most extreme conditions

(28°, 60 atm.) was still an equilibrium mixture of end-product and intermediate peroxides. The most obvious interpretation of the data obtained in this investigation would favor the latter conclusion.

The writer takes this opportunity to thank Professor H. S. Lukens for help and suggestions obtained from him during the course of this work. Thanks are also due Mr. J. G. Butz for helpful suggestions.

Summary

A study has been made of some of the factors which influence the composition of the precipitate formed by adding the solution of a lead salt to sodium rosinate solution.

An apparatus has been devised in which all the steps in the preparation of the rosinate may be carried out in an inert atmosphere.

A method for the analysis of the metal content of rosinates has been proposed.

The course, extent and reversibility of the autoxidation of lead rosinate has been studied, using a carefully prepared rosinate of known composition.

The results have been discussed from the viewpoint of the theory suggested by Dupont and Lévy for the autoxidation of abietic acid.

PHILADELPHIA, PENNSYLVANIA

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

COMPETITIVE HYDROGENATIONS. II

BY F. F. DIWOKY AND HOMER ADKINS

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Recently it was shown that there was no apparent relationship between the relative rates of the hydrogenation over platinum of pure compounds taken separately and their relative rates of hydrogenation in mixtures.[1] For example, *d*-α-pinene was much more rapidly hydrogenated than was cinnamic acid and yet in a mixture of pinene and cinnamic acid the latter was completely hydrogenated before the former took up any hydrogen. It was also ascertained that a reducible substance not undergoing hydrogenation may greatly accelerate the hydrogenation of another compound. For example, pure pinene, which was much more rapidly hydrogenated than was pure allyl alcohol, increased the rate of hydrogenation of allyl alcohol almost seven-fold without itself being hydrogenated to any considerable extent. The results given in this paper are concerned with an extension of this study to the use of nickel catalysts in the hydrogenation of mixtures of reducible compounds.

Originally it was intended to determine *(a)* the time required for hy-

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[1] Adkins, Diwoky and Broderick, THIS JOURNAL, 51,3418 (1929).

drogenation of certain representative compounds over a nickel catalyst; (*b*) the time required for the absorption of one-half the quantity of hydrogen necessary for the complete hydrogenation of the components of equimolecular mixtures of two compounds; (*c*) the distribution of hydrogen between the components of the mixture; (*d*) the time required for the absorption of all the hydrogen necessary for the complete hydrogenation of the components of the mixtures of compounds. However, the last of these objectives was reached in the case of only four mixtures (benzene with toluene, with diphenylamine and with phenol and of pyridine with phenol) because the hydrogenations could not be made complete under conditions which were comparable with those used for the pure compounds and the half hydrogenation of mixtures.

There are recorded in Table I the time required and the proportion of products in the hydrogenation of ten compounds and of thirty-two mixtures of these compounds with each other. The amount of each compound used in each experiment was 0.5 mole except for the mixtures containing acetanilide, for which the quantities were cut in half. A temperature of 175° was used for the hydrogenations involving aniline, acetanilide and diphenyl, and for the mixture of pyridine and toluene. A temperature of 132° was used for pure benzyl alcohol and 125° for the mixture of benzyl alcohol and benzene; while 150° was used for all the other hydrogenations. Two grams of catalyst was used for diphenylamine and the mixture of it with toluene. One gram of catalyst was used in all other experiments. The initial pressure (at 20°) in all experiments was 136 atmospheres: the hydrogenations took place at pressures from 125 to 200 atmospheres.

TABLE I

HYDROGENATION OF PURE COMPOUNDS AND MIXTURES

Hydrogen acceptors	% H_2	Time, min.	Product(s) and % yields
Benzene	100	0	Cyclohexane
Toluene	100	60	Methylcyclohexane
Ppidine	100	480	Piperidine
Phenol	100	120	Cyclohexanol
Aniline	69	1500	Cyclohexylamine (52); dicyclohexylamine (5)
Benzyl alcohol	100	230	Toluene (84); cyclohexylcarhinol (16)
Acetanilide	68	640	N-Acetylcyclohexylamine
Quinoline	100	0	Tetrahydroquinoline
Diphenylamine	100	960	Dicyclohexylamine
Acetone	100	26	Propanol-2
Benzene + toluene	100	34	Cyclohexane (56); methylcyclohexane (31)
Benzene + pyridine	94	510	Cyclohexane (0); piperidine (100)
Benzene + phenol	100	86	Cyclohexane (46); cyclohexanol (51)
Benzene + aniline	21	1010	Cyclohexane (0); cyclohexylamine (17)
Benzene + benzyl alcohol	70	250	Cyclohexane (9); toluene (65); cyclohexylcarhinol (35)

TABLE I *(Concluded)*

Hydrogen acceptors	% H_2	Time, min.	Product(s) and % yields
Benzene + acetanilide	100	360	Cyclohexane (71); N-acetylcyclohexylamine (20)
Benzene + quinoline	100	0	Cyclohexane (0); tetrahydroquinoline (100)
Benzene + diphenylamine	100	300	Cyclohexane (24); dicyclohexylamine (24); phenylcyclohexylamine (16)
Toluene + pyridine	100	420	Methylcyclohexane (0); piperidine (100)
Toluene + phenol	100	82	Methylcyclohexane (30); cyclohexanol (68)
Toluene + aniline	17	450	Methylcyclohexane (0); cyclohexylamine (11)
Toluene + acetanilide	91	480	Methylcyclohexane (38); N-acetylcyclohexyl amine (50)
Toluene + quinoline	100	0	Methylcyclohexane (0); tetrahydroquinolinr (100)
Toluene + diphenylamine	108	670	Methylcyclohexane (8); dicyclohexylaminc (46); phenylcyclohexylamine (8)
Pyridine + phenol	88	1600	Piperidine (92); cyclohexanol (8)
Pyridine + aniline	100	630	Piperidine (96); cyclohexylamine (0)
Pyridine + benzyl alcohol	98	1000	Piperidine (100)
Pyridine + acetanilide	107	550	Piperidine (100); N-acetylcyclohexylamine (5)
Pyridine + quinoline	114	1000	Piperidine (50); tetrahydroquinoline (67)
Pyridine + diphenylamine	95	1200	Piperidine (100)
Phenol + aniline	98	410	Cyclohexanol (24); dicyclohexylamine (33); cyclohexylamine (35)
Phenol + benzyl alcohol	106	280	Cyclohexanol (51); toluene (72); cyclohexylcarbinol (28)
Phenol + acetanilide	103	280	Cyclohexanol (87); N-acetylcyclohexylamine (8)
Phenol + quinoline	101	7	Cyclohexanol (0); tetrahydroquinoline (100)
Phenol + diphenylamine	101	220	Cyclohexanol (56); dicyclohexylamine (16); phenylcyclohexylamine (5)
Aniline + benzyl alcohol	94	1440	Cyclohexylamine (22); dicyclohexylamine (34); toluene (16); cyclohexylcarbinol (19)
Aniline + acetanilide	52	1200	Cyclohexylamine (45); N-acetylcyclohexylamine (0)
Aniline + quinoline	98	5	Cyclohexylamine (0); tetrahydroquinoline (100)
Aniline + diphenylamine	25	1000	Cyclohexylamine (24); dicyclohexylamine (3)
Benzyl alcohol + quinoline	103	0	Tetrahydroquinoline (100)
Benzyl alcohol + diphenylamine	62	170	Toluene (66); cyclohexylcarbinol (16); dicyclohexylamine (17)
Benzyl alcohol + acetanilide	100	60	Toluene (58); cyclohexylcarbinol (42); N-acetylcyclohexylamine (20)

In the case of the mixtures the reaction was allowed to proceed (when possible) until the amount of hydrogen absorbed was approximately equal to the amount of hydrogen required for the complete hydrogenation of one of the components. The bomb was then allowed to cool to room temperature and the amount of hydrogen actually absorbed determined. The amount of hydrogen actually absorbed is given in the second column of the table. One hundred per cent. hydrogen adsorption is that required for the complete hydrogenation of one of the two components of a mixture. In the case of mixtures this in general means 1.5 moles of hydrogen. For mixtures containing quinoline or acetanilide the amount is 1.0 and 0.75 mole of hydrogen, respectively. Benzyl alcohol presents a unique case since there are two reactions, one of which requires 3 moles and the other 1 mole of hydrogen for 1 mole of the alcohol. In the case of mixtures containing benzyl alcohol 100% absorption means 3 moles of hydrogen per mole of alcohol. The time (in minutes) given in column 3 of the table is that elapsing between the time at which the designated temperature was reached and the time at which the hydrogenation was stopped. The hydrogenation was stopped either because the desired amount of hydrogen had been taken up or because the catalyst had become inactive. A zero in this column means that hydrogenation was complete at the time that the designated temperature was reached. Eighty minutes were required to heat the bomb from 20 to 150° and fifteen minutes from 150 to 175°. There are given in column 4 of the table the name and yield of the various products of hydrogenation.

The rate of hydrogenation of phenol and quinoline at 2 to 3 atmospheres' pressure was determined for the sake of comparison with those at 125 to 200 atmospheres. Two grams of catalyst with 0.2 mole of each compound was used at 135°. Phenol was completely reduced in about two hundred and fifty minutes while quinoline was completely converted into tetrahydroquinoline in two hundred minutes

If the nine compounds which were hydrogenated are listed in the order of decreasing rate of hydrogenation, the order is (1) quinoline, (2) benzene, (3) toluene, (4) phenol, (5) benzyl alcohol, (6) pyridine, (7) diphenylamine, (8) acetanilide and (9) aniline. (This order is not independent of the pressure of hydrogen at which reaction occurs because phenol for example reduces readily at 2 or 3 atmospheres while some of the other compounds are not hydrogenated at all over the nickel catalyst at the lower pressures.) The relative rates of hydrogenation of these compounds in a mixture are in many cases very different from that which would be expected from the relative rates of hydrogenation of the single compounds. If the compounds are listed in the order of preferential hydrogenation in mixtures the sequence is (and using the numbers assigned to each compound above) (1) quinoline, (6) pyridine, (9) aniline, (5) benzyl alcohol, (4) phenol, (7) diphenylamine, (2) benzene, (8) acetanilide, (3) toluene. That is, if a mixture of any two compounds in the above list is partially hydrogenated under the experimental conditions used in this investigation, the compound which is higher in the list just given will receive the greater proportion of the hydrogen.

In the case of mixtures of some compounds having the same functional groups, the relative rates of hydrogenation of the components of a mixture are qualitatively what would be expected from a knowledge of the rates of hydrogenation of the single compounds. This is true for the mixture of benzene and toluene and for the one of quinoline and pyridine. The increased proportion of cyclohexanol from phenol in toluene as compared with the results in benzene is in agreement with the relative rates of hydrogenation of toluene and benzene. However, the relative rates of hydrogenation of benzene and phenol in a mixture are not at all what would be anticipated from a knowledge of the rates of hydrogenation of the compounds taken singly.

It appears that a compound such as aniline which is very slowly and never completely hydrogenated and which shows every sign of poisoning the catalyst for its own hydrogenation, may yet be almost without effect upon the hydrogenation of another compound. Quinoline for example hydrogenated practically as rapidly in the presence as in the absence of aniline. In a similar way aniline was almost without effect upon the hydrogenation of pyridine. In contrast with this is the effect of aniline, quinoline or pyridine in inhibiting completely the hydrogenation of the easily reduced benzene or toluene.

The time for the hydrogenation of a mixture of quinoline and pyridine was more than twice the sum of the times for the hydrogenation of the components, that is to say, each compound was inhibiting the hydrogenation of the other.

The hydrogenation of diphenylamine over nickel was accelerated by benzene and toluene although not so markedly as was the hydrogenation of allyl alcohol by pinene over platinum. The hydrogenation of aniline was also accelerated by the presence of phenol. Phenol and benzene in these experiments were also hydrogenated to the extent of 24% but toluene was almost completely resistant to hydrogenation just as was pinene in the mixture with allyl alcohol.

Benzyl alcohol is hydrogenated to both toluene and cyclohexylcarbinol, so that with this compound there is a competitive hydrogenation even with a single compound. For the catalyst and conditions used in this investigation for the hydrogenation of benzyl alcohol the ratio of the products was about 5 moles of toluene to 1 of the cyclohexylcarbinol. The ratio of alcohol to toluene was increased by the presence of phenol and diphenylamine and especially by benzene and acetanilide, which were themselves only reduced to the extent of 10 to 20%. This is all the more remarkable since at the temperature used for the hydrogenation of the mixtures (175°) pure benzyl alcohol is quantitatively reduced to toluene.

It is generally accepted that the combination of the catalyst and at least one if not both of the reactants is an essential step in such reactions as are here under consideration. Preferential adsorption would thus serve to account for many of the discrepancies in rate between the hydrogenation of single compounds alone and in mixture with other compounds. Upon this basis pyridine is preferentially hydrogenated in a mixture with the more easily hydrogenated benzene because it is adsorbed almost to the exclusion of benzene. It is noteworthy that the order of compounds quinoline, pyridine, aniline, benzyl alcohol, phenol, diphenylamine, benzene, acetanilide, toluene, which is the order of preferential hydrogenation in mixtures, is one which in general might reasonably be expected to hold for a tendency to form addition compounds.

Experimental Part

The apparatus and the general method of procedure were the same as those previously described.[2] The compounds submitted to hydrogenation were of the best grade sold by the Eastman Kodak Company and the Mallinckrodt Chemical Company and were in general not submitted to any purification other than a careful fractionation. The benzene and toluene were thiophene free. The catalysts were made as previously described. The values given for the hydrogen absorption are accurate to within plus or minus 4%. The accuracy of the values for the ratio of products varies a good deal in different analyses and in extreme cases may be as much as ±7%.

Analysis of Reaction Products.—The products of reaction were separated whenever possible by fractionations through a Widmer column at a suitable pressure. Whenever fractionation did not give a satisfactory separation of the components of a reaction mixture, advantage was taken of chemical as well as of physical differences between the components. The separation of cyclohexane from benzene, and methylcyclohexane from toluene was made with sulfuric acid containing 30% of sulfur trioxide. The separation of aniline, pyridine and piperidine from hydrocarbons was made by extracting a weighed portion of the product with a slight excess of hydrochloric acid, the extract made alkaline with solid sodium hydroxide, saturated with salt, extracted twice with 100 ml. of ether and the ethereal extract dried and fractionated. The absence of pyridine (except in one experiment) was shown by the test of Fiilnegg and Riesenfeld.[3] Piperidine was identified by its benzene sulfone piperidine, m. p. 92–93°. When necessary pyridine and piperidine were separated as by Arndt and Nachway.[4] The products from the hydrogenation of phenol and aniline were separated as follows. A weighed sample was put into solution with ether, treated with an excess over the calculated amount of dilute sodium hydroxide solution to remove phenol, the ether

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[2] Adkins and Cramer, THIS JOURNAL, 52, 4349 (1930).

[3] Fiilnegg and Riesenfeld, *Monatsh.*, 47, 185 (1926).

[4] Arndt and Nachway, *Ber.*, 59B, 448 (1926).

layer separated, dried over solid potassium hydroxide, separated again from the watery layer, the ether distilled off, product weighed and phenol calculated by loss in weight. This product consisted of cyclohexanol, cyclohexylamine, aniline and dicyclohexylamine. This weighed sample was extracted with dilute hydrochloric acid, extracted with two 75-ml. portions of ether and the layers separated. By the usual method cyclohexanol was obtained from the ether extract, the amines recovered from the hydrochloric acid extract and separated by fractional distillation. Cyclohexanol was separated from phenol by extracting a weighed amount with dilute sodium hydroxide, washing and drying the insoluble portion prior to distillation. Phenol was determined by difference. Mixtures of acetanilide and N-acetylcyclohexylamine were hydrolyzed as by Davis[5] and the amines separated by fractional distillation. Phenylcyclohexylamine and dicyclohexylamine were separated as by Fouque.[6] The former had a boiling point of 160–164° (22 mm.) and its picrate had a melting point of 163–164°.

Summary

The rates of hydrogenation of quinoline, benzene, toluene, phenol, benzyl alcohol, pyridine, diphenylamine, acetanilide and aniline have been determined over a nickel catalyst at 125–175° and under pressures of hydrogen from 125–200 atmospheres. The compounds have been listed in the order of decreasing rate of hydrogenation. Thirty-two mixtures of these compounds, each mixture containing two components, were subjected to the action of hydrogen over a nickel catalyst and the mixture allowed to take up as much hydrogen as would have been sufficient to completely hydrogenate one of the components of the mixture. The rate of absorption of the hydrogen and its distribution between the components of the mixture were determined by analysis of the reaction mixture. It was found that if the compounds were listed in the series, quinoline, pyridine, aniline, benzyl alcohol, phenol, diphenylamine, benzene, acetanilide and aniline, in any mixture containing two of them, the one higher in the series would receive the greater proportions of the hydrogen. Pyridine and quinoline in mixtures with other compounds took all, or practically all of the hydrogen. Apparently there is no relationship between the relative rates of hydrogenation of these compounds singly and in mixtures. The relative rates of hydrogenation of the components of a mixture are at least in part presumably dependent upon selective adsorption by the catalyst through two possible acceptors of hydrogen.

The hydrogenation of diphenylamine was accelerated by toluene and benzene, and the hydrogenation of aniline by the presence of phenol in the reaction mixture.

[5] Davis, *J. Chem. Soc.*, 95, 1397 (1909).

[6] Fouque, *Ann. chim.*, **15**, 291–32 (1921).

The ratio of cyclohexylcarbinol to toluene produced in the hydrogenation of benzyl alcohol, was increased by the presence of phenol or diphenylamine and especially of benzene or acetanilide in the reaction mixture.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SHARP & DOHME, INC.]

AMINO ALCOHOLS. VI. THE PREPARATION AND PHARMACODYNAMIC ACTIVITY OF FOUR ISOMERIC PHENYLPROPYLAMINES

BY WALTER H. HARTUNG AND JAMES C. MUNCH

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The commoner hypertensive amines are derivatives of β-phenylethylamine, that is, compounds containing the aromatic nucleus separated from the amino group by two carbons of an aliphatic side chain; e. g., tyramine $HOC_6H_4CH_2CH_2NH_2$, epinephrine, $(HO)_2C_6H_3CHOHCH_2NHCH_3$, and ephedrine, $C_6H_5CHOHCH(NHCH_3)CH_3$, all have this common structure.

Recorded pharmacological studies with compounds in which the relative position of these two functional groups is modified are rare.

Barger and Dale,[1] in their classical study on the relationship between chemical structure and sympathomimetic action, included a series of compounds in which the relative position of the amino portion with respect to the phenyl group varied. They found that aniline has no specific action; benzylamine gives a trace of the desired activity, a-phenylethylamine is feebly active, β-phenylethylamine highly active and most active of the series, while y-phenylpropylamine, $C_6H_5CH_2CH_2CH_2NH_2$, is again much less effective. While no allowance was made for any influence on the physiological activity that might be produced by the successive lengthening of the side chain, they nevertheless advanced the conclusion that "the optimum constitution of a fatty–aromatic amine for the production of sympathomimetic action is, therefore, that which is found in adrenaline itself, *viz.*, a benzene ring with a side chain of two carbon atoms, of which the second bears the amino group."

Concerning the value of the two-carbon side chain these conclusions must, in the light of recent findings, be amended, for it has been amply demonstrated that amino alcohols of the ephedrine type, that is, compounds with three carbons in the side chain, are not only very active pharmacologically but may even possess physiological and therapeutic virtues not resident in the corresponding compounds with but two carbons.[2]

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[1] Barger and Dale, J. *Physiol.*, 41, 19 (1910). Cf. Pyman, J. *Chem. Soc.*, 111, 1103 (1917).

(a) Chen, Wu and Henriksen, *J. Pharmacol.*, 36, 363 (1929); (b) Hartung and Munch, THIS JOURNAL, 51, 2262 (1929); (c) Hartung, Munch, Deckert and Crossley, *ibid.*, 52, 3317 (1930); (d) Piness, Miller and Alles, J. *Am. Med. Assn.*, 94, 790 (1930).

Aside from this work of Barger and Dale, comparatively little has been done to substantiate the other part of their conclusion, namely, the necessity for having the aryl and amino groups on adjacent carbons of an aliphatic side chain. Baehr and Pick[3] observed that if in hordenine, p-$HOC_6H_4CH_2CH_2N(CH_3)_2$, the dimethylamino group is removed from the aromatic portion by three or four carbons,[4] the pressor potency becomes correspondingly less. Hasama, in comparing the isomeric phenylethanolamines, $C_6H_5CH(NH_2)CH_2OH$ and $C_6H_5CHOHCH_2NH_2$, found the former to have no influence on the blood pressure,[5] whereas the activity of the latter is well established.

Matsuo and Mizuno[6] report that α-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, increased the contraction amplitude of the frog heart and the blood pressure of a rabbit, while the β-compound, $C_6H_5CH_2CH_2NH_2$, showed the opposite effect.

The present investigation was undertaken to determine, if possible, whether in the series of amino alcohols being studied in these Laboratories maximum activity is obtained when the aryl and amino groups are separated by two aliphatic carbon atoms. And in order to confine as nearly as possible any modification in physiological behavior to a corresponding change in the relative positions of these two functional groups, four isomeric phenylpropylamines were prepared and their behavior observed. These four compounds are given in Table I along with a summary of their pharmacological and toxicological behavior. β-Phenylethylamine and phenylpropanolamine are included for comparison.

TABLE I

DATA ON COMPOUNDS

	Base	M. L. D. of hydrochloride, mg./kg. Rats, subcutaneous	M. L. D. of hydrochloride, mg./kg. Rabbits, intravenous	Pressor activity of hydrochloride (Intravenous to dogs)
I	$C_6H_5CH_2CH_2NH_2$	..	60	1 Mg./kg. gave good rise that persisted about 20 min.
II	$C_6H_5CH(NH_2)CH_2CH_3$	1000	50	1 Mg./kg., very slight rise
III	$C_6H_5CH_2CH(NH_2)CH_3$	25	25	1 Mg./kg. gave rise equal to that of I. Effect persisted longer. Orally active[Zd]
IV	$C_6H_5CH_2CH_2CH_2NH_2$	100	50	1 Mg./kg. gave medium transitory rise
V	$C_6H_5CH(CH_3)CH_2NH_2$	500	50	Good pressor; also active after oral administration.
VI	$C_6H_5CHOHCH(NH_2)CH_3$	.	75–90	Equals ephedrine

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[3] Baehr and Pick, *Arch. exptl. Path. Pharmakol.*, *80*, 161 (1912).

[4] V. Braun, *Ber.*, 47,492 (1914).

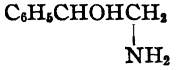
[5] Hasarna, *Arch. exptl. Path. Pharmakol.*, 153, 165 (1930).

[6] Matsuo and Mizuno, *Acta Schol. Med. Univ. Imp. Kioto*, [1] 7, 11 (1924); *Chem. Abst.*, 19,2705 (1925).

The data on comparative pressor potencies are not yet satisfactorily quantitative, but the information thus far obtained is very illuminating. For instance, it is readily seen that Barger and Dale are substantially correct in ascribing the optimum constitution for producing a rise in blood pressure to compounds containing at least a β-phenylethylamine skeleton. If any deviation is made from this elementary structure either by moving the amino closer to the phenyl (II) or by removing it farther away (IV), the degree of physiological response is very greatly diminished. But if this minimum skeleton is left unchanged (III, V and VI), substitutions in the other portions of the molecule may modify the nature of the pharmacodynamic behavior, but the ability to produce a rise in blood pressure is not diminished.

Chen, Wu and Henriksen[2a] attribute the oral efficacy of ephedrine to the presence of the third carbon in the side chain; thus, for instance, phenylpropanolamine (VI) is active when taken by mouth whereas phenylethanolamine, $C_6H_5CHOHCH_2NH_2$, is not.

Piness, Miller and Alles,[2d] who are interested clinically in phenylethanolamine, were desirous of determining what it lacked structurally to make it active when administered orally. Since phenylethanolamine differs from ephedrine by two methyl groups, one in the side chain and the other on the amino group, they investigated two methyl substituted derivatives of β-phenylethylamine, one in which the methyl was substituted on the nitrogen and the other in the side chain. They found the former ineffective when given by mouth and the latter, with three carbons in the side chain, very active when so administered. Hence, they also conclude that it is the three-carbon side chain that makes for oral activity.

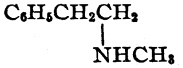


$$C_6H_5CHOH\underset{\substack{|\\ NH_2}}{CH_2}$$

Phenylethanolamine

$$C_6H_5CHOH\underset{\substack{|\\ NHCH_3}}{CH}CH_3$$

Ephedrine



$$C_6H_5CH_2\underset{\substack{|\\ NHCH_3}}{CH_2}$$

$$C_6H_5CH_2\underset{\substack{|\\ NH_2}}{CH}CH_3$$

Our results show that in extending the side chain of β-phenylethylamine, the entering methyl may be substituted on either of the two aliphatic carbons and in either case (III and V) oral activity is conferred. While quantitative values for pressor activity of these two isomers have not yet been determined, the wide differences in toxicity are very well defined and very striking indeed.

Phenylpropanolamine (VI) is included in the table in order to emphasize the importance of the alcoholic hydroxyl. Its elimination, which gives III, increases the intravenous toxicity to rabbits by 300% or more, a very significant extent.

Procedure

All the amines were prepared by the catalytic hydrogenation of an appropriate intermediate by the process already described.[7]

Experimental

Phenyl-1-amino-1-propane.—Propiophenone oxime[8] was dissolved in absolute alcohol containing three equivalents of hydrogen chloride and smoothly reduced to the corresponding amine, isolated as the hydrochloride The salt melted at 189.5° (corr.) and the base distilled at 100–105° at 35 mm.; a benzoyl derivative melted at 115–116° (corr.).[9]

Phenyl-I-amino-2-propane was obtained by reducing phenyl-1-chloro-1-amino-2-propane. Sixteen grams of phenylpropanolamine was heated in a bomb tube with 130 ml. of concentrated hydrochloric acid at 110–115° for four hours. No pressure developed. The solution was then chilled in an ice–salt bath and the hydrochloride of phenyl-1-chloro-1-amino-2-propane which settled out was filtered off, dried and recrystallized from absolute alcohol. The crystals melted at 201° (corr.); 8.5 g., a yield of 48%. Calcd. for $C_9H_{12}NClHCl$: Cl, 34.4. Found: Cl, 33.3. The organic chlorine seems to be very labile and further recrystallization gives a product with even less chlorine.

By shaking the chloro compound, dissolved in absolute alcohol, with palladium catalyst in an atmosphere of hydrogen, the chlorine was completely replaced by hydrogen; the resulting amine was isolated as hydrochloride, the salt melting at 144–147° and the base distilling at 200-201° (uncorr.).[10]

Phenyl-1-amino-3-propane.—An impure cinnamaldoxime[11] was reduced in an absolute alcoholic solution containing three equivalents of hydrogen chloride. Reduction ceased when 90% of the hydrogen calculated as required by the pure oxime had been taken up. The catalyst was removed and the filtrate evaporated to dryness on a steam-bath; the residue was taken up in water and an insoluble dark oily impurity removed by extraction with ether. The aqueous solution was treated with excess alkali, the liberated base extracted with ether, dried over sodium sulfate and distilled, boiling at 216–220° (uncorr.). For $C_6H_5CH_2CH_2CH_2NH_2$ the following boiling points are recorded 215°[12] 215–216°,[13] 221.5°.[14] The hydrochloride was precipitated from an ethereal solution of the base by addition of an absolute alcoholic solution of hydrogen chloride. The salt melted at 218" (corr.) From 11.6 g. of cinnamaldoxime 8.1 g. of the salt was obtained, a yield of 60%.

Phenyl-2-amino-1-propane was obtained from a-phenylpropionitrile. This intermediate nitrile was prepared from the sodium derivative of phenylacetonitrile and methyl iodide according to the directions of Victor Meyer[15] and Freund and König[16]

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[7] Hartung, THIS JOURNAL, 50, 3370 (1928).

[8] "Beilstein," 4th ed., Vol. VII, p. 301.

[9] Busch and Leefhelm, J. *prakt. Chem.*, [2] 77, 7 (1908), describe $C_6H_5CH(C_2H_5)$-NH_2·HCl as melting at 194°, the free base as distilling at 99-100" at 16 mm., and the benzoyl derivative as melting at 115–116°.

[10] Hey, J. *Chem. Soc.*, 18 (1930).

[11] Ref. 8, p. 351.

[12] Lasch, *Monatsh.*, 34, 1658 (1913).

[13] Tafel, Ber., 19, 1924 (1886).

[14] Tafel, *ibid.*, 22, 1854 (1889).

[15] Meyer, Ann., 250, 118 (1889).

[16] Freund and Konig, Ber., 26, 2874 (1893).

However, the good yields they report, as high as 79%, have not been duplicated; our yields were 10–14%

The reduction of α-phenylpropionitrile dissolved in absolute alcohol containing three equivalents of hydrogen chloride proceeded smoothly and completely, although about a third as rapidly as for the oximes, and the product was isolated as its hydrochloride salt, melting at 123–124° (corr.). Freund and König, by reducing the nitrile with sodium and absolute alcohol, obtained the base $C_6H_5CH(CH_3)CH_2NH_2$, whose hydrochloride melted at 124°.

Summary

Four isomeric phenylpropylamines were prepared by catalytic hydrogenation of an appropriate intermediate. A preliminary pharmacological examination of these compounds indicates that:

(1) The optimum skeleton for pressor compounds is β-phenylethylamine.

(2) A shift in the relative positions of the phenyl and amino groups very greatly decreases pressor potency.

(3) Substitution of a methyl on either of the two carbons in the side chain of this skeleton confers oral activity.

(4) The presence of the secondary alcoholic hydroxyl in phenylpropanolamine serves to decrease the toxicity to a degree that becomes significant therapeutically.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE PREPARATION OF ALIPHATIC AMIDES

BY JAMES A. MITCHELL AND E. EMMET REID

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The most satisfactory methods of preparing amides have involved dehydration of the ammonium salt of the corresponding acid. Hofmann[1] prepared various amides by heating ammonium salts of aliphatic acids for five or six hours at 230° under pressure. Kundig[2] prepared acetamide by the rapid distillation of ammonium acetate and by heating an alcoholic solution of acetic acid and ammonia in a sealed tube for a long time at 100°. He also obtained a yield of amide greater than 25% by passing dry ammonia through acetic acid and then heating to boiling. Grant and James[3] have prepared amides by saturating the acid with dry ammonia and boiling. Dunlap,[4] Keller[5] and Verley[6] have modified the procedure by heating sodium acetate and ammonium chloride at 240°.

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[1] Hofmann, Ber., 15, 977 (1882).

[2] Kundig, *Ann.*, 105, 277 (1858).

[3] Grant and James, THIS JOURNAL, 39,933 (1917).

[4] Dunlap, *ibid.*, 24, 762 (1902).

[5] Keller, *J. prakt. Chem.*, [2] 31, 364 (1885).

[6] Verley, *Bull. soc. chim.*, [3] 9, 691 (1893).

Acetamide is best prepared according to Coleman and Alvarado[7] by heating a mixture of ammonium acetate and acetic acid under a reflux condenser in such a manner that the excess acetic acid and the water formed in the reaction are slowly distilled off.[8] Noyes and Goebel have also shown that acetic acid catalyzes the reaction.

This method is very satisfactory for preparing acetamide, but is not economical for the higher aliphatic acids on account of the cost of the large excess of acid required. This suggested using an excess of the other reactant, ammonia, which is cheap.

Instances in which dimethyl amides were prepared in a similar manner are rare. Franchimont and Klobbie[9] prepared dimethyl heptoamide by heating the acid with dimethylamine at 230° in a sealed tube. Verley[6] prepared dimethyl formamide and acetamide by distilling a mixture of an alkali salt of the acid and dimethylamine hydrochloride.

Results

We have found that by passing ammonia gas through aliphatic acids kept at a suitable temperature in such a way that the water formed is continually removed, the equilibrium point of the reaction may be displaced far to the amide side and very high yields of amides obtained. The results with the aliphatic amides are indicated in Table I.

The temperature at which the acid is heated is sufficient to dehydrate a small proportion of the higher amides to form the nitriles. This reaction becomes appreciable with butyric and the higher amides.

The reaction velocity is appreciably slower with the higher acids. Heptoic acid reacts much more slowly than caproic and caprylic more slowly than heptoic. Lauric acid was heated at 185° for sixteen hours. Only a small fraction was converted to the amide. No amide was obtained from palmitic or stearic acid upon heating either at 125 or 190° for considerable intervals of time. The ammonium salts of these acids are probably unstable under the conditions of the experiments.

Similar experiments were performed in which anhydrous zinc chloride was added to acetic, propionic and caproic acids. No difference in rate of formation of the amide was observed when compared with parallel experiments with no zinc chloride.

Zinc chloride is a catalyst, however, for dehydration of the amide to the nitrile. At a temperature higher than that used in the preparation of the amide *a* considerable proportion of caproic acid is converted to the nitrile.

Although small amounts of nitrile are formed in distilling acetamide and

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[7] Coleman and Alvarado, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. 3, p. 2.

[8] Rosanoff, Gulick and Larkin, THIS JOURNAL, 33,974 (1911); Hitch and Gilbert, *ibid.*, 35,1780 (1913); Noyes and Goebel, *ibid.*, 44,2286 (1922).

[9] Franchimont and Klobbie, *Rec. trav. chim.*, 4 247 (1887).

TABLE I

ALIPHATIC AMIDES

Acid	Acid g.	Temp. of reflux cond., °C.	Temp. of acid, °C.	Time of heating, hrs	B. P. of product, °C	Yield of amide, %	M. p. of purified amide, °C
Acetic	**50**	80	170	6	210–20	77	81 5
Acetic	50	80	170 190	5 3		96	
Acetic	50	80	190	8		96	
Propionic	49	80	185	5.5	200–20	93	81.3
Propionic	50	80	190	5		95	
Butyric[a]	48	85	185	7	130–45 (22 mm.)	84	114.8
Butyric[a]	48	85	185	7		88	
Butyric[b]	48	85	180	7		85	115.0
Valeric	47	90	190	6	100–30 (6 mm.)	64	105.8
Valeric	47	90	180	15		82	
Caproic[c]	47	90	160	7	135–50 (10 mm.)	75	101.5
Caproic[c]	47	90	160	7		75	
Caproic[d]	47	90	180	7		75	101.0
Heptoic	46	90	160 190	7 4	130–50 (7 mm.)	75	96.5
Heptoic	46	90	125 180	3 8		75	
Caprylic	50	90	180	11	135–55 (4 mm.)	80	106.0

[a] Eastman. [b] Prepared by the oxidation of *n*-butyl alcohol. [c] Kindness of Sharp and Dohme. [d] Prepared by the malonic ester synthesis.

propionamide, they are satisfactorily purified by distillation at atmospheric pressure. It is better to fractionate the higher amides at reduced pressures.

Acetamide is best recrystallized from methyl alcohol and ether according to the method outlined by Wagner.[10] The amides become increasingly solu-

TABLE II

DIMETHYL AMIDES

Acid	Acid, g	Temp. of reflux cond., °C.	Temp. of acid, °C.	Time of heating, hrs.	B. p. of product, °C.	Yield of amide, %
Formic	110 (95%)	60	95	3	130–65	73
Formic	120 (85%)	60	120	3.5		50
Acetic	50	80	170	2.5	165–75	76
Acetic	30	80	150	3		84
Propionic	50	80	155	2.5	165–78	76
Propionic	50	80	155	3		78
Butyric	100	85	155	2.5	180–94	84
Valeric	100	85	165	3	205–15	87
Caproic	50	85	155	3	220–30	88
Caproic	50	85	155	3.5		88
Heptoic	92	85	160	3.5	165–75 (95 mm.)	81

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[10] Wagner, *J. Chem. Ed.*, 7, 1135 (1930). Wagner obtained a melting point as high as 83° for acetamide. We obtained a melting point of only 81 5° after a very rigid purification.

ble in ether as the molecular weight increases. This furnishes a satisfactory recrystallization medium for all but acetamide. The amides are more effectively recrystallized from hot benzene. The crystals, however, tenaciously absorb the solvent and it is advisable to centrifuge.

Dimethyl amides were prepared in the same manner, the ammonia being replaced by dimethylamine. The results are given in Table II. The dimethyl amides obtained were all liquids at ordinary temperatures and were purified by distillation.

Experimental

The apparatus employed consisted of a flask with a jacketed reflux condenser. The condenser was connected top and bottom with a side tube of the same length, which upon being filled with water could be kept at any desired temperature up to 90° by means of a Bunsen burner placed at the lower end of the side-tube. The flask containing the acid was heated to any desired temperature by an oil-bath. Temperatures were read from a thermometer which was placed inside the flask and extended into the condenser. The ammonia delivery tube entered at the top of the condenser and extended to the bottom of the flask.

For the preparation of the amides a stream of ammonia, taken directly from a cylinder, was passed through the delivery tube and bubbled through the acid the entire duration of the experiment. The water formed in the reaction was swept out through a tube just at the top of the condenser jacket into a bulb.

Samples of amides were carefully purified. After the preliminary vacuum distillation the amides were further purified by crystallization from pure benzene and absolute ether, frequently centrifuging and drying over sulfuric acid in a vacuum desiccator until accurate melting points were obtained, checking for several recrystallizations. The melting points were taken with a calibrated Anschiitz thermometer. Every precaution was taken to prevent overheating of the melting point bath and its temperature was kept uniform by efficient stirring. Melting points quoted in Table I are the corrected ones.

Acetamide was purified by recrystallizing four times from methyl alcohol and ether, centrifuging twice. Propionamide was crystallized once from methyl alcohol and ether, followed by centrifuging, and then recrystallized twice from ether. Butyramide" was crystallized from benzene, centrifuged and recrystallized three times from ether, followed by centrifuging. Butyramide[b] was crystallized three times from ether, and centrifuged. Valeramide was crystallized three times from ether and centrifuged. Caproamide[c] was crystallized three times from ether and centrifuged twice. Caproamide,[d] heptoamide and caprylamide were crystallized from benzene, centrifuged, and recrystallized twice from ether.

For the preparation of the dimethyl amides, the apparatus was attached to a water pump at the exit side and a current of air mixed with dimethylamine, prepared by dropping an aqueous solution of the amine[11] on solid potassium carbonate, was drawn through the acid during the course of the experiment. The gas was dried by passing it over solid potassium hydroxide. Certain experiments indicated, however, that drying was not essential. The reaction proceeds much faster with dimethylamine than with ammonia.

A study of the physical properties of dimethyl amides, together with methods of preparation and purification, is being continued in this Laboratory by other workers.

Summary

A satisfactory and economical method has been described for the preparation of amides and dimethyl arnides from the normal acids of the aliphatic series up to caprylic.

Accurate melting points of the amides from acetic to caprylic have been determined.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

THE POLARIMETRIC REDUCING SUGAR RELATIONSHIPS OF STARCH HYDROLYTIC PRODUCTS RESULTING FROM DIASTATIC ACTION

BY D. T. ENGLIS, G. T. PFEIFER AND J. L. GABBY

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The relationship between the specific rotation and copper reducing values of starch hydrolytic products as formed under the influence of diastatic action has been the subject of considerable study. In the early work of Brown and Heron[1] a close relationship was not observed but later work by Brown and associates[2] showed that the hydrolytic products first formed were in a condition of lower optical value and if equilibrium condition of the mutarotating mixture was reached, the rotation assumed the calculated value. Rolfe and Defren[3] claim the same close relationship when the hydrolysis of starch is brought about by acids. Using amylodextrin as the substrate in place of starch, Ford and Guthrie[4] have applied the principle to the estimation of the diastatic power of malt. By determining the change in rotation and multiplying by an appropriate factor

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[11] Kindly furnished by the du Pont Co.

[1] Brown and Heron, J. Chem. *Soc.*, **35**, 596 (1879).

[2] Brown, Morris and Millar, *ibid.*, **71**, 115 (1897).

[3] Rolfe and Defren, THIS JOURNAL, 18, 869 (1896).

[4] Ford and Guthrie, J. *Inst. Brewing*, 11, 206 (1905).

they arrive at a Lintner value for the preparation. More recently Gore[5] has employed a very similar procedure with Lintner's soluble starch as the substrate and proposes the method for the quantitative determination of diastatic activity of flour and various other products. In view of the probable complexity and the differences in character of the diastases which are obtained from different sources, as well as the changes in characteristics of the enzyme prepared by different methods of treatment of the same source materials, it is remarkable that the relationship between opticity and reducing power has been as close as it apparently has been. It may be due to the fact that most of the work in this connection has been done with malt diastase. While many investigators have assumed that the enzyme, maltase, is generally absent from malt preparations, the work of Daish[6] has shown that it is of wide occurrence in plant materials. That its presence is very significant has been emphasized by Davis.[7] It is with the consideration of the presence of a glucose-forming enzyme and its effect upon the polarimetric method for the determination of diastase activity that this paper is primarily concerned.

The hydrolysis of starch is usually represented as going through the following steps

Starch → dextrins → maltose → glucose

Since the reducing value and optical value of the products between starch and maltose are still matters of much uncertainty, these may be omitted from consideration for the moment and attention directed to the theoretical changes in the polarization and reducing values of the other products. The weight relations are as follows

1 g. of starch → 1.05 g. of maltose (or 1.10 g. of maltose hydrate) → 1.1 g. of glucose

If the specific rotations of the above substances are 199, 138 and 52.5, respectively, then the rotation for 1 g. of soluble starch and its hydrolytic products maltose and glucose if present in 100 cc. and polarized in a 4-dm. tube, Ventzke scale, would be

Starch		Maltose		Glucose
22.9°	→	16.8°	→	6.66°

and the drop in rotation assuming complete conversion to maltose or glucose would be 6.1 or 16.24° Ventzke, respectively. The reducing changes for 1 g. of starch expressed as apparent maltose hydrate would be

Starch		Maltose hydrate		Glucose
0	→	1.10	→	$\frac{1.10}{0.61\text{[8]}} = 1.8$

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[5] Gore, J. *Assoc. Official Agr. Chem.*, 364 (1923).

[6] Daish, *Biochem. J.*, 10, 49 (1916).

[7] Davis, *ibid.*, 10, 30 (1916).

[8] Average value of the reducing ratio of maltose to glucose from Munson–Walker table.

Hence if 1 g. of starch was completely converted to maltose the Polarization–Reduction ratio (P/R), expressed as Ventzke° 4-dm. tube/Apparent maltose hydrate would be 6.1/1.1 or 5.54 and if converted to glucose would be 16.24/1.8 or 9.04.

A calculation of this ratio from the data of Gore gives the following results

Interval of sample removal	1/2	1	1 1/2	2	2 1/2	3
Ratio for 1/2 hr. interval	5.58	6.00	4.73	6.44	...	4.62
Ratio for total interval	5.58	5.66	5.37	5.71	...	5.65

It is of interest that these values are reasonably close to 5.54, the theoretical value to be obtained assuming complete conversion to maltose.

The object of the experimental work was to determine the polarization–reduction ratio for different amylases and make certain of the general applicability of the method. It was believed that the study might also throw some light on the mechanism of the hydrolysis of starch.

Taka diastase is known to be capable of forming a large proportion of glucose from starch and methods have been devised for the estimation of starch,[9,10,11] assuming formation of maltose and glucose. On account of its glucose forming ability it was chosen as a representative amylase of somewhat different character than that of malt.

Experimental

The method of procedure followed was essentially that outlined by Gore[5] in all instances where the diastase was added in the form of a solution or an extract. In two instances where the diastase yielding material was added in the form of a flour the method of Rumsey[12] was followed. For this method several flasks containing identical quantities of reacting materials were prepared; then after different digestion periods flasks were removed, the solutions clarified and prepared for analysis for apparent maltose. In an article supplementary to one previously cited, Gore[13] recommends buffering the starch substrate so that the PH is 4.5–5.5. Using as he suggested the equivalent of 10 cc. of both normal acetic acid and sodium acetate per liter of substrate, a PH value of 4.6 was found. The reaction mixture was buffered in this way in most of the experiments.

Some of the digestion operations were made at room temperature, which was near to 21° at the time. In others the starch solution was brought to a slightly higher temperature, 25 or 39° before the diastase was added. It was then kept at the definite temperature in a thermostat throughout the reaction period. Duplicate determinations of the amount of copper reduced were made by the Munson and Walker method for each interval in all digestion operations and the average values taken. The polarimetric values were the average of six or more readings taken after mutarotation had reached equilibrium.

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[9] Davis and Daish, *J. Agr. Sci.*, 5, 454 (1912–1913).

[10] Horton, *ibid.*, 6, 152 (1914).

[11] Thomas, THIS JOURNAL. 46, 1670 (1924).

[12] Rumsey, Morrow's "Biochemical Laboratory Methods," John Wiey and Sons, 1927, p. 287.

[13] Gore, THIS JOURNAL, 47, 281 (1925).

As substrate material, Lintner's soluble starch supplied by Merck was used in the majority of the experiments. In a few of the later ones a special type of starch prepared as described recently by Gore[14] was employed. However, the concentration was still maintained near 2% instead of 4% as he suggests.

The materials which served as sources of the enzymes were different samples of Taka diastase from Parke, Davis and Company, several commercial malt diastase samples, samples of barley, flour and alfalfa meal.

Partial details of the results of two experiments are given in Table I. These and a number of others are summarized briefly in Table II.

TABLE I

OPTICAL ACTIVITY–REDUCING SUGAR RELATIONSHIPS DURING STARCH HYDROLYSIS UNDER THE INFLUENCE OF ENZYMES

(Experiment **4)**

Enzyme, Taka diastase equivalent to **0.05** g. per **100** cc. of substrate; substrate, Lintner's soluble starch, approx. 2%; digestion temperature, 21°

Interval, hrs	P optical value, Ventzke°, 4-dm tube	R Maltose hydrate, g per 100 cc.	Ratio of changes P/R For the interval	From initial observation
0	39.4	0.1389	..	..
0.5	38 2	4555	3.79	3.79
1	37.4	.7006	3.26	3.56
1.5	36.6	.8225	6.57	4.10
2	35.8	.9677	5.50	4.34
2.5	35.2	1.0602	6.48	4.56
3	34.4	1.1191	13.5	5.09

(Experiment **28)**

Enzyme, malt diastase; substrate, "Special" soluble starch, approx. 1.5%; digestion temperature, 25°

Interval, hrs	P optical value, Ventzke°, 4-dm. tube	R Maltose hydrate, g. per 100 cc.	Ratio of changes P/R For the interval	From initial observation
0	31.42	0.144	..	..
0 5	30.22	.427	4.24	4.24
1	28.42	.657	7.82	5.84
1.5	27.80	.870	2.91	4.98
2	27.16	.989	5.37	5.04
2.5	26.78	1.051	6.12	5.11
3	26.60	1.090	4.61	5.09

Discussion

In the first observations no particular attention was given to maintenance of a constant temperature during digestion, since it was assumed that both polarization and reduction changes would be similarly affected. More careful consideration made it apparent that if the amylase system is composed of several components each with its own particular optimum, the polarization–reduction ratio might vary with the temperature and other factors.

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[14] Gore, *Ind. Eng. Chem.*, **20, 865 (1928).**

TABLE II

OPTICAL ACTIVITY-REDUCING SUGAR RELATIONSHIPS DURING STARCH HYDROLYSIS UNDER INFLUENCE OF ENZYMES

Expt.	Diastase	G. per 100 cc	Digestion temp °C	Ratio P/R Hours 0 5	1	1.5	2	2.5	3	Total change in rotation, 4-dm. tube
2"	Takadiastase	0.05	21 ±	2.87	4.17	5.25	6.72	5.72	5.68	6.56
3"	Takadiastase	025	21 ±	2.41	403	4.37	4.78	5.13	4.91	5.10
4"	Taka diastase	025	21 ±	3.79	3 56	4.10	4.34	4.56	5 09	5.0
7	Takadiastase	0062	39	6 87	5.72	6.26	5.84	5.75	.	3.90
8	Taka diastase	0062	39	3.58	4.69	4 90	4.61	4.12	.	2.74
12	Taka diastase	0062	39	9 93	7.22	9 87	7.07	5.16	..	3 92
17	Takadiastase	0062	39	165	1.83	2.84	3.11	3.14	..	314
21	Taka diastase	025	25	2 31	2.99	3.18	4.63	5.48	6.02	5.80
22	Takadiastase	025	25	2.98	3.27	467	4.79	498	524	6.50
23	Taka diastase	050	25	3.01	3 65	4 25	4.37	5 04	4.31	6.42
24	'Taka diastase	050	25	2 23	2 87	3 07	3.45	3 99	4 07	5 1
26[b]	Taka diastase	050	25	4.57	4.84	4 75	5.00	5 21	5.16	4 93
27[b]	Taka diastase	050	25	3 67	3.77	3.70	5.37	5 39	5 62	5 56
5"	Malt	025	21	3.71	5.22	5 67	6.14	7.12	..	4 50
9	Barley flour	03	39	265	3.61	3.61	4.18	4.42	.	290
10	Barley flour	03	39	4.40	8.30	10.50	9.98	784	.	216
11	Barley flour	03	39	5.16	4.94	5.44	6 09	6.75	.	4 6
13	Malt	.020	39	6.45	6.00	5.57	5 91	5.44	..	3 95
14	Malt	.020	39	6.87	5.72	6.26	5.84	5.83	..	2.92
18	Malt	.0062	39	4.45	4 26	4.18	3.89	3.46	..	2.07
28[b]	Malt	.050	25	4 24	5.84	4.99	5 04	5.11	5 09	1.82
15	Barleyflour	10.0	39	4.67	4.36	4.87	..	..	..	4.99
16	Barley flour	10 0	39	4.79	5.07	5.07	..			6.3
6	Alfalfa	0.04	39	18 5	13 30	18.4	87.7	21.7	18.2	182

[a] No buffer. [b] Special starch.

Considerable difficulty was experienced at times in making the polarimetric observations. The solutions often became quite turbid and the end-point was uncertain. Even the special form of soluble starch prepared according to Gore's directions did not eliminate this trouble. Sometimes the results of duplicate experiments would show almost identical reducing sugar values but markedly different polarimetric changes and vice *versa.* On the whole the results were far from satisfactory and in many respects discouraging. Experiments 15 and 16 using barley flour according to Rumsey's[12] method gave results analogous to the samples of malt diastase. In these experiments the major portion of the change took place during the first half hour interval. If endocellular amylases were present they had very little effect on the P/R ratio.

In conclusion it may be said that although there seem to be differences in the hydrolytic characteristics of malt and Taka diastase materials the effect upon the polarization reduction ratio is such that the variation is probably no greater than other experimental errors in such determinations.

To be of value in throwing light on the mechanism of the hydrolysis of starch the method will have to be improved or give more consistent results for other investigators than it has been possible to attain in this study. It is evident that further attention in this connection must be given to the properties of the hydrolytic products intermediate between starch and maltose.

As can be noted in the data of Gore and those of Table I, the ratio P/R for each successive one-half hour unit interval fluctuates considerably, probably due to error in polarimetric readings, but these differences are smoothed out when the change is calculated from the initial point and some compensation of errors takes place.

In contrast to anticipated results, Taka diastase gave on the whole somewhat lower P/R ratios than malt diastase in the initial stages. This seemed to be more or less independent of the extent of hydrolysis (the latter being represented by the magnitude of the change in rotation given in the last column of Table II). This fact would tend to indicate the formation of reducing substances with relatively little change in optical activity from that of the original starch. It is probable that some glucose is formed from a saccharide unit other than maltose and that it may precede maltose or be formed simultaneously with it, thus giving the lower P/R ratio. Experiments 7 and 12 are out of harmony with others of the Taka diastase group in this respect and had other anomalous features in addition. They are included to indicate experimental variations which sometimes occur without apparent cause. From the results of the experiments completed, temperature, concentration of enzyme and buffering of the solution cannot be said to show any significant effect on the ratio.

Experiment 6 with an extract of alfalfa meal gave a rapid polarimetric change with very little saccharification and hence abnormally high P/R ratios.

Summary

Theoretical consideration of the properties of the final products of hydrolysis of starch resulting from diastatic conversion seemed to indicate that the assumed constant relationship between the polarimetric and reducing sugar values would not hold if glucose as well as maltose resulted from the action of the amylase system. It was further believed that the ratios found might furnish information on the mechanism of the hydrolysis of starch.

Determinations of the ratio have been carried out using Taka diastase as a glucose forming amylase system. The ratios found were different from those anticipated and indicate that the changes in the early stages of hydrolysis are probably unlike those of malt diastase.

While the ratios found were not constant, determinations of diastatic activity based upon the assumption of a constant value will probably not

involve an error more serious than those from other sources in such procedures.

Improvements in the procedure will be necessary to give definite information as to the course of hydrolysis of starch.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DIVISION OF CHEMICAL ENGINEERING, SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

CELLULOSE FUROATE[1,2]

BY KENNETH A. KOBE WITH RALPH E. MONTONNA

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The increasing industrial importance of cellulose esters presents an attractive field of investigation for new derivatives with desirable properties. One ester which has many desirable properties but which has not been used to any extent because of its excessive cost is cellulose benzoate. The great similarity of furoic acid[3] to benzoic acid made it desirable to prepare cellulose furoate with the hope that it would exhibit the same desirable properties as the benzoate. The recent extensive commercial development of furfural from which the acid can be readily obtained seemed to offer possibilities of obtaining this ester more cheaply than the corresponding benzoate derivative. This ester would be an "all cellulose" ester since furfural can be produced by distilling oxycellulose with dilute hydrochloric acid.

Discussion of Results

The preparation of furoic acid esters of cellulose was accomplished by means of a modified Schotten–Baumann reaction such as had been employed in the preparation of cellulose benzoate.[4] Tetrachloroethane was used as the diluent. Two types of products seemed to be formed as in the case of cellulose acetate, fibrous esters amounting to 65% of the theoretical and analyzing from 2.5 to 3 furoate residues per C_6 unit, and soluble, black, furoylated degradation products analyzing more than three furoate residues. This investigation was restricted mainly to the former product. The fibrous ester was always colored, varying in shade from light yellow to dark brown, and was insoluble in all the usual solvents for cellulose esters.

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[1] Abstracted from a thesis by Kenneth A. Kobe presented to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering in June, 1928.

[2] Presented before the Cellulose Division of the American Chemical Society at the 78th meeting, Minneapolis, Minnesota, September 9–13, 1929.

[3] Frankland and Aston, J. *Chem. Soc.*, 79, 515 (1901); Hill and Palmer, *Proc.* Am. *Acad. Arts Sci.*, 23, 188 (1888); Baum, *Ber.*, 37, 2949 (1904).

[4] Cross and Bevan, ibid., 34, 1514 (1901); *Chem. News*, 61, 87 (1890); Cross, Bevan and Beadle, J. *Chem. Soc.*, 63, 838 (1893); Wohl, *Z. angew. Chem.*, 16, 285 (1903); Ost and Klein, *ibid.*, 26, 437 (1913); German Patent 139,669.

The saponification values were obtained by the method of Cross and Bevan as modified by Woodbridge.[5] Analyses show that one acid residue is much more firmly bound than are the other two. This is in accord with the present accepted structure[6] of the hexose residues in cellulose, which show one primary and two secondary alcoholic hydroxyl groups. When the fibers stood for twenty-four hours with standard sodium alcoholate solution, only two furoate groups were removed, while on standing for seven days or refluxing for four hours all groups were removed. It was necessary to make a correction for increase of acid value due to decomposition of the furoic acid.

Experimental

Materials.—The cellulose was standard cellulose. The pyridine was of C. P. quality and was used without further purification. The furoyl chloride, tetrachloroethane and butyl acetate were technical grades and were redistilled before use.

Method.—Two grams of cellulose was covered with 100 cc. of diluent, usually tetrachloroethane, and the pyridine and furoyl chloride then added. The flask was attached to a reflux condenser and placed in a paraffin-bath which was heated so that the solvent just boiled. It was usually allowed to heat for three hours and then cooled The contents of the flask were poured onto a Büchner funnel and the fibers were sucked dry, then washed with chloroform and with alcohol. The fibers were boiled in several portions of water to remove any traces of solvent or reagents. They were sucked dry and all water removed in an oven at 100°. The material in solution was precipitated with petroleum ether, boiled with water and dried.

The maximum yield of fibers (3.6 g. = 65.7%) was secured with 15 cc. each of pyridine and furoyl chloride (2.6 times the theoretical), using 100 cc. of tetrachloroethane as the diluent and heating for three hours. Excess pyridine causes the fibers to lose tensile strength and become dark brown in color; excess furoyl chloride causes a lowered yield. When butyl acetate was used as a solvent, a horn-like mass having a very low saponification value was obtained. Heating for longer periods of time causes a decreased yield of fibers and an increased yield of soluble material of which 1.3 g was obtained by heating for twenty-four hours while but 0.2 to 0.3 g. forms in the three-hour period.

Analysis of Product.—The fibers were rubbed through a 10-mesh screen and mixed to give a uniform sample. A 0.3-g. sample was covered with 50 cc. of an alcohol solution of sodium alcoholate and allowed to stand for twenty-four hours, seven days or refluxed for four hours. The excess alkali was titrated using thymol blue as the indicator. When furoic acid was heated with sodium alcoholate solution for four hours, the acid value increased from 90.1 to 105.3% so that a correction was made in all samples treated in this manner.

Expt.	Stand 24 hrs., %	Reflux 4 hrs., %	Reflux corrected, %	Acid groups per C_6 unit
16	57.6	70.1	66.0	2.2
17	62.4	71.1	67.0	2.3
18	59.3	69.2	65.1	2.1
19	65.2	74.4	74.4	2.9
20	59.5	70.5	70.5	2.5

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[5] Woodbridge, THIS JOURNAL, 31, 1067 (1909).

[6] Hibbert, *J. Ind. Eng. Chem.*, 13,256,334 (1921).

The 1.3 g. of soluble material gave 82.2% furoic acid on standing for twenty-four hours with the sodium alcoholate solution (values from other experiments were 83.5 and 81.6%).

Calculated saponification values: trifuroate, $C_6H_7O_2(OOCC_4H_3O)_3$ = 75.75% of C_4H_3OCOOH; difuroate, $C_6H_8O_3(OOCC_4H_3O)_2$ = 64.0%.

Summary

1. Cellulose di- and trifuroates have been prepared by treating standard cellulose with furoyl chloride in the presence of pyridine. The esters were fibrous, dark colored and insoluble in the usual solvents for cellulose esters.
2. A considerable degradation of cellulose takes place during the reaction with the production of furoylated degradation products of cellulose which are black amorphous substances.
3. The analysis of cellulose trifuroate by saponification shows very clearly the fundamental difference of two of the alcoholic hydroxyl groups in the hexose residue from the third or primary hydroxyl and thus confirms the present accepted structure of the hexose residue.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE E. F. HOUGHTON & CO. RESEARCH LABORATORIES]

SOME HETEROCYCLIC DERIVATIVES OF DIPHENYL

BY J. M. F. LEAPER

RECEIVED FEBRUARY 19, 1931 PUBLISHED MAY 6, 1931

The production on a large scale of diphenyl in order to supply the demand for this very useful heat-transfer medium has already resulted in the price of this material being brought down to a figure comparable with that of any of the polynuclear hydrocarbons, except naphthalene.

Its applications in the chemical industry for synthetic purposes are in consequence destined to become of increasing importance, especially as it appears likely that the price can be further reduced.

The recent work by Jenkins, McCullough and Booth[1] has indicated for instance that the simple mono-chloro, nitro and amino derivatives can be produced readily on a commercial basis, and the work of C. H. Penning[2] has extended the knowledge of the polychlorinated derivatives.

The present paper covers some new heterocyclic compounds derived from 4-amidodiphenyl, the derivatives chosen for study being such as might be expected to be of possible commercial application in the rubber industry, in froth flotation of ores, as inhibitors in steel pickling or in dyestuff manufacture.

Use has been made in this work of the method described by R. Herz[3] for introducing sulfur into the ring by the action of sulfur chloride on the

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[1] Jenkins, McCullough and Booth, *Ind. Eng. Chem.*, 22, 31 (1930).

[2] Penning, *ibid.*, 22, 1180 (1930).

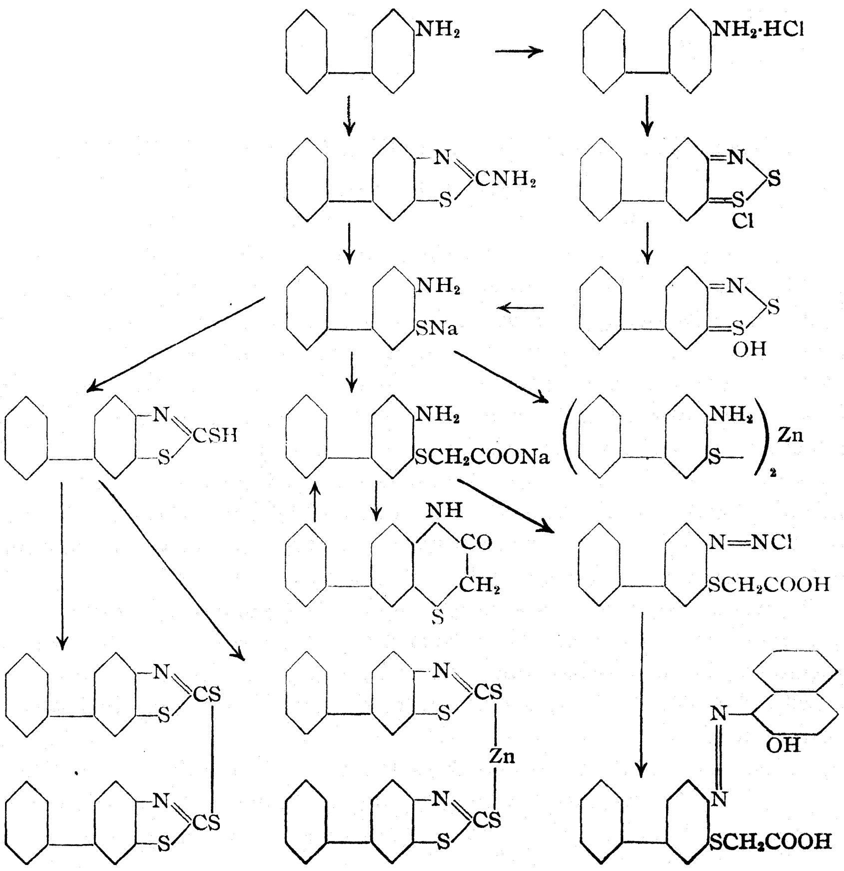
[3] Herz, German Patent 360,690.

hydrochlorides of amino compounds having a free ortho position. This reaction is the keystone of many important industrial syntheses, for example, in the Hydron Pink and Orange series of thioindigoids (Truttwin, "Enzyklopaedie der Kuepenfarbstoffe"), as also in the excellent method of A. H. Ney[4] for the manufacture of substituted mercaptothiazoles

Besides the characteristic ring grouping formed by the Herz reaction, chlorination of the amino compound also usually occurs if a free para position is present or if certain groups are in this position, and it appeared to the writer possible that in the case of diphenyl the tendency for chlorine substitution might extend through to the 4'-position. This, however, proved not to be the case since all derivatives obtained were unsubstituted in this part of the nucleus.

The course of the reactions described is graphically shown in the Flow Sheet.

FLOW SHEET



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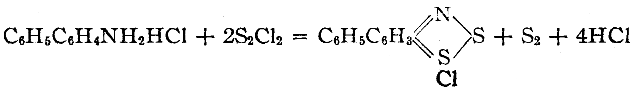
[4] Ney, U. S. Patent 1,788,585

Experimental Part

The diphenyl used for the work was the ordinary commercial product marketed by the Federal Phosphorus Company. Its setting point was 68" and it was considered unnecessary to subject it to recrystallization.

At the inception of this work the 4-aminodiphenyl used was prepared by the method of Bell, Kenyon and Robinson;[5] later the methods of Jenkins, McCullough and Booth[1] became available and were found somewhat more convenient for preparing the finely divided hydrochlorides necessary for the Herz reaction. The 4-nitro compound used for the reduction was crystallized once from methanol, when it had a melting point of 113°. The 4-amino hydrochloride was obtained from the benzene solution of the base by first drying the latter over calcium chloride and then passing in dry hydrochloric acid gas with rapid agitation. The benzene was filtered on a Biichner funnel and air drawn through the hydrochloride until dry. The product was then ready for the Herz reaction

Phenylphenylene Thiazthionium Chloride.—Seven hundred grams of sulfur monochloride was placed in a three-necked flask provided with an efficient agitator; 100 g. of thoroughly dry 4-aminodiphenyl hydrochloride was slowly added at 20° and agitation continued at this temperature overnight The next morning 400 cc. of benzene was added and the temperature then raised to 75–80" and kept at this point with good agitation under a reflux condenser for four and one-half hours Hydrogen chloride gas is evolved during this period and the color of the reaction mass changes from yellow to a reddish-brown. The reaction mixture was now allowed to cool to room temperature and filtered on a dry Biichner funnel. It was washed with enough benzene to remove yellow mother liquor and allowed to dry at room temperature, yield, 140 g. (calcd. 129 g.) The main impurity present is free sulfur formed in the reaction.



$$\mathrm{C_6H_5C_6H_4NH_2HCl + 2S_2Cl_2 = C_6H_5C_6H_3{<}\overset{N}{\underset{\underset{Cl}{S}}{}}{>}S + S_2 + 4HCl}$$

The excess sulfur chloride and benzene can be recovered readily from the filtrate by distillation. The product is a finely crystalline brownish-red powder, slightly soluble in ring hydrocarbons and in acetic acid. It may be purified by dissolving in cold acetic acid, filtering and adding to the filtrate sufficient dry ether to slowly precipitate the thiazonium chloride.

Anal. Calcd. for $C_{12}H_8NS_2Cl$: N, 5.28; S, 24.15; Cl, 13.37. Found: N, 5.20; S, 24.72; Cl, 13.13.

On attempting to obtain a melting point, the product charred at about 130°.

Phenylphenylene Thiazthionium Hydrate.—The chloride is stirred at room temperature with water overnight. The chloride appears to go partly into solution at first with a yellow color, quickly precipitating out again as a purplish powder, the solution meanwhile becoming strongly acid (HCl). On further stirring the precipitate becomes lighter colored until after about sixteen hours it is almost white when the reaction is complete. It is filtered off, washed with water until free from acid and dried. The weight obtained is the theoretical. A sample of the hydrate prepared from the purified chloride by the above method gave a negative test for chlorine, proving that the only chlorine in the chloride was that attached to the labile thiazonium sulfur.

Anal Calcd. for $C_{12}H_9ONS_2$: N, 5.67; S, 25.91. Found: N, 5.59; S, 26.24

The "hydrate" is soluble in alcohol, from which it may be precipitated in fine needles by careful addition of water and allowing to stand It melts at about 135° with charring and decomposition.

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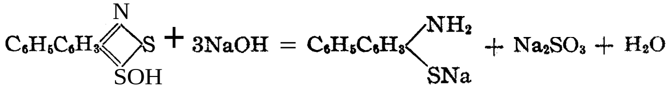
[5] Bell, Kenyon and Robinson, *J. Chem. Soc*, 1239 (1926).

4-Amido-3-mercaptodiphenyl (**Zinc** Salt).—The reaction is as follows



$$C_6H_5C_6H_3(N)(S)(SOH) + 3NaOH = C_6H_5C_6H_3(NH_2)(SNa) + Na_2SO_3 + H_2O$$

the sodium salt being then precipitated as the zinc salt.

Forty grams of the hydrate, figured on the dry basis, preferably the still wet filtrate from the conversion of the chloride, are slurried with enough water to make about **400** cc. A little ice is added and **64** cc. of 35° BC. sodium hydroxide with stirring. The hydrate goes into solution immediately with the exception of a small portion of insoluble impurity. The solution should now color Clayton yellow paper pink, indicating excess of sodium hydroxide over the sodium salt of the thiophenol. The solution is filtered and zinc chloride solution added until no further precipitate is obtained. The precipitate is redissolved in a mixture of dilute hydrochloric acid and alcohol Excess of sodium acetate solution is added to precipitate zinc mercaptide.

Anal. Calcd. for $(C_{12}H_{10}NS)_2Zn$: Zn, **14.05.** Found: Zn, **13.55.**

The pure zinc mercaptide may be used for any of the condensation reactions, but the crude solution of sodium mercaptide obtained by dissolving the hydrate in sodium hydroxide is quite suitable for all purposes and is much more convenient. The sodium salt may also be precipitated out with excess of sodium hydroxide if desired.

Air passed into the sodium hydroxide solution of the thiophenol precipitates the disulfide as a somewhat resinous mass, which is difficult to purify. No analysis was made of this.

2-Mercapto-6-phenylbenzothiazole.—Forty grams of crude phenylphenylene thiazthionium chloride is converted to the hydrate as described above, the latter filtered off, washed well and re-slurried with enough water to make about **180** cc. and **40** cc. of 35" Bé. sodium hydroxide is added. The mixture is agitated for ten minutes and transferred to a flask; **10** cc. of carbon disulfide is added and the whole heated to refluxing temperature under a condenser. After about five minutes a crystalline magma appears in the reaction mass. With further heating the deep yellow color of trithiocarbonate changes to a light brownish color and at the end of about forty minutes the crystalline precipitate all goes into solution. The reaction of the solution is now alkaline to Brilliant yellow paper but not to Clayton yellow. The solution is diluted to 800 cc., cooled to room temperature and dilute hydrochloric acid added with agitation until neutral to Brilliant yellow. The thiazole comes out as an almost white precipitate. It is filtered, washed and dried; yield, **29.5** g. **(87%** of calcd. figured on the 4-aminodiphenyl), m. p. **220".** Recrystallized twice from benzene containing 10% "Cellosolve." the melting point remained constant at **230.5°**.

Anal. Calcd, for $C_{13}H_9NS_2$: N, 5.76; S, **26.33.** Found: N, **5.68;** S, **26.16.**

The product is soluble in sodium and potassium hydroxides but practically insoluble in ammonia (distinction from 2-mercaptobenzothiazole, which is soluble in ammonia), very slightly soluble in alcohol, somewhat more so in benzene and in glycol mono-ethyl ether ("Cellosolve").

Bis-6-phenyl-2-benzothiazole Disulfide.—Four and nine-tenths grams of phenylmercaptobenzothiazole is dissolved in **2.2** cc of **35" Bé.** sodium hydroxide **and 100** cc. of water; **2.5** g. of iodine dissolved in *75* cc. of water containing potassium iodide are added to the thiazole solution. The creamy white precipitate of disulfide is filtered off, washed well and dried; yield, **4** g. The product is insoluble in alcohol, soluble in benzene, and very soluble in chloroform. Crystallized once from a mixture of alcohol and benzene and once from benzene, the product melts at **163°**.

Anal. Calcd. for $C_{26}H_{16}N_2S_4$: N, **5.78;** S, 26.45. Pound: N, **5.71;** **S, 26.72.**

Zinc and Lead Salts of 2-Mercapto-6-phenylbenzothiazole.—The thiazole dissolved in alcohol is precipitated by the calculated amount of zinc sulfate in aqueous solution, the precipitated zinc salt washed and dried; it is a white powder.

Anal. Calcd. for $C_{26}H_{16}N_2S_4Zn$: Zn, 11.90. Found: Zn, 11.41.

The lead salt was made similarly using diethylene glycol monoethyl ether ("Carbitol") for dissolving the thiazole and an aqueous solution of lead acetate, and is a yellow crystalline powder.

Anal. Calcd. for $C_{26}H_{16}N_2S_4Pb$: Pb, 29.97. Found: Pb, 30.55

It was thought desirable to prepare the 2-mercapto-6-phenylbenzothiazole by the method suggested by Herz and Schubert[6] from 4-amidodiphenyl by treating with sodium thiocyanate and bromine in acetic acid solution giving 2-amido-6-phenylbenzothiazole, the latter then being heated with a considerable excess of potassium hydroxide, splitting the thiazole ring and giving the amidothiophenol. The alkaline solution of the latter is then treated with carbon disulfide as in the previous method.

2-Amido-6-phenylbenzothiazole.—8.3 g. of 4-amidodiphenyl and 3.2 g. of sodium thiocyanate are agitated with 120 cc. of glacial acetic acid at 50°; 2 cc. of bromine is added drop by drop and agitation continued for one hour. The mixture is then cooled, diluted and sodium hydroxide added until slightly alkaline. The amidothiazole precipitated as a creamy white powder. It was filtered, washed and dried; yield, 8.8 g. The product is soluble in hot dilute hydrochloric acid and is purified by filtering this hot solution and allowing the hydrochloride to crystallize out. This is washed a little and basified by treatment with sodium hydroxide, then washed, dried and recrystallized from hot benzene, separating in creamy white plates of m. p. 227–228°.

Anal. Calcd. for $C_{13}H_{10}N_2S$: N, 12.38; S, 14.16. Found: N, 12.46; S, 14.15.

This product was treated for four to five hours with strong potassium hydroxide in considerable excess, when ammonia was evolved and the heterocyclic ring split back to the amidothiophenol. The resulting solution was divided into two parts One portion was treated with carbon disulfide as above, precipitated with hydrochloric acid and the separated yellow precipitate dried and recrystallized once from benzene. The product obtained melted at 229° and when mixed with 2-mercapto-6-phenylbenzothiazole previously obtained, there was no diminution in melting point. The second portion of the thiophenol solution was heated with sodium chloroacetate, the solution precipitated with hydrochloric acid and heated to form the thioglycolic anhydride. This was filtered off. dried and crystallized once from benzene. The product melted at 210° and when mixed with the anhydride obtained from the thiazthionium chloride described below, melted at 211°.

2-Amido-5-phenylthioglycolic Acid.—Forty grams of the thionium chloride was converted to the hydrate as above described, the latter filtered off, washed, mixed with water to make 400 cc., 65 cc. of 35° Bé. sodium hydroxide added, agitated for five minutes, filtered, 21 g. of chloroacetic acid previously neutralized with dilute sodium hydroxide added and the mixture heated for a half hour to 60° with agitation. The condensation is now complete and hydrochloric acid is added, precipitating the crude amidophenylthioglycolic acid. On heating the acidiied mixture the precipitate, which is at first somewhat resinous, becomes crystalline, indicating a change to the inner anhydride. This is filtered off, washed and dried; yield, 31 g. (about 94% figured on amidodiphenyl). Recrystallized twice from hot benzene it gives white leaflets of m. p. 212–212.5°.

Anal. Calcd. for $C_{14}H_{11}ONS_3$: N, 5.81; S, 13.28. Found: N, 5.73: S, 13.41.

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[6] Herz and Schubert, U. S. Patent. 1,788,297.

On heating with concd. sodium hydroxide the anhydride is converted back to the sodium salt of amidothioglycolic acid.

Diazotization of Amidothioglycolic Acid.—A solution of the crude sodium salt obtained by addition of sodium hydroxide to the hydrate as described above was mixed with an equimolecular amount of sodium nitrite solution, and the mixture added slowly at 10° with good agitation to dilute hydrochloric acid, keeping the solution acid to Congo paper. Agitation is continued for one hour. The diazo solution was filtered and added to an alkaline β-naphthol solution as usual. The dye precipitates at once Some acetic acid was added and the dye filtered off, washed, dried and crystallized from acetic acid, giving reddish needles with a metallic appearance.

Anal. Calcd. for $C_{24}H_{18}O_3N_2S$: N, 6.76; S, 7.73. Found: N, 6.73; S, 7.79.

A similar coupling was made also using o-phenylphenol (Dow) instead of β-naphthol. This gave a dyestuff having an orange color in acetic acid solution, the β-naphthol dye giving a bluish-red solution.

Preliminary Experiments Made on the Preparation of the Substituted Thioindigoid Dyestuff According to the Methods of Herz.[7]—Starting from the diazotized *o*-amidothioglycolic acid, it was converted to the nitrite by the Sandmeyer reaction and then to the substituted thionaphthene by saponification, the latter then being oxidized to the thioindigo, gave a dyestuff which dyed cotton bluish-red shades from a hydrosulfite vat. Further investigation of this dyestuff is reserved for later publication.

In connection with the sodium salt of the amidothioglycolic acid, an interesting fact was noted. It was at first intended to salt out this sodium salt from the crude solution obtained by heating the amidothiophenol with excess of sodium chloroacetate in order to obtain a purer product for diazotization, etc. It was found, however, that the sodium amidothioglycolate thus obtained was almost insoluble in cold water after salting out, whereas in the presence of the usual impurities, *i. e.*, sodium sulfide, sodium sulfite, sodium chloroacetate, etc., a quite concentrated cold solution could be obtained, which was more convenient for diazotization.

Summary

1. The course of the Herz reaction as applied to 4-amidodiphenyl was established.
2. Some new heterocyclic derivatives related to 3-mercapto-4-aminodiphenyl have been prepared and described.
3. 6-Phenyl-2-mercaptobenzothiazole was made by two methods.
4. A new azo dye was prepared.

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[7] Herz, U. S. Patents 1,243,170 and 1,243,171

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

A STUDY OF THE TOXICITY OF TOXICAROL, DEGUELIN AND TEPHROSIN USING THE GOLDFISH AS THE TEST ANIMAL

BY W. A. GERSDORFF

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The goldfish (*Carassius auratus*), having proved to be a good test animal in the study of toxicity, has been used in the toxicological examination of various substances that is now in progress in this Laboratory. The substances tested have been constituents of fish-poisoning plants and their derivatives. The method used by the author has been described in a previous paper,[1] and a study by that method of the toxicity of rotenone and two of its derivatives, isorotenone and dihydrorotenone, has also been published.[2] This paper presents the results of a similar examination of toxicarol, deguelin and tephrosin, toxic constituents of two fish poisoning plants of the genus Cracca (*Tephrosia*).

Toxicarol (m. p. 219°) and deguelin[3] (m. p. 171°) were isolated from the roots of C. *toxicaria* by *E. P.* Clark of this Laboratory.[4] It was shown by him that both substances are found also in the roots of *Deguelia (Derris) elliptica*, and in addition deguelin occurs in the roots of *Lonchocarpus nicou* ("cubé") and the leaves of C. *vogelii*.

Tephrosin (m. p. 198°) was isolated from the leaves of *C. vogelii*.[5] It may also be obtained, however, from derris and cubé roots.

The chemical structure of these three substances is not yet fully known. Toxicarol is an optically inactive compound of the molecular formula $C_{23}H_{22}O_7$, possessing two hydroxyl and two methoxyl groups. Deguelin is an optically inactive dimethoxy lactone having the molecular formula $C_{23}H_{22}O_6$. Tephrosin is a dimethoxy lactone with the molecular formula $C_{23}H_{22}O_7$. It is suggested by Clark that tephrosin is an hydroxydeguelin. It is to be noted that the molecular formulas for toxicarol and tephrosin differ from that of rotenone by having one more atom of oxygen, whereas the formula for deguelin is identical with that of rotenone.

On account of the slight solubility of the compounds in water, acetone was used as the solvent. It was found necessary early in these toxicological studies with rotenone and some of its derivatives to work with freshly prepared stock solutions of the compounds in acetone, since such solutions when allowed to stand underwent appreciable chemical change, as evidenced by a change in the color of the solution, with a concomitant loss in

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[1] W. A. Gersdorff, THIS JOURNAL, 52, 3440–3445 (1930).

[2] W. A. Gersdorff, *ibid.*, 52, 5051–5056 (1930).

[3] Deguelin was not named until later and is referred to in the reference as "the second compound."

[4] E. P. Clark, THIS JOURNAL, 52, 2461–2464 (1930); 53, 313–317 (1931).

[5] E. P. Clark, *ibid.*, 53, 729–732 (1931).

toxicity. The loss of toxicity of solutions of rotenone has also been noted by Jones and Davidson, who used insects as the test animals.[6] That the solutions change on standing was observed in the present study especially with toxicarol and deguelin. Acetone solutions of toxicarol suffer a rapid loss in toxicity to goldfish; acetone solutions of deguelin, however, undergo an appreciable increase in toxicity. Acetone solutions of tephrosin either do not undergo a change in toxicity or the change is slow as compared to that of the other two compounds.

The data are given in Tables I to III. The survival time curves and the velocity of fatality curves which were plotted from these data are given in Figs. 1 and 2. In the former curves the ordinates are survival times in minutes; in the latter, they are the reciprocals of the survival times multi-

TABLE I

TOXICITY OF TOXICAROL TO GOLDFISH AT 27.0 ± 0.3°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Me $\frac{100}{\text{surv. time}}$
1.0	17	38	1.8	91	1.12
0.5	17	39	1.9	112	0.90
.25	15	39	1.9	138	.74
.10	14	39	1.9	158	.64
.075	11	39	1.9	185	.58
.060	12	39	1.9	239	.43
.050	24	40	2.0	310	.34
.025	11	38	1.8	960[b]	.11[b]

[a] Estimated from length. [b] One additional fish was apparently unaffected after forty-four hours in the test solution.

TABLE II

TOXICITY OF DEGUELIN TO GOLDFISH AT 27.0 ± 0.3°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$
5.0	6	40	2.0	60	1.68
0.40	17	38	1.8	124	0.83
.25	16	40	2.0	158	.66
.175	27	40	2.0	186	.56
.125	13	40	2.0	208	.50
.090	20	40	2.0	261	.39
.075	16	39	1.9	278	.38
.060	13	39	1.9	312	.33
.050	4	37	1.7	400	.26
.040	15	40	2.0	478	.21
.035	21	[b]	Mean of 17 fishes, 1800. Four fishes still active after 64 hrs.		.09
.025	11		Apparently unaffected in 61 hrs.		

[a] Estimated from length. [b] Fishes not measured, but of same approximate size.

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[6] H. A. Jones and W. M. Davidson, J. *Econ. Entomology,* 24, 258–262 (1931).

TABLE III

TOXICITY OF TEPHROSIN TO GOLDFISH AT 27.0 ± 0.3°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$
2.0	12	40	2.0	134	0.75
1.5	12	41	2.2	158	.64
1.0	15	43	2.4	137	.74
0.75	15	38	1.8	156	.65
.50	13	38	1.8	181	.56
.30	18	38	1.8	222	.47
.20	21	39	1.9	274	.40
.15	12	41	2.2	349	.30
.10	12	42	2.3	576	.19
.075	12	40	2.0	1360	.09
.050	9	[b]	...	Apparently unaffected in 30 hrs.	

[a] Estimated from length. [b] Fishes not measured, but of same approximate size.

plied by 100. In both types of curves the abscissas are concentrations in milligrams per liter.

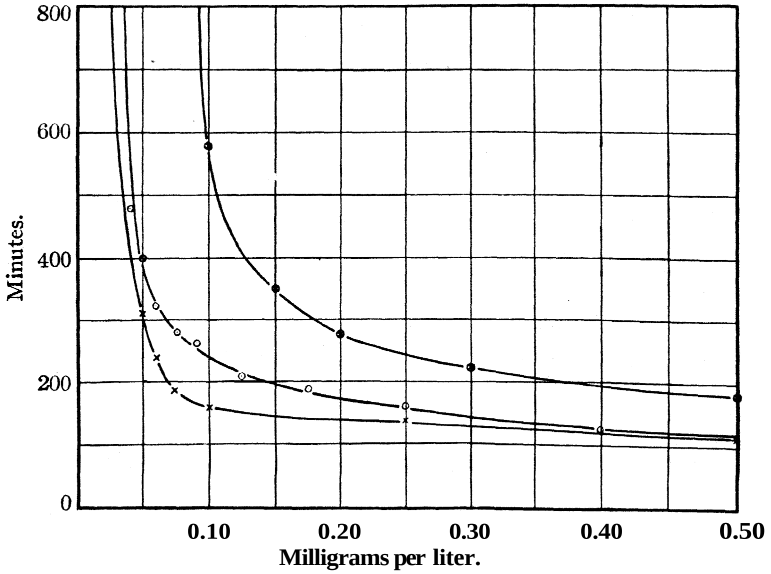

Fig. 1.—Survival time curves: X, toxicarol; ⊙, deguelin; ⊗, tephrosin.

Until an equation better expressing the course of toxic action is found acceptable, the formula used in the preceding papers, that is, Powers' formula, toxicity = $\sqrt{\tan \theta / a}$, will again be used as a measure of the relative toxicities of the three substances studied here. In this formula data obtained from the velocity of fatality curve are used. A portion of this curve approximates a straight line since its corresponding portion of the survival time curve approximates an equilateral hyperbola. This straight line, representing the theoretical velocity of fatality, is prolonged to cut the x-axis at a point designated a; tan Θ is the slope of this line. In this way values are obtained for the theoretical threshold of toxicity, that is, the concentration below which the substance does not cause death, and the rate of increase of the theoretical velocity of fatality with increase in concentration. The formula expresses the opposite effect of these two variables.

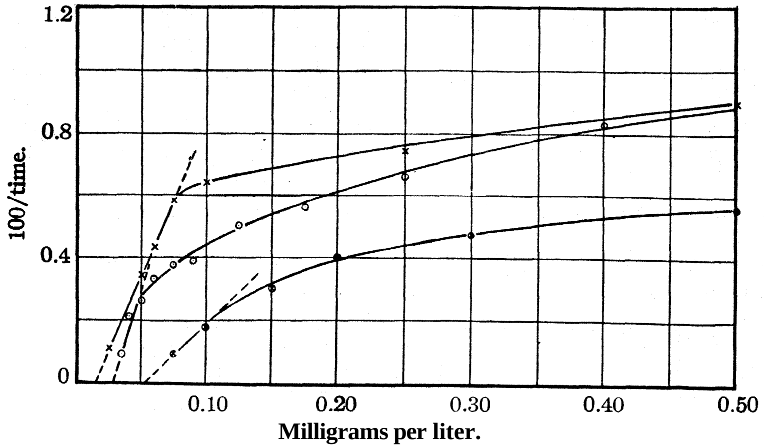

Fig. 2.—Velocity of fatality curves: X, toxicarol; ⊙, deguelin; ⊗, tephrosin.

The comparative toxicities of the substances under consideration derived according to this equation are shown in Table IV. The values given for a and tan Θ are based on the expression of concentration in milligrams per liter and time in minutes. The values for the toxicities are compared to that for rotenone since rotenone was the first as well as the most toxic of the compounds studied.

TABLE IV

COMPARATIVE TOXICITY AT 27°C. OF TOXICAROL, DEGUELIN, AND TEPHROSIN TO GOLDFISH

Substance	a, mg. per liter	Tan Θ		Relative toxicity with respect to rotenone
Toxicarol	0.015	0.097	2.5	0.65
Deguelin	.030	.150	2.2	.56
Tephrosin	.055	.043	0.88	.23

Conclusions

Of the three compounds studied, toxicarol has the lowest threshold of toxicity, 0.015 mg. per liter. That of deguelin is twice as great and that of tephrosin nearly four times as great. The threshold of toxicity of rotenone is slightly lower than that of toxicarol. The velocity of fatality of deguelin increases with increase in concentration at a higher rate than that of toxicarol (half again as high), but this rate is lower for tephrosin (less than half that of toxicarol). The rate of increase for rotenone is double that of toxicarol. At higher concentrations, when the rate of increase decreases, toxicarol is slightly more toxic than deguelin and tephrosin is considerably less toxic; for example, at a concentration of 0.20 mg. per liter the survival times are, respectively, 139, 175 and 274 minutes. Rotenone at higher concentrations is considerably more toxic than toxicarol; at a concentration of 0.20 mg. per liter the survival time is sixty-five minutes. According to Powers' formula, which is an expression of relative toxicity considering the first two factors only, the three substances studied have the following decreasing order of toxicity: toxicarol, deguelin and tephrosin. Their toxicities are 65, 56 and 23%, respectively, of that of rotenone.

WASHINGTON, D. C.

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY AND THE LABORATORY FOR PURE RESEARCH OF MERCK AND COMPANY]

CATALYTIC REDUCTION OF MIXTURES OF PARA-NITRO- AND NITROSOPHENOLS WITH ALDEHYDES AND KETONES

BY RANDOLPH T. MAJOR

RECEIVED FEBRUARY 24, 1931 PUBLISHED MAY 6, 1931

In connection with an attempt to prepare certain O-arylhydroxylamines it was noted that when the product that was formed by the catalytic reduction of 2,4-dinitrophenol in solution in acetone was benzoylated by the usual method of Schotten–Baumann, the compound expected, (2,4-bis-benzaminophenyl) benzoate, m. p. 233°,[1] was not obtained. Analyses indicated that the new compound contained one C_3H_6 group more than does (2,4-bis-benzaminophenyl) benzoate. When, however, the solvent that was used was either dioxane or isopropyl alcohol instead of acetone the expected (2,4-bis-benzamino-phenyl) benzoate was formed.

These facts pointed to the probability of a condensation taking place between acetone and the phenol during the reduction.

A solution of 2,4-dinitrophenetole[2] was then catalytically reduced and benzoylated. The compound that was obtained was found to be the expected new compound (2,4-bis-benzamino)-phenetole.

Thinking that the phenol group might have something to do with the peculiar course of the reduction in the first case mentioned, ortho, meta and para nitrophenols were catalytically reduced in solution in acetone.

When *p*-nitrophenol was catalytically reduced in the presence of acetone

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[1] Post and Stuckenberg, *Ann.*, 205, 69 (1880).

[2] Willgerodt, *Ber.*, 12,764 (1879).

some p-aminophenol was formed, but there was also obtained another product which was soluble in alkalies and acids and which could be separated from p-aminophenol by shaking a solution of the two in acids with benzaldehyde, which combined with and precipitated the *p*-aminophenol.[3] This other product was shown to be the same compound that was formed by the catalytic reduction of 4-(isopropylidene-amino)-phenol, $(CH_3)_2C=NC_6H_4OH$,[4] and corresponded in every way to 4-(isopropyl-amino-phenol which had previously been prepared by the action of isopropyl chloride on *p*-aminophenol.[5] Various derivatives were made, including the hydrochloride, dibenzoyl derivative, the nitroso derivative and the phenyl isocyanate addition product.

When, however, o-nitrophenol was catalytically reduced in the presence of acetone no (2-isopropylamino)-phenol was formed but when the reduction product was benzoylated (2-benzamino-phenyl) benzoate[e] was obtained. Also when m-nitrophenol was reduced in the presence of acetone, no m-isopropylaminophenol could be detected.

Obviously, therefore, the compound that was formed by the benzoylation of the reduction product of the mixture of 2,4-dinitrophenol and acetone was (2-benzamino-4-benzoyl-(isopropyl)-amino)-phenylbenzoate, $2,4\text{-}(C_6H_5CONH)(C_6H_5CONCH(CH_3)_2)C_6H_4\text{–}OCOC_6H_5$.

The course of the reaction was not simply a condensation between the p-aminophenol formed during the reduction and the acetone which was present, followed by further reduction. This was shown by catalytically reducing a mixture of p-aminophenol and of acetone. No 4-(isopropylamino)-phenol was obtained.

By a similar process (4-*sec.*-butylamino)-phenol was formed by the reduction of a mixture of *p*-nitrophenol and methyl ethyl ketone, and 4 (amyl-3-amino)-phenol hydrochloride, $p\text{-}(C_2H_5)_2CHNHC_6H_4OH\cdot HCl$, was formed from the reduction products of a mixture of *p*-nitrophenol and diethyl ketone.

However, when *p*-nitrophenol was reduced in the presence of acetophenone or menthone, only p-aminophenol was obtained.

Also, when nitrobenzene was catalytically reduced in the presence of acetone, no n-isopropylaniline was formed.

On the other hand, good yields of 4-(isopropylamino)-phenol were obtained by the reduction of p-nitrosophenol in the presence of acetone.

Attention was next directed to the possibility of condensation between 4-nitrophenols and aldehydes during reduction. No definite, crystalline

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[3] German Patent 208,434.

[4] Haegel, Ber., 25, 2755 (1892); Michaelis and Luxembourg, *ibid.*, 27, 3006 (1894).

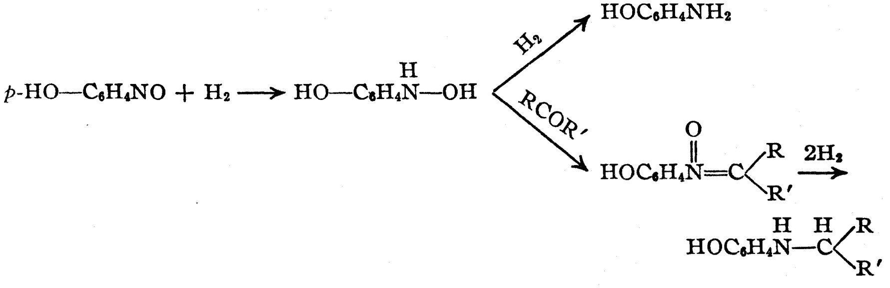
[5] Buc, U. S. Patent 1,555,452, September 29, 1925.

[6] (a) Ladenburg, Ber., 9, 1529 (1876). (b) Hinsberg and Udranszky, Ann., 254, 256 (1889).

condensation products were isolated when p-nitrophenol was catalytically reduced in the presence of either formaldehyde or acetaldehyde. However, when a mixture of p-nitrophenol, benzaldehyde and an inert solvent such as methanol was catalytically reduced, a considerable yield of 4-(dibenzylamino)-phenol[7] was obtained.

It was also found that reduction of a mixture of *p*-aminophenol and benzaldehyde gave a good yield of 4-(dibenzylamino)-phenol.

A complete explanation of the rather peculiar reactions that have been recorded is not at present clear. However, in the case of the reduction of mixtures of ketones and p-nitro- and nitrosophenols it seems clear that some intermediate product formed during reduction of the substituted phenols condensed with the ketone and the condensation product was, in turn, reduced. The most likely intermediate products that could behave in this way are the corresponding hydroxylamines. It has been shown by Hoffmann and Victor Meyer that hydroxylamines are formed as intermediate products in the reduction of many nitro compounds.[8] According to this conception the reaction must proceed in the following manner



Apparently a hydroxy group in the para position to the nitrogen atom must increase the chemical activity of the hydroxylamine group which is formed during the reduction. That this is probably true is indicated by the fact that while zinc dust and water reduce nitrobenzene and most of its derivatives to phenyl hydroxylamines,[9] the same agents reduce *p*-nitrophenols to *p*-aminophenols.[10]

In the case of the reduction of a mixture of *p*-nitrophenol and benzaldehyde, the same sort of reaction probably occurred at first and then due to the greater activity of aldehydes as compared with ketones condensation took place between the aldehyde and the secondary amine which had been formed. Finally, there was reduction of the new condensation product. The reaction may be represented as follows

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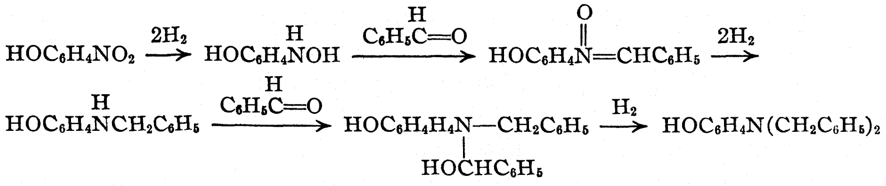
[7] Bakunin, *Gazz. chim. ital.*, II, 36, 211 (1906); *Chem. Centr.*, II, 1413 (1906).

[8] Hoffmann and V. Meyer, *Ber.*, 24, 3528 (1891).

[9] Bamberger, *ibid.*, 27, 1348, 1548 (1894); Wohl, *ibid.*, 27, 1432 (1894).

[10] Bamberger, *ibid.*, 28, 250 (1895).



$$HOC_6H_4NO_2 \xrightarrow{2H_2} HOC_6H_4\overset{H}{N}OH \xrightarrow{\overset{H}{C_6H_5C{=}O}} HOC_6H_4\overset{O}{\overset{\|}{N}}{=}CHC_6H_5 \xrightarrow{2H_2}$$

$$HOC_6H_4\overset{H}{N}CH_2C_6H_5 \xrightarrow{\overset{H}{C_6H_5C{=}O}} HOC_6H_4H_4\underset{\underset{HOCHC_6H_5}{|}}{N}{-}CH_2C_6H_5 \xrightarrow{H_2} HOC_6H_4N(CH_2C_6H_5)_2$$

Experimental Part

General Method of Reduction.—All of the reductions described in this paper were carried out in a Burgess–Parr Reduction Apparatus." The hydrogenation catalyst was in every case platinum oxide.[12]

Reduction Followed by Direct Benzoylation of the Reduction Product.—The appropriate mixtures shown in Table I were reduced. The reduction products were diluted with water and benzoylated with a mixture of benzoyl chloride and sodium hydroxide.

TABLE I

REDUCTION EXPERIMENTS

Mixture reduced		Solid product obtained			Nitrogen, %	
Solid	Solvent	M. p., °C.	Crystallized from	Formula	Calcd.	Found
2,4-Dinitrophenol	Acetone	171	Alc.	$C_{30}H_{26}O_4N_2$	5.86	6.11
2,4-Dinitrophenol	Isopropyl alc.	233[b]	..[c]	....	..	..
2,4-Dinitrophenetole	Acetone[a]	189	Alc.	$C_{22}H_{20}O_3N_2$	7.78	7.80 7.57[d]

[a] The same compound was obtained when other solvents such as 1,4-dioxane, methanol and glacial acetic acid were used in place of acetone. [b] Post and Stuckenberg, Ref. 1, give 231–233° as them. p. of 2,4-(bis-benzamino)-phenyl benzoate and state that the compound is insoluble in alcohol. [c] Insoluble in alcohol. [d] Mol. wt. Calcd. for $C_{22}H_{20}O_3N_2$: 360. Found: 362,365 (Menzies–Wright method).[13]

Hydrolysis of 2,4-(Bis-benzamino)-phenetole.—A solution of 2.5 g. of 2,4-(bis-benzamino)-phenetole in concentrated hydrochloric acid was heated in a sealed tube at 155–160° for four hours. After the tube had been cooled long needle-like crystals were found in the solution. These were filtered and the filtrate extracted with ether. The solid which was left after the ether had been evaporated and the above-mentioned solid precipitate were identified as benzoic acid by their solubility in organic solvents and alkalies, relatively slight solubility in water and the melting point of 121–122°,[14] yield 71%.

The acid filtrate described above was evaporated to dryness in *vacuo.* One gram of solid remained. To 0.3 g. of this was added a dilute aqueous solution of picric acid.

A pale yellow precipitate formed which was recrystallized from dilute alcohol; decomposition point 120°.[15]

Another portion of the solid left after excess of hydrochloric acid had been evaporated was dissolved in water and benzoylated with benzoyl chloride and sodium hydroxide. A

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[11] Manufactured by the Burgess–Parr Company, Moline, Illinois.

[12] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

[13] Menzies and Wright, Jr., *ibid.*, 43, 2314 (1921).

[14] Reissert, *Ber.*, 23, 2244 (1890), gives 121.25° as them. p. of benzoic acid.

[15] Lumière and Seyewetz, *Bull. soc. chim.*, *[111]9*, 597 (1893), give 120° as the decomposition point of 2,4-diaminophenol picrate.

solid was obtained which was relatively insoluble in alcohol; m. p. 233°. A mixture with 2,4-(bis-benzamino)-phenyl benzoate also melted at 233°.

Reduction of a Mixture of *p*-Nitrophenol and Acetone.—A solution of 0.18 mole of *p*-nitrophenol in one mole of acetone was reduced. When the reduction was complete the solution was evaporated to dryness. The residue was then extracted with hot benzene. The portion which did not dissolve was soluble in hot acetone, m. p. 184° with decomposition.[16]

When the above-mentioned solution in hot benzene was cooled, a solid precipitated which melted with decomposition at 143°. The filtrate from this was evaporated to dryness. An oil remained, most of which was insoluble in dilute acids. It was accordingly washed with dilute hydrochloric acid and extracted with ether. Evaporation of the ether left a solid which was recrystallized from benzene; m. p. 115°. A mixture of p-nitrophenol with this compound also melted at 115°. It was soluble in dilute alkalies.

The above-mentioned solid, m. p. 143°, was dissolved in dilute acetic acid and the solution shaken with an excess of benzaldehyde for ten minutes. The excess benzaldehyde and any condensation product with it was extracted with ether. The acid layer was neutralized with sodium carbonate. A cream colored precipitate formed which was recrystallized from benzene; m. p. 155–156° with some decomposition; yield, 45%. It occurred in the form of fine white needles.

Anal. Calcd. for $C_9H_{13}ON$: C, 71.47; H, 8.67; N, 9.27; mol. wt., 151.11. Found: C, 71.4, 71.72; H, 8.95, 8.77; N, 9.64; mol. wt. (Menzies–Wright method),[13] 150.

4-(Isopropyl-(nitroso)-amino)-phenol, *p*-$C_3H_7N(NO)C_6H_4OH$.—A cold solution of 0.5 g. of 4-(isopropylamino)-phenol in dilute hydrochloric acid was treated with an aqueous solution of 0.25 g. of sodium nitrite in water. After standing for a short while, salt solution was added and the solution was extracted with ether. When the ether was evaporated a yellow solid was left which was soluble in dilute alkalies but insoluble in acids. It gave the Liebermann nitroso reaction.[17] It was recrystallized from benzene; m. p. 112–113°.

Anal. Calcd. for $C_9H_{12}N_2O_2$: N. 15.54. Found: N, 15.05.

4-(Phenylcarbamino-(isopropyl)-amino)-phenol.—A solution of 0.4 g. of *p*-isopropylamino-phenol and 0.6 g. of phenyl isocyanate in dry benzene was heated to boiling. A white precipitate formed. The solution was cooled and the solid was filtered off. It was insoluble in dilute acids but soluble in dilute alkali. It was recrystallized from benzene; m. p. 214–215° with some decomposition.

Anal. Calcd. for $C_{16}H_{18}O_2N_2$: N, 10.38. Found: N, 10.80. 10.79.

4-Isopropylamino-phenol.—A solution of 2.5 g. of 4-(isopropylidene-amino)-phenol in alcohol was reduced. After completion of the reduction the alcohol was evaporated A solid remained which was recrystallized from benzene; m. p. 155–156°. A mixture of this solid with the compound, m. p. 155–156°, obtained by the catalytic reduction of a mixture of p-nitrophenol and acetone also melted at 155–156°.

Reduction of a Mixture of a Nitrophenol and a Ketone Followed by Treatment of the Reduction Product with Nitrous Acid.—A solution of the nitrophenol in the ketone, and methanol, also when the ketone was diethyl ketone, was reduced. The volatile material was then evaporated in *vacuo* at room temperature. The residue was dissolved in cold dilute hydrochloric acid. A cold aqueous solution of sodium nitrite was then added. The nitroso derivative of the *sec.*-alkylaminophenol precipitated.

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[16] Lossen, *Ann.*, 175, 296 (1875), gives 184° as the decomposition point of *p*-aminophenol.

[17] Liebermann, Ber., 7, 248, 806, 1098 (1874).

TABLE II

RESULTS OF EXPERIMENTS

Nitrophenol	Ketone	Nitroso derivative yield, %	M. p., °C.	Formula	Nitrogen, % Calcd.	Found
Ortho	Acetone	Negl.[a]	....	....	...	....
Para	Diethyl	60	89–90[b]	$C_{11}H_{16}O_2N_2$	13.44	13.21 13.57

[a] A portion of the residue left after acetone had been evaporated was benzoylated with a mixture of benzoyl chloride and dilute sodium hydroxide. A solid formed which was recrystallized from alcohol; m. p. 182°.[18] [b] Purified by dissolving in alcohol. treating with decolorizing carbon, filtering and reprecipitating with water. It was then twice recrystallized from a one to one mixture of benzene and petroleum ether and finally dissolved in glacial acetic acid and reprecipitated with water.

Separation of the **Alkyl Aminophenols** by Treatment of the Reduction Products with **Benzaldehyde.**—After the reduction was complete the volatile solvents were evaporated in *vacuo.* The residue was dissolved in dilute acetic acid. The solution was shaken with a slight excess of benzaldehyde and then extracted with ether. The aqueous solution was then made neutral with sodium carbonate. Any alkylaminophenol which had been formed during the reduction precipitated. These phenols darkened when they were exposed to air and light. All were soluble in acids and alkalies.

TABLE III

EXPERIMENTAL DATA

Mixture reduced Solid	Ketone	Product obtained Yield, %	M. p., °C.	Formula	Nitrogen, % Calcd.	Found
m-Nitrophenol	Acetone	Negl.	.....	......	..	....
p-Aminophenol	Acetone	No	.....	......	..	....
p-Nitrophenol	Methyl ethyl[a]	34	118–119[c]	$C_{10}H_{15}ON$	8.50	8.80 8.68
p-Nitrophenol	Menthone[a]	No	.....	......	..	....
Nitrobenzene	Acetone	No[b]	.....	......	..	....
p-Nitrosophenol	Acetone	54	155–156[d]	$C_9H_{13}ON$	9.27	9.12 9.22

[a] The mixture to be reduced was diluted with methyl alcohol.

[b] No oil precipitated when the acid solution was treated with sodium carbonate, nor could any be extracted with ether. Another portion of the oily residue from the reduction was treated with benzoyl chloride and sodium hydroxide. The solid which formed was recrystallized from alcohol. White platelets were obtained; m. p. 161°. A mixture of this compound with pure benzanilide also melted at 161°. The last portion of the oily residue was distilled. After a small amount of acetone and other low-boiling material had distilled over, the rest all distilled at about 184°,[19] and the temperature of the distilling liquids never rose to the boiling point of N-isopropylaniline.[20]

[c] Recrystallized three times from toluene.

[d] Recrystallized from benzene.

Reduction of a Mixture of p-Nitrophenol and Acetophenone.—A solution of 0.05 mole of *p*-nitrophenol, and 0.05 mole of acetophenone in alcohol was reduced. A precipitate formed. It was filtered off; m. p. 184° with decomposition;[16] yield, 4 g. Water

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[18] Hinsberg and Udranszky, Ref. 6b, give 182° as the m. p. of 2-(benzamino)-phenyl benzoate.

[19] Thorpe, J. Chem. *Soc.*, 37, 221 (1880), gives 184° as the b. p. of aniline.

[20] Pictet and Crepieux, *Ber.*, 21, 1109 (1888), give 209–210° as the b. p. of N-isopropylaniline.

was added to the filtrate and the mixture benzoylated with benzoyl chloride and sodium hydroxide. The solid which formed was recrystallized from alcohol; m. p. 233°.[21]

4-(Isopropylamino)-phenol Hydrochloride.—Dry hydrogen chloride was passed into a solution of 4-(isopropylamino)-phenol in a mixture of chloroform and dry ether. The solid which formed was dissolved in absolute alcohol and reprecipitated with dry ether. The 4-(isopropylamino)-phenol from the reduction of 4-(isopropylidene-amino)-phenol and that formed by the reduction of a mixture of *p*-nitrophenol and acetone both gave hydrochlorides which melted at 189°; a mixture of the two also melted at 189°.

Hydrochloride of the **4-(Isopropylamino)-phenol** Obtained by the Reduction of a Mixture of ***p*-Nitrophenol** and Acetone.—Anal. Calcd. for $C_9H_{14}ONCl$: Cl, 18.91. Found: Cl, 19.31, 19.18.

Hydrochloride of the **4-(Isopropylamino)-phenol** Obtained by the Reduction of **4-(Isopropylidene-amino)-phenol.**—*Anal.* Calcd. for $C_9H_{14}ONCl$: Cl, 18.91. Found: Cl, 18.88.

4-(*Sec*.-alkylamino)-phenol Hydrochloride.—A solution of **4-(*sec*.-alkylamino)**-phenol or its nitroso derivative in concentrated hydrochloric acid was evaporated to dryness *in vacuo* at room temperature. Of course, oxides of nitrogen were evolved when acid was added to the nitroso derivative. The solid residue was dissolved in absolute alcohol and reprecipitated with dry ether. These hydrochlorides had no definite melting point but decomposed when heated.

TABLE IV

EXPERIMENTAL DATA

		Nitrogen. % of chloride	
Substituted phenol dissolved	**Formula**	**Calcd.**	**Found**
4-(*Sec*.-butylamino)-phenol	$C_{10}H_{16}ONCl$	6.96	6.93 6.96
4-(Amyl-3-(nitroso)-amino)-phenol	$C_{11}H_{18}ONCl$	6.51	6.39 6.23

Reduction of a Mixture of ***p*-Nitrophenol** and **Benzaldehyde.—A** solution of 0.1 mole of *p*-nitrophenol and **0.3** mole of benzaldehyde in methanol was catalytically reduced in the usual manner. The reduced solution was then evaporated in *vacuo* to remove methanol. Ether was added to the residue. White crystals remained which decomposed at 184°,[16] were insoluble in water but soluble in acids and alkalies and were darkened by standing in the air in the light. The ethereal filtrate from these crystals was washed with sodium bisulfite and then sodium carbonate in order to remove benzaldehyde and acids. The ether solution was then extracted with dilute hydrochloric acid. During this extraction a solid precipitated. It was treated with dilute sodium carbonate solution and this solution was extracted with ether. Evaporation of the ether left a solid which was recrystallized from 75% alcohol; m. p. 127–128°. The same solid was obtained by addition of sodium carbonate to the extract in hydrochloric acid described above. In that case an oil precipitated which was extracted with ether. This solution was evaporated and the residue was recrystallized from 75% alcohol; m. p. 127–128°.[22]

Anal. Calcd. for $C_{20}H_{19}ON$: N, 4.85. Found: N, 5.05.

Benzoylation of Substituted ***p*-Aminophenols.—A** solution of the substituted *p*-aminophenol in sodium hydroxide was shaken for several minutes with benzoyl chloride. **A** solid benzoate was formed.

Reduction of a Mixture of ***p*-Aminophenol and Benzaldehyde.—A** solution of 0.05 mole of *p*-aminophenol and 0.15 mole of benzaldehyde in 20 cc. of methanol and 50

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[21] Hinsberg and Udranszky, Ref. 6b, give 231" as the m. p. of 4-(benzamino)-phenyl benzoate.

[22] Bakunin, *Gazz. chim.* ital., **II**, 36, 211 (1906); Chem. *Centr.*, **II**, 1413 (1906), gives 127" as the m. p. of 4-(dibenzylamino)-phenol.

TABLE V

EXPERIMENTAL DATA

Substance	M. p., °C.	Recrystallized from	Nitrogen, % Calcd.	Found
4-(Benzoyl-(isopropyl)-amino)-phenyl benzoate, $C_6H_5CON(C_3H_7)C_6H_4OCOC_6H_5$	174–175[a]	EtOH	3.90	3.97
4-(Dibenzylamino-phenyl) benzoate	143–144	Iso-PrOH	3.56	3.84 3.63

[a] Occurred in the form of white needles.

cc. of 1,4-dioxane was reduced. When reduction was complete the solution was evaporated to dryness. An oil remained which was dissolved in ether. The ethereal solution was shaken for some time with an aqueous solution of sodium bisulfite. The ethereal layer was then washed with a solution of sodium carbonate. The ether was then evaporated. An oil remained which solidified. The solid was twice recrystallized from 75% ethyl alcohol. Needle-like almost colorless crystals were obtained, m. p. 127°; yield 73%. A mixture of these crystals with 4-dibenzylaminophenol also melted at 127°.

Anal. Calcd. for $C_{20}H_{19}ON$: N, 4.85. Found: N, 5.07, 5.08.

A study of the condensation which takes place between ketones and aldehydes with *p*-nitroaniline and *p*-phenylenediamine during reduction has also been made and will shortly be submitted for publication.

The author wishes to express his appreciation to Mr. Douglass F. Hayman for many of the analyses which are recorded in this paper.

Summary

1. Catalytic reduction of a mixture of *p*-nitrophenol or *p*-nitrosophenol and an aliphatic ketone led to the formation of 4-(*sec.*-alkyl-amino)-phenols.

2. Various derivatives of 4-(*sec.*-alkyl-amino)-phenols have been prepared.

3. Catalytic reduction of 2,4-dinitrophenol and acetone led to the formation of 2-amino-4-isopropylamino-phenol.

4. There is no appreciable condensation between ketones and any of the following nitro compounds during catalytic reduction: nitrobenzene, #-nitrophenetole, o-nitrophenol, and m-nitrophenol.

5. There was no appreciable condensation between p-nitrophenol and either acetophenone or menthone during catalytic reduction.

6. 4-(Dibenzylamino)-phenol was prepared by the catalytic reduction of a mixture of benzaldehyde and p-nitrophenol, and also of a mixture of benzaldehyde and *p*-aminophenol.

RAHWAY, NEW JERSEY

[CONTRIBUTION PROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ORGANIC ACIDS OF SPINACH, BROCCOLI AND LETTUCE[1]

BY E. K. NELSON AND H. H. MOTTERN

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The value of acids in food metabolism depends upon whether the acid is easily metabolized, as are citric and malic, or difficultly metabolized, as oxalic or benzoic, since by the oxidation of the organic acid radical the alkaline mineral is left in the system and helps to maintain a proper alkaline reserve.

Much work has been done to determine the organic acids of fruits, but little seems to be on record as to their presence in the common vegetables, no doubt for the reason that the acids in fruits are free or partly free, whereas in vegetables they are, for the most part, present as salts.

The examination of certain green vegetables for oxalic acid prompted an extension of the work to include identification of other organic acids present.

Arbenz[2] and Esbach[3] have reported the presence of considerable amounts of oxalic acid in spinach. Arbenz found 0.29% and Esbach 0.32% of oxalic acid in the fresh material.

A more recent investigation by Alice E. Ryder[4] appeared while the present investigation was in progress. In three samples of spinach Ryder found 0.486, 0.652 and 0.692% of oxalic acid.

Examination of Spinach

The spinach used for the present investigation was purchased on the Washington market early in February, 1930.

Oxalic acid was determined by the method of Arbenz.[2] Twenty grams of dry spinach was extracted with 150 cc. of 15% boiling hydrochloric acid, the mixture was filtered, and the filtrate was evaporated to dryness, dissolved in 20 cc. of water and extracted with ether in a perforation ouffit to complete extraction. The residue from the ether was dissolved in water, and ammonia was added until the solution was alkaline. It was then reacidified with acetic acid and precipitated hot with calcium chloride solution. The precipitate was redissolved in hydrochloric acid and reprecipitated as above until the crystals were pure calcium oxalate as determined by the microscope. The precipitate was ignited over the blast lamp and weighed as calcium oxide. By this method the dried spinach was found to contain 3.72% of anhydrous oxalic acid, equivalent to 0.31% on the basis of the fresh material (the spinach contained 8.3% dry matter).

For the separation of the other non-volatile acids of spinach, 500 g. of the dried spinach was extracted with boiling water, and the acids were precipitated from the extract with lead subacetate. The acids recovered from the lead precipitate were allowed to crystallize and filtered from the greater part of the oxalic acid. When esterified the sirupy filtrate afforded 6 g. of crude esters.

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[1] Food Research Division Contribution No. 92.

[2] Arbenz, *Mitt. Lebensm. Hyg.*, **8,** 98 (1917).

[3] Esbach, *Bull. Gen. Ther. Med. Chir.,* 114,385 (1883).

[4] Ryder, *J. Home Econ.,* 22,309 (1930).

Two fractionations at 10 mm. yielded 0.7 g. boiling at 120°, 0.7 g. boiling at 120–140°, and 2.0 g. boiling at 140–160°. The lower fraction, on treatment with hydrazine hydrate, afforded an abundant precipitate of needles of oxalic acid hydrazide, melting at 235°. The intermediate fraction yielded l-malic hydrazide melting at 178–179°. The higher boiling fraction gave two hydrazides, one evidently l-malic hydrazide, crystallizing in nodules, and another crystallizing in clear rosets of prisms which melted at 107°, showing that it was citric hydrazide. It was further identified as citric hydrazide by optical crystallographic examination.[5]

Examination of Broccoli

The broccoli used, described as *Brassica Oleraceae,* var. Botrytis, or sprouting variety, was purchased on the Washington market. As no complete analysis of broccoli has been published, a thorough examination was made.

The buds, leaves and stems were examined separately. The methods of analysis used were those prescribed in "Methods of Analysis" of the A.O.A.C.

An investigation was also made of the organic acids of broccoli according to the ester distillation method.

The results of the analysis of broccoli are given in Table I.

TABLE I

ANALYSIS OF BROCCOLI, *Brassica Oleraceae*

	Buds		Leaves		Stems	
	Fresh, %	Dry, %	Fresh, %	Dry, %	Fresh, %	Dry %
Moisture	88.1		88.3		90.9	
Ether extract	0.74	6.19	0.84	7.17		
Crude fiber	1.42	11.91	1.11	9.45		
Protein	4.39	36.93	4.04	34.41		
Invert sugar		Trace				
Sucrose		None				
Starch	1.30	10.88				
Pentosans	0.91	7.61				
Ash	1.69	14.23	2.41	20.55		
Acid insol. ash	0.028	0.24	0.061	0.52		
P_2O_5	.17	1.39	.12	1.03		
CaO	.30	2.56	.38	3.27		
Ferric and aluminum oxides	.012	0.10	.026	0.22		
Mn_3O_4	.006	.051	.005	0.041		
MgO	.021	.18	.16	1.33		
K_2O	.30	2.51	.34	2.90		
Alkalinity of ash, cc. $N/10$ per 100 g.	93.4	785	144	1485		
Nitrates as KNO_3	0.09	0.76	0.12	1.05	0.25	2.74
Oxalic acid	0.02	0.16	0.02	0.15	0.01	0.11

Oxalic acid was determined by the method of Arbenz.[2]

For the investigation of the non-volatile acids twenty and one-half kilograms of broccoli was extracted with boiling water and the extract concentrated to two liters. After dilution with an equal volume of alcohol, the acids were precipitated with lead subacetate, and after being washed the lead salts were decomposed with sulfuric acid. After removal of the excess of sulfuric acid, the solution of organic acids was concentrated

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[5] Optical examinations were made by G. L. Keenan of the Food, Drug and Insecticide Administration.

to small volume and thoroughly extracted with ether. The residue from the ether was partly crystalline and weighed slightly less than one gram. The crystalline acid, after recrystallization, did not have a sharp melting point, but succinic and oxalic acids were identified in it by optical crystallographic methods.

The acids unextracted by ether were esterified in the usual manner and afforded 26.5 g. of the ethyl esters of organic acids.

The mixed esters were fractionated three times at 10 mm. The following fractions were obtained

1	90–125°	0.9 g.	
2	125–135°	5.1 g.	α_D −10.5°
3	135–145°	0.4 g.	
4	145–155"	1.0 g.	
5	155–165°	1.6 g.	
6	165–170°	10.8 g.	

Residue and loss, 6.7 g.

The hydrazides of the acids were prepared from these fractions and purified. Fractions 1, 2, 3 and 4 yielded *l*-malic hydrazide, melting at 178–179°; fraction 5 was a mixture of ethyl malate and ethyl citrate; fraction 6 yielded citric hydrazide in its hydrated form melting at 104–106°.

The non-volatile acids of broccoli are therefore *l*-malic and citric acids with small amounts of oxalic and succinic acids.

Examination of Lettuce

Thirty-nine and seven-tenths kilos of lettuce, purchased on the Washington market, was dried. yielding 2630 g. of the dried vegetable.

Twenty grams examined by the Arbenz[2] method for oxalic acid yielded 0.164% of oxalic acid, equivalent to 0.01% on the basis of the undried lettuce.

Two and one-half kilos of the dried vegetable was extracted with boiling water and the extract was concentrated and mixed with an equal volume of alcohol. The lead salts were precipitated with lead subacetate, and the acids recovered from the lead precipitate were converted into the ethyl esters; 73.5 g. of crude ethyl esters was obtained. The ester mixture was fractionated three times at 10 mm. Fractions were obtained as follows

1	100–110°	1.0 g.	
2	127–135°	32.5 g.	α_D −10.6°
3	135–145°	0.9 g.	
4	145–155°	1.0 g.	
5	155–165°	1.3 g.	
6	165–170°	24.5 g.	

Residue 5.0 g.

The hydrazides were prepared from these fractions. Fraction 1 yielded *l*-malic hydrazide and a little levulinic hydrazide. Fraction 2 afforded *l*-malic hydrazide, melting at 178–179°, as did also fractions 3 and 4. Fraction 5 was a mixture. Fraction 6 yielded citric hydrazide, hydrated form, melting at 104–106° and identified by optical crystallographic examination.

The proper ester fractions, calculated to *l*-malic and citric acids, show that fresh lettuce contains approximately 0.065% of *l*-malic acid and 0.048% of citric acid.

Summary

Fresh spinach was found to contain 0.31% of oxalic acid. Citric acid and a small quantity of malic acid were separated by the ester distillation method.

Analysis of broccoli shows that the leaves and buds have materially the same composition and nutritive value. Both buds and leaves contain proteins somewhat in excess of that reported in spinach.[6]

The predominating organic acid in broccoli is citric acid. It also contains *l*-malic acid and small amounts of oxalic and succinic acids. The proportion of citric and malic acids is 3:2.

The organic acids of lettuce were found to be oxalic acid, 0.011%, *l*-malic acid, about 0.065%, and citric acid, about 0.048%.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS. IV. DETERMINATION OF THE STRUCTURE OF MIXED BENZOINS BY THE BECKMANN REACTION[1]

BY JOHANNES S. BUCK AND WALTER S. IDE

RECEIVED FEBRUARY 28, 1931 PUBLISHED MAY 6, 1931

The rigid determination of the structure of a number of mixed (unsymmetrically substituted) benzoins would allow important generalizations to be made as to the reactivity of various aromatic aldehydes, and would also contribute to the wider use of benzoins in synthetic work. Up to the present time a few mixed benzoins have been assigned structures, largely on the basis of their production (or the production of the isomer) by the Grignard reaction. Benzanisoin,[2a] benzfuroin[2b] and p-dimethylaminobenzoin[3] have been so determined. In addition, the structure of benzfuroin has been deduced by a Beckmann reaction,[4] that of p-dimethylaminobenzoin by an indirect method,[5] and that of benzanisoin by synthesis from the desoxy compound.[6] The structures of the three foregoing benzoins may therefore be taken as definitely settled, and the authors have taken these compounds as standards in this paper.

For determining the structure of mixed benzoins, the Grignard reaction, although probably trustworthy, is anything but convenient. Indirect

[6] Werner, "Die Pflanzenstoffe, 1911, p. 180.

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[1] Since submitting this paper, a note has appeared by Tiffeneau and Lévy, *Compt. rend.* 192, 287 (1931), in which the structures of some mixed benzoins are determined by fission with potassium hydroxide. The results with benzfuroin, benzpiperoin and benzanisoin agree with those of the present authors. Horbye, Ref. 11, has determined the structures of benzpiperoin and benzanisoin by an oxidation method.

[2a] McKenzie, Luis, Tiffeneau and Weill, *Bull. soc. chim.*, [4] 45, 414 (1929).

[2b] Asahina and Terasaka, *J. Pharm. Soc. Japan*, 494, 219 (1923).

[3] Jenkins, Bigelow and Buck, THIS JOURNAL, 52, 5198 (1930).

[4] Werner and Detscheff. Ber., 38, 69 (1905).

[5] Jenkins, Buck and Bigelow, THIS JOURNAL, 52, 4495 (1930).

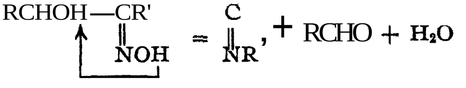
[6] Meisenheimer and Jochelson. Ann., 355, 249 (1907).

methods are of limited application. The authors therefore decided to examine further the reaction of Werner and Detscheff[4] in order to work out a more facile and general method, and found that, with some modifications in technique, the reaction leaves little to be desired from a practical point of view. Seven mixed benzoins (the same as were used in Part III)[7] were investigated, and structures assigned to them and to their oximes.

The Beckmann reaction, using benzenesulfone chloride, does not generally give an amide with benzoin oximes, but a mixture of an aldehyde and a nitrile or isonitrile. This is known as a Beckmann reaction of the second type and is formulated by Werner and Detscheff[4] as follows

$$\begin{array}{l} \mathrm{RCHOH{-}CR'} \\ \ \uparrow \qquad \| \\ \mathrm{HO{-}N} \end{array} = \mathrm{RCHO} + \begin{array}{c} \mathrm{CR'} \\ ||| \\ \mathrm{N} \end{array} + \mathrm{H_2O}$$

(1)



$$\begin{array}{l} \mathrm{RCHOH{-}CR'} \\ \ \uparrow \quad \| \\ \ \ \mathrm{NOH} \end{array} = \begin{array}{c} \mathrm{C} \\ \| \\ \mathrm{NR'} \end{array} + \mathrm{RCHO} + \mathrm{H_2O}$$

(2)

involving in the first case the elimination of water between the two adjacent hydroxyl groups and in the second case the wandering of a hydroxyl group and a radical, with the elimination of a molecule of water. The authors prefer to regard the reaction as taking place by the usual vicinal transposition of the first type, followed by the fission of the enol form of the amide. Oxime (1) would give the amide, RCHOHN=C(OH)R'(RCHOHNHCOR'), which, after the manner of the von Braun fission,[8] would (spontaneously) give RCHO and R'CN, as before. The alternative (improbable) fission between the N and C(OH) groups would give RCN and R'CHO, corresponding, on Werner and Detscheff's views, to the isomeric benzoin. If *trans* groups were concerned, then RCHO and R'N=C would be expected.

In the case of oxime (2) the normal product would be the amide RCHOH-C(OH)=NR' (RCHOHCONHR'), which might lose water between the two hydroxyl groups, giving RCHO and R'N=C.[9] If *trans* groups were involved, RCHO and R'CN (corresponding to oxime (1)) would be formed. Fission between the C(OH) and N groups would give products never observed in this type of reaction.

The conception of the Beckmann reaction involving the transposition of vicinal groups has been attacked by several workers, notably by Meisen-

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[7] Buck and Ide, THIS JOURNAL, 53, 1536 (1931).

[8] Von Braun and Müller, *Ber.*, 39, 2018 (1906), where, for example, benzylbenzamide, with phosphorus pentabromide gives benzyl bromide and benzonitrile.

[9] In this connection the authors have found that mandelic anilide with phosphorus pentachloride gives phenylisonitrile. Werner and Piguet, *Ber.*, 37, 4309 (1904), have obtained mandelic anilide from β-benzoin oxime (*syn*-phenyl) by using benzenesulfone chloride with pyridine. The same oxime, using alkali in place of pyridine, gives benzaldehyde and phenylisonitrile.

heimer (who, however, worked chiefly on benzil oximes). The matter cannot be regarded as settled, and the present authors prefer to interpret their results on the basis of vicinal transposition, or on Werner and Detscheff's theory, both giving the same structure. The reason for so doing is the complete agreement of the structures so deduced with those found by other methods in the three cases cited above.

It will be seen that the aldehyde formed determines the structure of the parent benzoin, while the formation of a nitrile or of an isonitrile discriminates between the two oximes, the *syn*-phenyl oxime giving the isonitrile and the *anti*-phenyl oxime the nitrile. For practical purposes only the aldehyde need be isolated to determine the position of the carbonyl group in the benzoin. Either oxime, or indeed a mixture of the two, could be used for this purpose.

The benzoins examined in the present paper, together with the desoxy compounds derived from them (as main product) by reduction, are listed below (letters as in Part III, Ref. 7).

$ClC_6H_4CHOHCOC_6H_3(OMe)_2$	A	$ClC_6H_4CH_2COC_6H_3(OMe)_2$
$ClC_6H_4CHOHCOC_6H_4OMe$	B	$ClC_6H_4CH_2COC_6H_4OMe$
$ClC_6H_4CHOHCOC_6H_4NMe_2$	C	$ClC_6H_4CH_2COC_6H_4NMe_2$
$ClC_6H_4CHOHCOC_6H_3O_2CH_2$	D	$ClC_6H_4CH_2COC_6H_3O_2CH_2$
$C_6H_5CHOHCOC_6H_4OMe$	E	$C_6H_5COCH_2C_6H_4OMe$
$C_6H_5CHOHCOC_6H_3O_2CH_2$	G	$C_6H_5CH_2COC_6H_3O_2CH_2$
$C_6H_5CHOHCOC_6H_4NMe_2$	H	$C_6H_5CH_2COC_6H_4NMe_2$

In the majority of cases the desoxy compound is formed by the replacement of the CHOH group by CH_2. The case of benzoin E shows that the reduction is not simple and that the hydrobenzoin or the isohydrobenzoin is involved[10] and that it is not permissible to infer the structure of the benzoin from that of the desoxy compound produced by reduction.

It will be seen that, so far as they go, the results obtained support Hörbye's[11] view that the CHOH group takes the position adjacent to the unsubstituted phenyl group. To this group may now be added the o-chlorophenyl group. The results are at variance with some of Staudinger's[12] views but support the contentions of Jenkins.[3,5]

Experimental

Oximes.—Three general methods were used to prepare the oximes of the mixed benzoins. (1) The benzoin was allowed to stand in alcoholic solution at room temperature with hydroxylamine acetate and the product precipitated by gradual addition of water. (2) The benzoin was warmed on the bath with hydroxylamine and excess of sodium hydroxide, all in alcoholic solution, usually for three hours. The oxime was precipi-

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[10] Orékhoff and Tiffeneau, *Bull soc. chim.*, [4] 37, 1410 (1925).

[11] Ch. Horbye, "Dissertation," Dresden, 1917. Cf. Tiffeneau and Lévy, footnote.

[12] Staudinger, *Ber.*, 46, 3530, 3535 (1913).

tated by carbon dioxide. This method is useful when the benzoin is sparingly soluble in alcohol. (3) The benzoin, in pyridine solution, was warmed on the bath for three hours with hydroxylamine hydrochloride and the reaction mixture then gradually diluted with water.

The method was selected by trial, yield being the consideration. In no case was more than one oxime isolated, although the isomer was carefully sought for. When the yield was mediocre, the remainder of the material was recovered as a thick gum, probably containing unchanged starting material and decomposition products as well as the isomeric oxime. It is quite possible that the isomer could be obtained by other methods. All of the oximes obtained were of the a-(anti-phenyl) form, except that from p-dimethylaminobenzoin, which was the β-isomer. The oximes were recrystallized from alcohol, in which they are moderately soluble, until pure. As a rule, they are sparingly soluble in other solvents, except pyridine. The compounds are tabulated below.

TABLE I

OXIMES

Benzoin	No. in Pt. III	Form	No. of prep.	Yield. %	M. p., °C.	Appearance	Formula	Nitrogen analyses Calcd.	Nitrogen analyses Found	Structure of benzoin (*v. s.*)	No. of oxime
1-Chloro-α-hydroxybenzyl-3′,4′-dimethoxyphenyl ketone (1-chlorophenyl-3′,4′-dimethoxybenzoyl carbinol)	1	a	2	99	149	White rhombs	$C_{16}H_{16}O_4NCl$	4.35	4.53	A	A
1-Chloro-α-hydroxybenzyl-4′-methoxyphenyl ketone (1-chlorophenyl-4′-methoxybenzoyl carbinol)	2	a	1	99	144	Glittering crusts[a]	$C_{15}H_{14}O_3NCl$	4.80	4.97	B	B
1-Chloro-α-hydroxybenzyl-4′-dimethylaminophenyl ketone (1-chlorophenyl-4′-dimethylaminobenzoyl carbinol)	3	a	3	80	156-158	Yellow rhombs	$C_{16}H_{17}O_2N_2Cl$	9.19	9.08	C	C
1-Chloro-α-hydroxybenzyl-3′,4′-methylenedioxyphenyl ketone (1-chlorophenyl-3′,4′-methylenedioxybenzoyl carbinol)	4	a	2	81	149	White rhombs	$C_{15}H_{12}O_4NCl$	4.58	4.64	D	D
a-Hydroxybenzyl-4′-methoxyphenyl ketone[1] (phenyl-4′-methoxybenzoyl carbinol)	5	a	1	68	140	Crusts of thin prisms	$C_{15}H_{15}O_3N$	5.44	5.47	E	E
α-Hydroxybenzyl-3′,4′-methylenedioxyphenyl ketone (phenyl-3′,4′-methylenedioxybenzoyl carbinol)	6	a	1	50	168	Crusts of prisms[a]	$C_{15}H_{13}O_4N$	5.16	5.09	G	G
a-Hydroxybenzyl-4′-dimethylaminophenyl ketone (phenyl-4′-dimethylaminobenzoyl carbinol)	7	β	2	57	140	Glittering crusts[o]	$C_{16}H_{18}O_2N_2$	10.36	10.60	H	H

[a] Form obscure.

Beckmann Reaction.—The Beckmann reaction was carried out in alkaline (sodium hydroxide) solution, using benzenesulfone chloride as the transforming agent. The chloride was added in portions to the alkali–oxime mixture, the whole being shaken vigorously and care being taken that the mixture remained alkaline. The temperature was not allowed to rise more than a few degrees. The reaction mixture was shaken until the chloride had disappeared, then cooled and the oily layer exhaustively extracted with ether, the extract dried over sodium sulfate and the ether driven off. The oil remaining was fractionated under low pressure, using a fine capillary. When benzaldehyde was present, this was removed at 10-mm. pressure, and the pressure then lowered to 0.5–1.0 mm. and the second product distilled off. This usually solidified in the receiver. In other cases (*o*-chlorobenzaldehyde) the oil was all fractionated at 0.5–1.0 mm. The fractions, which, however, were usually sharply separated, were redistilled if necessary under reduced pressure. Benzaldehyde was identified by its properties and by its conversion into benzoin (mixed melting point determinations). o-Chlorobenzaldehyde, after purification via the bisulfite compound, was identified by its properties and by mixed melting point determinations of its oxime with 2-chlorobenz-anti-aldoxime. The nitriles were identified by mixed melting point determinations with the authentic nitrile when this was available, but they were always hydrolyzed, by the Radziscewski[13] method, to the amide and identified by properties and by mixed melting point determinations with the authentic amide.

It is doubtful whether an isonitrile odor (cf. Ref. 4) is of much significance. Its presence in the case of oximes D and E must be ascribed to a side reaction or (unlikely) to a trace of the other oxime. In the case of oxime H the odor was intense, but it was not possible to isolate the isonitrile. Werner and Detscheff[4] encountered the same difficulty. The absence of any nitrile (obtained without difficulty from oxime C) is evidence for the-formation of the isonitrile. This observation also answers the possible objection that the nitriles might be formed from the isonitriles by distillation, although this is unlikely at the temperatures to which

TABLE II

BECKMANN REACTION

Oxime	Taken, g.	1st Fraction Name	G.	%	2d Fraction Name	G.	%
A	20.0	o-Chlorobenzaldehyde	6.8	78	Veratronitrile	6.2	61
B	15.0	o-Chlorobenzaldehyde	7.0	96	Anisonitrile	6.7	98
C	20.0	o-Chlorobenzaldehyde	7.1	77	*p*-Dimethylaminobenzonitrile	7.9	83
D	20.0	o-Chlorobenzaldehyde	6.0	65	Piperonitrile	5.4	56
E	15.0	Benzaldehyde	5.8	94	Anisonitrile	7.2	93
G	12.0	Benzaldehyde	4.3	92	Piperonitrile	6.4	98
H	12.0	Benzaldehyde	4.1	86	[*p*-Dimethylaminophenylisonitrile]	0	

Oxime	Isonitrile smell	Resin residue, g.	Reaction mixture
A	–	Large	Brown-black, some dirt
B	–	0.5	Light yellow, clean
C	–	5.2	Green-black
D	+	Large	Dark brown, much dirt
E	+	2.2	Yellow
G	–	0.3	Little color
H	++++++	Large	Brown-black, much dirt

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[13] Technique of Rupe and Majewski, Ber., 33,3401 (1900), using somewhat stronger peroxide.

they were exposed (the nitriles distil at about 120° below 1.0 mm.). In the case of oximes A, D and H much black, amorphous matter was formed in the reaction. Some of this was separated from the ether extract; the rest appeared as residue in the distilling vessel. The residue is not formed by decomposition during distillation, as can be seen by the small residues from oximes B and G. The results are given in tabular form.

Summary

The structures of seven mixed benzoins, obtained by the usual potassium cyanide condensation, have been determined by means of a second-type Beckmann reaction. The results, interpreted according to Werner's views of the Beckmann rearrangement, give structures in agreement with those determined by independent methods.

TUCKAHOE, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

CROTYL ETHERS OF PHENOL

BY CHARLES D. HURD AND FRANK L. COHEN

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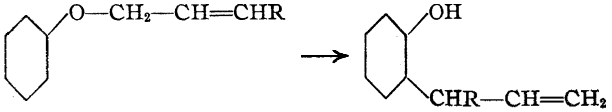
When allyl aryl ethers are heated, rearrangement into o-allylphenols usually occurs with ease. The same has been shown to be true in some cases when substituted allyl aryl ethers undergo pyrolysis. Only the following groups seem to have received study in this connection: (1) crotyl, $CH_3CH=CHCH_2-$, with phenol,[1,2] β-naphthol,[2] and hydroxynaphthoquinone;[3] *(2)* cinnamyl, $C_6H_5CH=CHCH_2-$, with phenol;[4] **(3)** a-methylcrotyl, $CH_3CH=CH-CH(CH_3)-$, with phenol;[5] (4) γ-methylcrotyl, $(CH_3)_2C=CHCH_2-$, with phenol;[6] (5) α,α-dimethylallyl, $CH_2=CH-C(CH_3)_2-$, with phenol;[7] (6) geranyl, $CH_2=C(CH_3)-(CH_2)_3-C(CH_3)=CHCH_2-$, with catechol.[8]

The first four groups undergo rearrangement of the type exemplified in the equation



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[1] Claisen and Tietze, *Ber.,* 59, 2350 (1926).

[2] Von Braun and Schirmacher, *ibid.,* 56, 544–5 (1923).

[3] Fieser, THIS JOURNAL, 48, 3205 (1926).

[4] Claisen, Kremers, Roth and Tietze, *Ann.,* 442, 233 (1925).

[5] Claisen and Tietze, *Ber.,* 58, 277 (1925); Claisen, Kremers, Roth and Tietze, *Ann.,* 442, 226 (1925).

[6] Claisen and Tietze, Ref. 5; the reference by these authors in *Ber.,* 59,2349 (1926), gives a conflicting notation and evidently refers to $CH_2=CH-C(CH_3)_2-O-C_6H_5$.

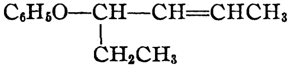
[7] Claisen, Kremers, Roth and Tietze, J. *prakt. Chem.,* 105, 67 (1922).

[8] Kawai, *Sci. Papers Inst. Phys. Chem. Research, 6,* 53 (1927).

With $C_6H_5—O—C(CH_3)_2CH{=}CH_2$, however, the pyrolysis leads to isoprene and phenol.

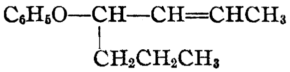
In the case of a-methylcrotyl phenyl ether, we corroborated the results of Claisen[4] in all essential details. To extend this study, the following substituted allyl ethers of phenol were investigated

a-Ethylcrotyl phenyl ether



$$C_6H_5O—\underset{\displaystyle CH_2CH_3}{\underset{|}{C}H}—CH{=}CHCH_3$$

α-*n*-Propylcrotyl phenyl ether



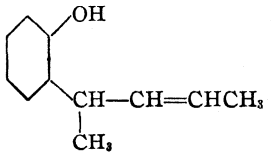
$$C_6H_5O—\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{C}H}—CH{=}CHCH_3$$

α,α,γ-Trimethylcrotyl phenyl ether, $C_6H_5O—C(CH_3)_2CH{=}C(CH_3)_2$

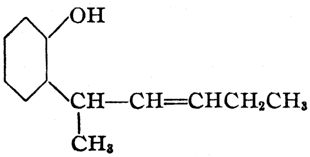
a-n-Propylallyl phenyl ether, $C_6H_5O—CH(C_3H_7(n))—CH{=}CH_2$, was also synthesized and studied. This will be reported in a later paper.

Synthesis of these ethers was effected by refluxing phenol, potassium carbonate and the corresponding crotyl chloride in an ether–acetone solution for several hours. The a-ethyl- and a-propylcrotyl ethers could be purified by vacuum distillation but the trimethylcrotyl ether underwent pyrolysis with such treatment. All of these ethers were liquids.

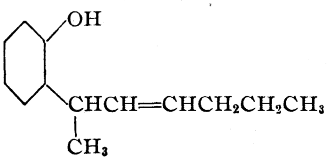
Pyrolysis.—Normal rearrangements of a-methyl-, a-ethyl- and α-*n*-propylcrotyl phenyl ethers occurred when they were heated. A temperature of 200° sufficed for the first two, and with the third an exothermic reaction was noticed at 228°. The products formed in the three cases, respectively, were o-a-methylcrotylphenol (I), *o*-α,δ-dimethylcrotylphenol (11), and o-a-methyl-6-ethylcrotylphenol (III). The yields in the three cases were **83,** 75 and **52%.** All of these phenols were very viscous oils and were alkali-soluble.



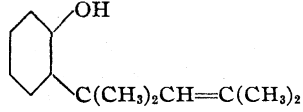
I



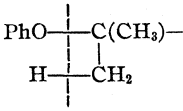
II



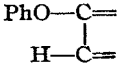
III

For a similar type of rearrangement, trimethylcrotyl phenyl ether should have given rise to *o*-α,α,γ-trimethylcrotylphenol,  but none was found. Instead, the reaction followed an entirely different course, yielding phenol, 2,4-dimethylpentadiene-1,3 and tar. The yield of the diene was about 33%.

The course of pyrolysis of these crotyl ethers is sufficiently analogous to the course of pyrolysis of similar allyl and propargyl ethers which have already been studied that two generalizations may be made. (1) Rearrangement into an ortho or para substituted phenol is the chief effect in the heating of allyl or crotyl aryl ethers, and the same holds if the allyl or crotyl groups contain one alpha substituent. Thus, compounds of the types $Ar—O—CH_2CH{=}CH_2$, $Ar—O—CH_2CH{=}CHR$, $Ar—O—CHRCH{=}CH_2$ and $Ar—O—CHRCH{=}CHR$ may be expected to rearrange if there is an available o- or *p*-position in the aromatic nucleus. (2) When α,α-disubstituted allyl, crotyl or propargyl aryl ethers are heated, they undergo scission into a phenol and a hydrocarbon. These ethers of phenol have been studied: α,α-dimethylallyl,[7] trimethylcrotyl (this paper), and trimethylpropargyl.[9] All of these contain the grouping $Ph—O—C(CH_3)_2—z$ and all pyrolyze into $PhOH + CH_2{=}C(CH_3)—z$. It might be argued that the reason for hydrocarbon formation in these cases is the presence of the hydrogens on the a-methyl substituent, thereby making it easy for the phenol to be detached, thus



$$\begin{array}{l} PhO\,\vdots\,C(CH_3)—z \\ \quad\ \ \vdots\quad | \\ H\,\vdots\,CH_2 \end{array}$$

However, the alpha monosubstituted allyl and crotyl ethers with a similar structure fail to give this scission into phenol and hydrocarbon. Furthermore, triphenylpropargyl phenyl ether,[9] with no structure of the  $\begin{array}{l} PhO—C{=} \\ \quad\ \ | \\ H—C{=} \end{array}$ type, also yields phenol and a hydrocarbon on pyrolysis.

The rearrangement of aryl crotyl ethers is a special case of the "three-carbon system": $xCH_2—CH{=}CHR \longrightarrow CH_2{=}CH—CHxR$. Undoubtedly the mechanisms of both[10] are similar. In turn, the three-carbon system is but a special case of the general formulation: $xE—E{=}E' \longrightarrow E{=}E—E'x$, wherein E represents any element such as C, N, O or S. The union between E and x is a loose one. Applied to the phenyl crotyl ethers, the products of the reaction seem to be most readily explained by assuming an initial scission at the position of weakness, $PhO\,\vdots\,\text{crotyl}$, into radicals which immediately readjust themselves. With a primary or secondary crotyl radical, the PhO— radical rearranges to  before attaching

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[9] Hurd and Cohen, THIS JOURNAL, 53, 1068 (1931).

[10] For a survey of the three-carbon system, see "Annual Reports on the Progress of Chemistry," 25, 119–130 (1929).

itself to the y-crotyl carbon. If the crotyl group is tertiary, the PhO- radical selects a hydrogen from the crotyl radical, giving phenol and a hydrocarbon.

The triphenylmethyl alkyl ethers[11] resemble the crotyl (or allyl) aryl ethers in being far less stable than most other ethers. With them, heat induces a rupture of the carbon-to-oxygen bond on the side of the radical with low electron attraction, namely, the triphenylmethyl radical. Evidence for this is the isolation of triphenylmethane and an aldehyde (or ketone) as pyrolytic products. Undoubtedly, the initial effect of heat with both series of ethers (Ar—O—crotyl and R—O—CPh_3) is very similar, if not identical.

Experimental Part

The β-unsaturated alcohols were synthesized by literature methods. Pentene-3-ol-2,[12] hexene-2-ol-4[13] and heptene-2-ol-4 were prepared by the interaction of crotonaldehyde in the cold with a Grignard reagent (Me-, Et- and n-Pr-MgBr, respectively). The yields of the three alcohols were 47, 60 and 68%. 2,4-Dimethylpentene-3-ol-2 was prepared in 30% yield[14] from mesityl oxide and methylmagnesium iodide. Simultaneously, a 57% yield of 2,4-dimethylpentadiene-1,3 was realized.

Chlorides from the Alcohols.—2-Chloropentene-3 was synthesized[15] by interaction of the alcohol (in absolute ether) with phosphorus trichloride. The reaction was left for three days at room temperature, whereupon a 37% yield was realized. In the preparation[13,16] of 4-chlorohexene-2 and 4-chloroheptene-2, phosphorus pentachloride was used instead of the trichloride. The yields were 54 and 73%, respectively.

Trimethylcrotyl chloride (2,4-dimethyl-2-chloropentene-3) was too unstable for purification by distillation. It was prepared in solution as follows. To 5.0 g. of 2,4-dimethylbutene-3-ol-2 dissolved in 25 cc. of dry ether was added 2.0 g. of phosphorus trichloride. The reaction mixture was kept at ice temperature for an hour and then it was left for two days at room temperature. The ether solution was decanted from the phosphorus acid layer, after which it was washed with water and dried over sodium sulfate. This solution of trimethylcrotyl chloride was used in subsequent reactions with no further purification, since all attempts to distil it gave almost quantitative yields of 2,4-dimethylpentadiene-1,3.

Synthesis of the Phenyl Ethers

a-Methylcrotyl phenyl ether was prepared by Claisen's method.[5] Our yield of the ether from 2-chloropentene-3 was only 30% instead of 40%, and our boiling point at 12 mm. was 103–104° instead of 96–98°. A weight of tarry material was formed which was equal to the weight of the desired ether.

a-Ethylcrotyl Phenyl Ether.—To a solution of 10 g. of 4-chlorohexene-2 (0.08 mole) in 100 cc. of dry ether was added 10 g. of anhydrous potassium carbonate, 40 cc. of pure

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[11] Norris and Young, THIS JOURNAL, 52, 754 (1930).

[12] Courtot, *Bull. soc. chim.*, [3] 35, 657 (1906). See also, Baudrenghien, *Bull. sci. acad. roy. Belg.*, 15, 53 (1929).

[13] Reif, *Ber.*, 39, 1603 (1906).

[14] Grignard, *Compt. rend.*, 130, 1324 (1898); von Fellenberg, *Ber.*, 37, 3578 (1904); Kohler, *Am. Chem. J.*, 31, 647 (1904); 38, 514 (1907).

[15] Reif, *Bm.*, 41, 2741 (1908).

[16] Reif, Ref. 15. p. 2742.

acetone and 7.6 g. of phenol (0.09 mole). The reaction mixture was refluxed vigorously for eleven hours. Water was then added to dissolve the salts and to remove some of the acetone and excess phenol. The ether solution was washed with dilute alkali until it was free from phenol. After drying over calcium chloride, the solution was distilled at reduced pressure. Four grams of the unreacted chloride, b. p. 50–53° at 15 mm., 4.2 g. of a-ethylcrotyl phenyl ether, b. p. 116–118° at 15 mm., and 1.8 g. of *o*-α,δ-dimethylcrotylphenol, b. p. 140–143° at 15 mm., were obtained. The 4.2 g. yield of the ether is a 30% yield.

Anal. Subs., 0.1512, 0.1413: CO_2, 0.4525, 0.4216; H_2O, 0.1240, 0.1157. Calcd. for $C_{12}H_{16}O$: C, 81.75; H, 9.15. Found: C, 81.4, 81.5; H, 9.11, 9.10.

a-n-Propylcrotyl Phenyl Ether.—A mixture of 20 g. of 4-chloroheptene-2 (0.14 mole), 40 cc. of pure acetone, 26 g. of potassium carbonate (0.2 mole), 100 cc. of dry ether and 16.8 g. of phenol (0.2 mole) was placed in a liter round-bottomed flask and refluxed vigorously for six hours. Water was then added, the ether layer separated and washed with small portions of normal alkali, dried over calcium chloride and fractionated. Propylcrotyl phenyl ether, b. p. 153–154° at 23 mm., was obtained as a colorless viscid oil, which almost immediately turned to a dark red on cooling. The tarry residue decomposed on further heating. The yield was 17.4 g., or 65%.

Anal. Subs.. 0.1408: CO_2, 0.4219; H_2O, 0.1197. Calcd. for $C_{13}H_{18}O$: C, 82.04; H, 9.54. Found: C, 81.8; H, 9.44.

α,α,γ-Trimethylcrotyl Phenyl Ether.—To the ether solution which contained the trimethylcrotyl chloride (see above) was added 25 cc. of acetone, 5.0 g. of potassium carbonate and 3.7 g. of phenol. This was refluxed for several hours and 50 cc. of ether was added. The ether solution was then washed with dilute sodium hydroxide and water, dried over sodium sulfate and carefully distilled. After removing the ether and the 2,4-dimethylpentadiene-1,3 which was formed simultaneously, an almost colorless but quite viscous oil remained. Its index of refraction n_D^{20} was 1.3047. The oil did not distil at 150" and 1.5 mm., whereas above 150" decomposition ensued.

Mol. wt. Subs., 0.2114; benzene, 21.96 g.; freezing point lowering, 0.240°. Calcd. for $C_{13}H_{18}O$: mol. wt., 190.1. Found: 189.0.

Pyrolysis of the Ethers

From 2 to 10 g. of the ether specimens was placed in a side-arm test-tube or in a small distilling flask which was connected with a small condenser. In turn, this was attached to a receiver which was immersed in an ice–salt bath. A thermometer was extended into the ether, and the reaction tube was heated by immersion in an oil-bath.

With a-methylcrotyl phenyl ether, a temperature of 200° was maintained for one hour. The pyrolytic mixture was then cooled, dissolved in ether and the alkali-soluble material washed out with 5% sodium hydroxide. The alkali-soluble material was then obtained fairly pure by acidifying the alkaline solution. The yellowish oil which resulted was ether-extracted, dried and distilled. o-a-Methylcrotylphenol was a colorless, viscous oil with a strong phenolic odor. The boiling point of 120–121" at 11 mm. corresponded to that given by Claisen.[5] The yield from 4 g. was 3.3 g., which is 83% of the theoretical.

α-Ethylcrotyl Phenyl Ether.—Four grams of this ether was heated slowly until the temperature was 200–205°. At this point the ether darkened appreciably and seemed to reflux slightly. No volatile material was evolved. The temperature was maintained for thirty minutes without any further apparent change. After cooling, the reaction product was dissolved in 50 cc. of ether and washed with dilute alkali. The alkaline solution was acidified and a red oil separated. The reaction product was then ex-

tracted with more alkali until no more alkali-soluble material remained. Four extractions with **10-cc.** portions of normal sodium hydroxide solution were **sufficient.** The alkali-soluble material, which was obtained as an oil when acid was added, was extracted with ether, dried, and the solution distilled.

o-α,δ-Dimethylcrotylphenol was obtained as a red oil. At **15 mm.** it boiled at **143–145°.** The **yield** was **3.1** g., or 75%.

Anal. Subs., **0.1030, 0.1650: CO_2, 0.3090, 0.4958; H_2O, 0.0843, 0.1343. Calcd.** for $C_{12}H_{16}O$: C, **81.75;** H, **9.10.** Found: C, 81.9, 81.8; H, 9.10, 8.98.

α-*n*-Propylcrotyl Phenyl Ether.—A **9.5-g.** sample of this ether was pyrolyzed. At **228–230°** rearrangement occurred exothermically. No volatile distillate was observed. After continued heating for one-half hour, the pyrolyzed mixture was fractionally distilled and 5.2 g. of alkali-soluble material, b. p. 154–155° at 14 mm., was obtained. Also, **2.1** g. of unchanged ether, b. p. 143–145° at **14** mm., was recovered. The pyrolyzed material, α-methyl-δ-ethylcrotylphenol, $HO—C_6H_4—CH(CH_3)—CH{=}CHCH_2CH_2CH_3$ was completely alkali-soluble. It was light yellow in color and very viscous. The yield was 54% of the theoretical value.

Anal. Subs., **0.1614, 0.1531: CO_2, 0.4853, 0.4595; H_2O, 0.1375, 0.1309.** Calcd. for $C_{13}H_{18}O$: C, **82.04;** H, **9.54.** Found: C, 82.0, 81.9; H, **9.46, 9.49.**

α,α,γ-Trimethylcrotyl Phenyl Ether.—Two grams of **α,α,γ-trimethylcrotyl** phenyl ether was heated at such a rate that the difference in temperature between the bath and the ether did not exceed 5°. At 150° the ether showed an appreciable darkening. At **160–170°** there was an evolution of vapor which was condensed and collected in a small receiving flask. The material in the test-tube reaction flask rapidly became darker. The temperature of **160–170°** was maintained for half an hour until evolution of the volatile material ceased. The residual material in the reaction tube was a thick black tar after it had cooled.

The volatile distillate was shown to be 2,4-dimethylpentadiene-1,3.[17] Its boiling point was **92–93'.** The yield of this material was **0.3 g.,** or **33%** of the theoretical. The tarry residue was extracted with small portions of normal alkali, the **alkaline** extract acidified and treated with bromine water until no more bromine was absorbed. Half a gram of **tribromophenol** was obtained, which corresponded to **0.2** g. of phenol. No other alkali-soluble material was isolated.

Summary

The following ethers of phenol have been synthesized and studied: **α-methylcrotyl,** a-ethylcrotyl, a-n-propylcrotyl and a,a,y-trimethylcrotyl. The first three of these ethers rearranged into phenolic isomers on heating, namely, into o-a-methylcrotylphenol, *o*-α,δ-dimethylcrotylphenol, and o-ar-methyl-6-ethylcrotylphenol. The trimethylcrotyl ether was less stable than the others and it pyrolyzed into phenol and 2,4-dimethylpentadiene-1,3.

It was pointed out that the substituted **allyl aryl** ethers with the grouping $Ar—O—CH_2—C{=}C$ or $Ar—O—CHR—C{=}C$ may be expected to rearrange on heating, whereas with a grouping such as $Ar—O—CR_2—C{=}C$ pyrolysis leads to phenol (ArOH) and a hydrocarbon.

EVANSTON, ILLINOIS

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[17] Von **Fellenberg,** Ber., **37,3578 (1904).**

[CONTRIBUTION PROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

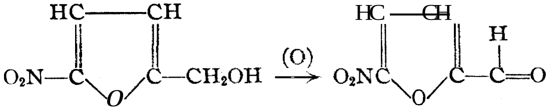
NITROFURFURYL ALCOHOL

BY HENRY GILMAN AND GEORGE F. WRIGHT

RECEIVED MARCH 2, 1931 PUBLISHED MAY 6, 1931

Introduction

In continuation of studies on direct substitutions of the furan nucleus, a first nitrofurfuryl alcohol has been prepared. The synthesis has been effected by the nitration of furfuryl acetate, followed by hydrolysis of the nitro ester to the nitro alcohol. The nitrofurfuryl alcohol can be oxidized to the recently prepared nitrofurfural.[1]



The nitro group in nitrofurfural has been placed provisionally[2] in the 5 position. It is highly significant that the aldehydic group and the alcoholic (acetate) group orient to the same position. Very probably the mode of substitution in both cases is that described earlier, namely, a 1,4-addition to a conjugated system.[3] Again,' the nitro group has a marked stabilizing effect on the furan nucleus.

Experimental Part

Nitration of **Furfuryl** Acetate.—To 286 g. of acetic anhydride, kept at a temperature below −5" is added dropwise 87.4 g. (1.38 moles) of fuming nitric acid (sp. gr. 1.61). Then 70 g. (0.5 mole) of furfuryl acetate[4] dissolved in 102 g. of acetic anhydride is added, with stirring and at −20°, to the nitrating mixture.[5] When addition is complete the reaction is stirred for one hour at −20°, and then poured upon cracked ice. Sodium hydroxide solution, together with ice to maintain the low temperature, is added with vigorous stirring until the solution is exactly neutral. The oil which separates is drawn off and the solution extracted once with about 700 cc. of ether. The combined oil and ether extract is treated with about 200 cc. of pyridine; after a few hours the ether is evaporated, and the residue diluted with water and chilled. Thereupon, the oil which separates becomes solid, and gives 55 g., a 59.5% yield, of nitrofurfuryl acetate melting at 40°. Crystallization from an alcohol–water solution gives pure white crystals melting at 47°.

Anal. Calcd. for $C_7H_7O_5N$: N, 7.57. Found: N, 7.46.

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[1] Gilman and Wright, THIS JOURNAL, 52, 2550, 4165 (1930).

[2] The definite position of this and other substituents is being determined by a miscellany of methods including an absolute method of orientation, concerning which reference might be made to a recent study by Gilman and Wright, ***Iowa State College J. of Sci.***, 5, 85 (1931).

[3] Gilman and Wright, THIS JOURNAL, 52,3349 (1930).

[4] Prepared in accordance with the procedure described in "Organic Syntheses," 1927, Vol. VII, p. 44.

[5] The temperature was maintained by chilling with a solid carbon dioxide–furfural mixture.

The direct nitration of the so-called water-insoluble form of furfuryl alcohol proceeds smoothly, but decomposition sets in on subsequent treatment with pyridine.[1] Apparently nitrofurfuryl nitrate is among the products which are being investigated.

Hydrolysis of Nitrofurfuryl Acetate.—Eighteen and one-half g. (0.1 mole) of nitrofurfuryl acetate is refluxed for twenty minutes with 200 cc. of 5% sulfuric acid. The solution is chilled and filtered by suction to remove 0.2 g. of an as yet unidentified compound[6] melting at 73°. The filtrate is extracted thrice with 50-cc. portions of ether and the combined ether extracts are dried over sodium sulfate. The residue, after removal of the ether, is distilled under reduced pressure (157°, 8 mm.), to give a yellow oil which solidified overnight to the nitrofurfuryl alcohol melting at 32°. The yield is 9–10 g. or 49–55%.

Anal. Calcd. for $C_5H_5O_4N$: C, 41.95; H, 3.52. Found: C, 41.96; H, 3.76.

Oxidation of Nitrofurfuryl Alcohol.—The nitrofurfuryl alcohol was oxidized by heating for two days at 40–50° with a mixture of manganese dioxide and 50% sulfuric acid. The ether extract from this oxidation gave nitrofurfural melting at 36°. This showed no depression in a mixed melting point determination with an authentic specimen.'

The authors are grateful to R. R. Burtner for assistance in this study. He has shown that furfuryl chloride and furfuryl methyl ether also undergo ready substitution, the chloromethyl and alkoxymethyl groups orienting like the acetate group.

Summary

The first nitrofurfuryl alcohol has been prepared by the hydrolysis of nitrofurfuryl acetate, which was obtained by the direct nitration of furfuryl acetate. The nitro group markedly stabilizes the furan nucleus.

AMES, IOWA

[194TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, AND THE MICROANALYTICAL LABORATORY, FOOD AND DRUG ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

THE IDENTIFICATION OF PHENOLS AS THE ESTERS OF 3,5-DINITROBENZOIC ACID

BY MAX PHILLIPS AND GEORGE L. KEENAN

RECEIVED MARCH 4, 1931 PUBLISHED MAY 6, 1931

In connection with an investigation on the chemistry of lignin which one of the authors has been conducting, an occasion arose requiring the identification of the phenols produced when lignin is subjected to destructive distillation or is distilled with zinc dust in an atmosphere of hydrogen. Attempts were made to prepare the usual derivatives of phenols such as the benzoyl derivatives, the phenyl, diphenyl and α-naphthyl urethans, and the *p*-nitrobenzyl ethers, but all these were found to be liquid at room temperature and therefore unsuitable for the purpose of identification. It was found, however, that 3,5-dinitrobenzoyl chloride condensed with the phenols under investigation and yielded products which could be

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[6] The same compound has been isolated in small quantities from the direct nitration of water-insoluble furfuryl alcohol in acetic anhydride.

readily purified by crystallization. The 3,5-dinitrobenzoyl chloride was first used as a reagent for the identification of alcohols[1] and has been applied by Brown and Kremers[2] to the identification of phenols. The method prescribed by these investigators is; however, difficult to carry out, particularly when only a small quantity of a phenolic substance is available.

In this paper a new and simple method for the preparation of the 3,5-dinitrobenzoyl derivatives of phenols is described. Some of the more important physical properties of these derivatives, including the data on the optical properties of the crystals, are recorded.

Experimental

Materials Used.—The 3,5-dinitrobenzoyl chloride used in all our experiments was obtained from the Eastman Kodak Company.

Phenols.—All the phenols except those listed below were obtained from the Eastman Kodak Company.

Phenol.—This was the regular U. S. P. product

5-Hydroxy-1,3-dimethylbenzene.—This was prepared through the diazo reaction from 5-amino-1,3-dimethylbenzene.

Thymol.—This was the U S. P. product.

Isoeugenol.—This was a Kahlbaum product.

Creosol (**1-Methyl-3-methoxy-4-hydroxybenzene**).—The creosol was synthesized from vanillin by the application of the Clemensen[3] reduction method. The procedure was briefly as follows. To 20 g. of vanillin and 400 cc. of hydrochloric acid (200 cc. of hydrochloric acid *d* 1.19 and 200 cc. of water), 100 grams of amalgamated zinc was added, and the mixture was boiled under a reflux condenser for eight hours. The reaction product was allowed to cool to room temperature, and extracted with ether. The ether solution was extracted with a solution of sodium bisulfite, dried over anhydrous sodium sulfate, and the ether distilled off. The residue was fractionally distilled, and the fraction which distilled over at 219–221° was retained; yield, 5 g. (27.6%). A methoxyl determination gave the following results.

Anal. Subs., 0.1254: AgI, 0.2111. Calcd. for $C_8H_{10}O_2$: CH_3O, 22.46. Found: CH_3O, 22.23.

1-*n*-Propyl-3-methoxy-4-hydroxybenzene.—This was prepared by the catalytic reduction of eugenol. The procedure was as follows. One-tenth of a mole of eugenol (16.4 g.) was dissolved in 150 cc. of 95% ethanol, 0.2 g. of platinum catalyst was added (prepared according to the directions given by Adams, Voorhees and Shriner)[4] and the mixture was shaken in a shaking machine in an atmosphere of hydrogen until the calculated amount of hydrogen was absorbed. The platinum was filtered off and the filtrate distilled. At first alcohol came over, then the temperature rose rapidly and an oil distilled over at 250–255°. This was redistilled, and the main portion came over at 251–253° (corrected for stem exposure) (765.8 mm.); yield, 12 g. (72.2%).

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[1] S. P. Mulliken, "A Method for the Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, New York, 1905, p. 168.

[2] Brown and Kremers, *J. Am. Pharm. Assoc.*, **11**, 607 (1922).

[3] Clemensen, *Ber.*, 46, 1837 (1913); 47, 51 (1914).

[4] Adams, Voorhees and Shriner, "Organic Syntheses," Vol. VIII, John Wiley and Sons, New York, 1928, p. 92.

Anal. Subs., 0.1552: AgI, 0.2170. Calcd. for $C_{10}H_{14}O_2$: CH_3O, 18.67. Found: CH_3O, 18.47.

Preparation of the 3,5-Dinitrobenzoyl Esters of the Phenols.--4.01 mole of the phenol and 2.3 g. (0.01 mole) of 3,5-dinitrobenzoyl chloride were added to 20 cc. of c. p. pyridine, and the mixture was heated over a free flame under the reflux condenser for one hour. The reaction product was cooled and poured into about 400 cc. of cold 5% sulfuric acid. If the crude reaction product separated as a solid, it was filtered off and washed with water until the wash water was acid free. The product was added to 200 cc. of 2% sodium hydroxide solution, the mixture was well stirred, filtered, washed with water, and then crystallized. When the reaction product separated out as an oil or as a gummy mass, it was dissolved in ether and the ether solution washed successively with water, 2% sodium hydroxide, and finally with water. The ether was distilled off and the residue crystallized. In all cases except one the reaction products were crystallized from 95% ethanol. The 3,5-dinitrobenzoyl derivative of isoeugenol was crystallized from n-butyl alcohol.

Melting Point Determinations.—The melting points were determined in a Roth[5] type of apparatus with Anschiitz thermometers which had been standardized by the Bureau of Standards.

Nitrogen Determinations.—The nitrogen was determined by the Kjeldahl method, modified for the determination of nitrogen in nitro compounds. The modified Pamas–Wagner micro Kjeldahl apparatus[6] was used. Approximately twenty milligrams of substance were taken for each determination.

The results of the melting point and nitrogen determinations are given in Table I.

TABLE I

MELTING POINTS AND NITROGEN CONTENT OF 3,5-DINITROBENZOYL DERIVATIVES OF PHENOLS

3,5-Dinitrobenzoyl derivatives	M. p., (corr.), °C.	Formula	Nitrogen, % Calcd.	Found
Phenol	145.8	$C_{13}H_8O_6N_2$	9.72	9.69
o-Cresol	138.4	$C_{14}H_{10}O_6N_2$	9.27	9.14
m-Cresol	165 4	$C_{14}H_{10}O_6N_2$	9.27	9.14
p-Cresol	188 6	$C_{14}H_{10}O_6N_2$	9.27	9.14
4-Hydroxy-1,2-dimethylbenzene	181.6	$C_{15}H_{12}O_6N_2$	8.86	8.83
2-Hydroxy-1,3-dimethylbenzene	158.8	$C_{15}H_{12}O_6N_2$	8.86	8.82
4-Hydroxy-1,3-dimethylbenzene	164.6	$C_{15}H_{12}O_6N_2$	8.86	8.96
5-Hydroxy-1,3-dimethylbenzene	195 4	$C_{15}H_{12}O_6N_2$	8.86	8.90
2-Hydroxy-1,4-dimethylbenzene	137.2	$C_{15}H_{12}O_6N_2$	8.86	8.68
Thymol	103.2	$C_{17}H_{16}O_6N_2$	8.13	8.17
p-Cyclohexylphenol	168.0	$C_{19}H_{18}O_6N_2$	7.56	7.43
Guaiacol	141.2	$C_{14}H_{10}O_7N_2$	8.80	8.60
Creosol (1-methyl-3-methoxy-4-hydroxybenzene)	170.6	$C_{15}H_{12}O_7N_2$	8.43	8.33
1-*n*-Propyl-3-methoxy-4-hydroxybenzene (n-propylguaiacol)	116.2	$C_{17}H_{16}O_7N_2$	7.77	7.72
Eugenol	130.8	$C_{17}H_{14}O_7N_2$	7 82	7 86
Isoeugenol	158.4	$C_{17}H_{14}O_7N_2$	7.82	7.70
a-Naphthol	217.4	$C_{17}H_{10}O_6N_2$	8.28	8.08
β-Naphthol	210.2	$C_{17}H_{10}O_6N_2$	8.28	8 29

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[5] Roth, *Ber.*, 19, 1970 (1886).

[6] Parnas and Wagner, Biochem. *Z.*, 125, 253 (1921); Clark and Collip, *J. Biol. Chem.*, 67, 621 (1926).

TABLE II

OPTICAL PROPERTIES OF CRYSTALS OF 3,5-DINITROBENZOYL DERIVATIVES OF PHENOLS

3,5-Dinitrobenzoyl deriv. of	Habit	Color	Extinction	Elongation	Class	Figures	Refractive indices α	Refractive indices β	Refractive indices γ	Common index
Phenol	Rods	Colorless	Parallel	Negative	Biaxial	Rare	1.505	1.690	>1.740	a
o-Cresol	Plates	Colorless	.....	......	Biaxial	Infrequent	1.490	Indet.	>1.720	a
m-Cresol	Plates	Colorless	Parallel	Negative	Biaxial	Rare	1.475	1.700	1.740	a and γ
p-Cresol	Plates	Colorless	.....	......	Biaxial	Rare	1.500	Indet.	1.740	α and γ
4-Hydroxy-1,2-dimethylbenzene	Rods, needles	Colorless	Parallel	Negative	Biaxial	Rare	1 508	1 670	>1.740	α and γ
2-Hydroxy-1,3-dimethylbenzene	Rods, plates	Cream-white	Parallel	Negative	Biaxial	Rare	1.512	1.670	>1.740	a and γ
4-Hydroxy-1,3-dimethylbenzene	Rods, plates	Colorless	Parallel	Negative	Biaxial	Rare	1.517	1.645	>1.690	α
5-Hydroxy-1,3-dimethylbenzene	Rods	Cream-white	Parallel	Negative	Biaxial	Rare	1.485	1.650	>1.740	α and β
2-Hydroxy-1,4-dimethylbenzene	Needles	Cream-white	Parallel	Negative	Biaxial	Rare	1.487	1.665	1.740	α
Thymol	Needles	Colorless	Parallel	Negative	Biaxial	Rare	1.480	1.625	1.705	a
p-Cyclohexylphenol	Needles	Brownish-white	Parallel	Positive or negative	Biaxial	Frequent	1 515	1.625	1.702	All
Guaiacol	Needles	Yellow	.....	......	Biaxial	Rare	1.530	Indet.	>1.740	α
Creosol (1-methyl-3-methoxy-4-hydroxybenzene)	Rods. needles	Colorless	Parallel	Positive	Biaxial	Rare	1.550	1.570	1.640	γ
1-n-Propyl-3-methoxy-4-hydroxybenzene (*n*-propylguaiacol)	Needles	Light yellow	Parallel	Positive	Biaxial	Infrequent	1.520	Indet.	1.650	a and γ
α-Naphthol	Needles	Yellow	Parallel	Negative	Biaxial	Rare	1.400	1.615	>1.740	β
β-Naphthol	Needles	Colorless	Parallel	Negative	Biaxial	Rare	1.475	1.740	>1.740	α

Optical Properties of the Crystals.—The optical properties of the crystals were determined by the immersion method[7] which has been used successfully by one of the authors in the identification of several types of organic compounds.[8] The 3,5-dinitrobenzoyl derivatives of the phenols were most satisfactorily studied in solutions of potassium mercuric iodide in glycerol and water, although for rapid determinative work, oily liquids consisting of mixtures of mineral oils, monochloronaphthalene and methylene iodide can be used.

The results obtained are given in Table II. Because of the peculiar cleavage properties of the 3,5-dinitrobenzoyl derivatives of eugenol and isoeugenol the optical properties of the crystals could not be determined with any degree of accuracy and therefore are not included in the table.

Summary

1. A method for the preparation of the 3,5-dinitrobenzoyl derivatives of phenols is described. This method can be conveniently used for the identification of phenols.
2. The melting points and the optical properties of the crystals of the 3,5-dinitrobenzoyl derivatives of several phenols were determined.
3. Methods for the preparation of creosol and of 1-n-propyl-3-methoxy-4-hydroxybenzene are given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

THE REARRANGEMENT OF SATURATED ALKYL PHENYL ETHERS. SYNTHESIS OF ISOPROPYL PHENOL AND CRESOLS[1]

BY JOSEPH B. NIEDERL AND SAMUEL NATELSON

RECEIVED MARCH 5, 1931 PUBLISHED MAY 6, 1931

Theoretical Part

In an earlier publication[2] a report was given on the condensation of olefins with phenols under the influence of concentrated sulfuric acid in the cold. The results obtained differed from those already reported in the literature, ethers being obtained and not the corresponding substituted phenols. It was suggested that the condensation process used by the other authors brought about rearrangement of the ethers first formed.

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[7] Wilson and Keenan, *J. Assoc. Official Agr. Chem.*, **13,** 389 (1930).

[8] Keenan, *J. Biol. Chem.*, **62,** 163 (1924); *J. Wash. Acad. Sci.*, **16,** 433 (1926); Keenan and Weisberg, *J. Phys. Chem.*, **33,** 791 (1929).

[1] Constructed from the second half of the thesis presented by Samuel Natelson to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy, 1931. Presented at the Indianapolis meeting of the American Chemical Society, April 3, 1931.

[2] Niederl and Natelson, THIS JOURNAL, **53,** 272 (1931).

Koenigs,[3] and Schrauth and Quasebarth[4] used a mixture of sulfuric and acetic acids as condensing agents and obtained the corresponding substituted phenols on warming. This condensation process is close to the one employed by the authors, concentrated sulfuric acid in the cold, yet the results were different.

For the conclusive proof of the reaction mechanism offered in such condensations, it was necessary that it be shown that saturated alkyl phenyl ethers would rearrange under the conditions used by Koenig. In all the ethers obtained (*sec.*-amyl phenyl and cresyl ethers; di-isobutyl phenyl and cresyl ethers) the oxygen is at a secondary or tertiary carbon atom. Since no data on the rearrangement of such types of compounds could be found in the literature, the simplest case, the various isopropyl phenyl and cresyl ethers, was then chosen for study.

There have been numerous cases of rearrangement already reported.[5] Where the alkyl group is a negative one, mere heat is necessary.[6] As the alkyl group becomes less and less negative, various reagents, such as zinc chloride and hydrogen chloride, have to be used to effect rearrangement.[5b,e]

A mixture of concentrated sulfuric and glacial acetic acid should then be an excellent means for rearranging alkyl phenyl ethers. This reagent has the advantage of bringing the whole reaction mixture into homogeneous solution, while at the same time the concentration of the active rearranging agent, sulfuric acid can be reduced to any desired quantity. The ease with which the resultant product may be isolated is apparent, it only being necessary to add water to separate the rearranged product.

From the reactions studied there appears to be very little side reaction, the only product obtained other than the rearranged ether being the original ether itself, which can be again subjected to rearrangement.

The mechanism for this type of rearrangement as offered by Van Alphen involves oxonium formation. Kursanov suggests hydrolysis of the ether to the phenol and the alkyl halide and then recombination with the formation of a substituted phenol. Neither of these authors explains the rearrangement of alkyl ethers in the absence of a rearranging agent. Claisen's mechanism is a special one and requires the presence of the unsaturation in the alkyl residue. From Latimer's considerations,[7] the

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[3] Koenigs and Carl, *Ber.*, 24, 3889 (1891).

[4] Schrauth and Quasebarth, *ibid.*, 57, 856 (1924).

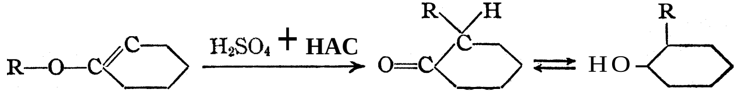
[5] (a) Claisen, *Ann.*, 237, 261 (1887); 401, 21–119 (1914); *Z. angew. Chem.*, 36, 478–9 (1923); *Ber.*, 58b, 275–81 (1925); 45, 3157–66 (1912); (b) Van Alphen, *Rec. trav. chim.*, 46, 799 (1927); (c) Heller, *Ber.*, 45, 418 (1912); (d) Bucherer and Grolee, *ibid.*, 39, 986 (1906); (e) Kursanov, *J. Russ. Phys.-Chem. Soc.*, 48, 1172–4 (1914); (f) Eijkman, *Chem. Centr.*, I, 1597 (1904); I, 814 (1905); (g) Smith and Niederl, THIS JOURNAL, 53, 806 (1931).

[6] Claisen and Godesberg, *Ann.*, 418, 69–120 (1919).

[7] Latimer, THIS JOURNAL, 51, 3185 (1929).

substituted phenol structure is a more stable configuration than that of the ether and therefore when placed in a suitable medium or under suitable conditions, readjustment to the more stable configuration should be expected.

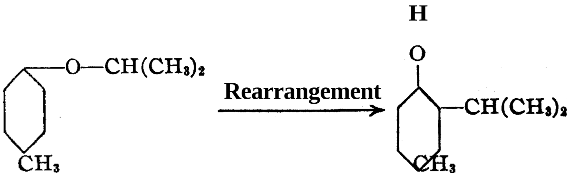
Drawing an analogy from keto–enol tautomerism and rearrangement of vinyl alkyl ethers to the corresponding aldehydes, the series of reactions may be represented as



As mentioned before, the ethers chosen for study were the isopropyl phenyl and cresyl ethers. Some of these ethers and the corresponding phenols obtained after rearrangement had not been previously prepared and had to be characterized.

The complete identification of the substituted phenols formed would involve determination of the position of the alkyl groups introduced. This would permit us to draw conclusions and generalizations which would be of great value in the identification and structure proof of a number of new longer chain phenols obtained by a similar process and to be described later.

The rearrangement of isopropyl *p*-cresyl ether was first studied. The reaction went smoothly and the rearranged phenol was isolated.



The isopropyl group could migrate to the ortho position only, the para position being occupied and meta rearrangement being rare.

The rearrangement of isopropyl phenyl ether gave rise to a product the main portion of which distilled in the neighborhood of the boiling point of o-isopropyl phenol as reported in the literature.[8]

The product obtained on treating this product with bromoacetic acid was identical with that reported in the literature for *o*-isopropylphenoxyacetic acid.[9]

The product therefore appears to be identical with o-isopropylphenol and the alkyl group in the ether has apparently migrated ortho to the hydroxyl group

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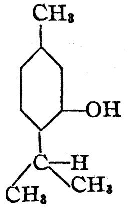
[8] Spica, *Gazz. chim. ital.*, *9*, 442 (1879); *Jahresb.*, 663 (1880).

[9] Fileti, *Gazz. chim. ital.*, *16*, 129 (1886).

It was expected that by the rearrangement of the isopropyl *m*-cresyl ether, thymol would be obtained. Actually a strong odor of thymol was observed, the total product boiling between 230-240°. From the fraction boiling between 231-235° a derivative with bromoacetic acid was made which melted 4° lower than that of thymol. According to Crum-Brown's rule there are three isomeric products possible upon the introduction of an isopropyl group into m-cresol.

I



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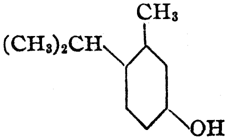

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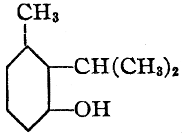
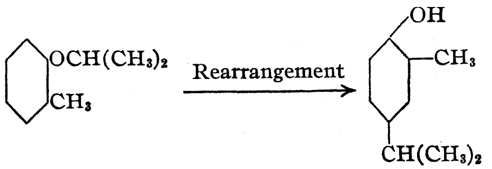


Thymol **3-Methyl-4-isopropylphenol** **2-Isopropyl-3-methylphenol**

Of these only I (thymol) has been identified conclusively. A condensation product furnished by Read[10] was studied and was found to be different from thymol and the rearranged isopropyl m-cresyl ether.

Usually upon treatment of an alcohol with phenol in the presence of a condensing agent the alkyl radical enters in a position para to the hydroxyl group.[11] Structural Formula II may then be assigned to these types of products. The only possible structure for the substituted phenol obtained from isopropyl m-cresyl ether by the rearrangement process mentioned before, would then be Formula I or III, which would be in harmony with the fact observed that whenever the ortho positions are free migration to this place is preferred. Formula III would involve readjustment to a position which should be particularly non-reactive due to such phenomena as steric hindrance. A definite stand as to the position occupied is not being taken until the behavior of this compound is studied further.

The rearrangement of the o-cresyl isopropyl ether gave rise to a product which was identified by its physical and chemical properties and by its bromine derivative as *p*-isopropyl-*o*-methylphenol. The compound appears to be identical with that obtained by Kelbe and Spica,[12] the structure of which is given as



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[10] (a) Read, Sharp and Dohme, private communication; (b) Mazzara, *Gazz. chim. ital.*, 12,505 (1882).

[11] Senkowski, *Ber.*, 24,2974 (1891); Anschütz and Beckerhoff, *ibid.*, 28,407 (1895).

[12] Kelbe, Ann., 210, 40 (1881); Spica, *Gazz. chim. ital.*, 12,552 (1882).

With a methyl group occupying an ortho position, migration para to the hydroxyl group appears to be favored.

Experimental Part

Preparation of Isopropylphenyl and Cresyl Ethers.--One molecular weight of the phenol or cresol was placed in a three-necked flask fitted with a reflux condenser. Fifty-eight grams (excess) of finely powdered potassium hydroxide was added and the whole heated with a low flame, when a homogeneous viscous mass is formed; 125 g. (excess) of isopropyl bromide was then slowly added through a dropping funnel extending below the level of the liquid. Constant warming was necessary to keep the whole mass from solidifying. After all the halide had been added refluxing was continued for two hours more. The mass was allowed to cool and then 500 cc. of water was added to dissolve the separated sodium bromide. A light oil appeared at the top of the liquid. This was removed in a separatory funnel and washed successively with 10% alkali and then twice with water. The separated light yellow oil was dried over calcium chloride and then distilled. One fractionation was sufficient to give a colorless constant boiling oil.

Rearrangement of Isopropylphenyl and Cresyl Ethers.—The rearrangement mixture consists of a solution of 150 cc. of concentrated sulfuric acid in sufficient glacial acetic acid to make up to a liter: 80 cc. of the ether prepared as above was placed in a flask fitted with a reflux condenser and a calcium chloride addition tube; 200 cc. of the rearrangement mixture was added and the whole shaken. Two layers are formed at first, but the mixture becomes homogeneous on warming. The solution was then refluxed gently for five hours. The temperature of the solution on refluxing is constant between 125–130°. The reaction mixture was then allowed to stand overnight. It assumed a deep red color. The whole was transferred to a 500-cc. separatory funnel and 200 cc. of water added. Sufficient solid hydrated sodium carbonate was added to neutralize the sulfuric acid (180 g.). The separatory funnel was then filled with a saturated salt solution. On standing, a heavy viscous oil separated to form the upper layer. The lower layer was allowed to drain off and discarded and the upper layer extracted with 10% potassium hydroxide solution. The alkali-insoluble portion was redistilled to reclaim unchanged ether. The alkali extract was neutralized with cold concentrated hydrochloric acid, ice being thrown in to keep the reaction mixture cool, when a deeply colored oil separated. The mixture was extracted with ether, the ether distilled off and the residue fractionated.

From 72 g. of ether. 39 g. of rearranged alkali-soluble product was obtained. and 16 g. of unchanged ether in the case of *m*-cresyl isopropyl ether. This corresponds to a 54% yield on the basis of the total ether at the outset, or a 70% yield taking into consideration the ether recovered.

Preparation of Isopropylphenoxy- and Cresoxyacetic Acids.—About one gram of the substituted phenol was weighed out carefully on an analytical balance. The exact quantity of 1 N potassium hydroxide was added and the whole gently warmed. A slight excess of bromoacetic acid was weighed into a separate flask and carefully neutralized with 1 *N* potassium hydroxide. The two solutions were mixed and then gently boiled for five minutes. Decolorizing charcoal was added and the whole filtered while hot. While still warm the calculated quantity of concentrated hydrochloric acid was added and the mixture allowed to stand. The separated crystalline product was filtered off and recrystallized from hot water.

Isopropylphenyl Ether.[13]—A colorless oil with an odor resembling anise; b. p. 178°, sp. gr. 0.975 (20°), n^{20}_D 1.4992.

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[13] Perkin, J. Chem. *Soc.*, 69, 1187, 1250 (1896).

o-Isopropylphenol (2-Oxy-1-isopropylbenzene).[8]—Colorless oil with phenolic odor, soluble in alkali. Its alcoholic solution gave a deep violet color with ferric chloride solution; b. p. 213–214°, sp. gr. 1.012 (20°), n_{D}^{20} 1.5315.

o-Isopropylphenoxyacetic Acid.*—White needle-like crystals; soluble in hot water; m. p. 130° (uncorr.).

Anal. Calcd. for $C_9H_{12}O$: C, 68.04; H, 7.27; neut. equiv., 194. Found: C, 68.21; H, 7.62; neut. equiv., 200.

Isopropyl o-Cresyl Ether.—Light oil with a characteristic aromatic odor; b. p. 192° (uncorr.), sp. gr., 0.953 (20°), n_{D}^{20} 1.5040.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.15; H, 9.39.

6-Oxy-1-methyl-3-**isopropylbenzene** (2-Methyl-4-**isopropylphenol**).[12]—Colorless liquid with phenolic odor; b. p. 232–234° (uncorr.), sp. gr. 0.989 (20°), n_{D}^{20} 1.5178.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.29; H, 9.38.

(2-Methyl-4-isopropylphenoxy)-acetic Acid—Prepared from the above compound by treating it with bromoacetic acid as described above; m. p. 87–88° (uncorr.).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 68.97; H, 7.46; neut. equiv., 203.

2,4,5-Tribromo-6-oxy-1-methyl-3-isopropylbenzene.[14]—Prepared by treating the 2-methyl-4-isopropylphenol in water with an excess of bromine. Upon recrystallization from alcohol lustrous, golden-yellow plates were obtained; m. p. 223° (uncorr.).

Isopropyl m-Cresyl Ether.—Faint pleasant aromatic odor; b. p. 195°, sp. gr. 0.931 (20°), n_{D}^{20} 1.4959.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.32; H, 8.95.

(3-Oxy-1-methyl-*x*-isopropylbenzene), 3-Methyl-*x*-**isopropylphenol.**—Odor strongly resembles that of thymol, alkali soluble. Its alcoholic solution was colored a deep lavender by ferric chloride solution; b. p. 230–235°, sp. gr. 0.994 (20°), n_{D}^{20} 1.5280.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.84; H, 9.39.

x-Isopropyl-m-cresoxyacetic Acid—Prepared from the above compound; small white crystals soluble in hot water; m. p. 141° (uncorr.).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 69.43; H, 7.86; neut. equiv., 213.

y-Isopropylm-cresoxyacetic Acid (3-Methyl-y-isopropylphenoxyacetic Acid).—This compound was prepared from a condensation product (b. p. 95–110° (4 mm.)),[10a] m. p. 125–126° (uncorr.).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 69.75; H, 7.36; neut. equiv., 209.

Isopropyl *p*-**Cresyl Ether.**—Strong disagreeable odor with a trace of anise; b. p. 195° (84°, 12 mm.), sp. gr. 0.927 (20°), n_{D}^{20} 1.4952.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.10; H, 9.39.

4-Oxy-1-methyl-3-isopropylbenzene(4-Methyl-2-isopropylphenol).—Characteristic odor, rather disagreeable; alkali soluble. Gives rise to a purple color with ferric chloride in alcohol solution. In aqueous solution, a greenish turbidity is obtained with ferric chloride; b. p. 234–237° (uncorr.), sp. gr. 0.989 (20°), n_{D}^{20} 1.5277.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.80; H, 9.36.

(4-Methyl-2-isopropylphenoxy)-acetic Acid.—Long silky needles; soluble in hot water, difficultly soluble in the cold; m. p. 126° (uncorr.).

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[14] Jesurun, *Ber.*, 19, 1414 (1886).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 69.13; H. 7.53; neut. equiv., 212.

The quantitative determinations were performed microanalytically according to Pregl.[15]

Acknowledgment is made here to Mr. Franz K. Silbert of this Laboratory for performing the analyses, and to Mr. Louis Krautmann for his assistance in preparing some of the above mentioned compounds.

Summary

Saturated alkyl phenyl ethers (isopropylphenyl and cresyl ethers) were rearranged to the corresponding substituted phenols by means of a mixture of concentrated sulfuric and glacial acetic acid. Proofs for the probable structure of the products obtained were advanced and a general rule as to the way of migration of the alkyl groups was given.

As the possibility of rearranging even short chain, saturated phenyl ethers has now been demonstrated, a series of related problems such as the rearrangement of some of the more important phenyl ethers of mono and poly functional alkanes are now being investigated.

The physiological properties of the substituted phenols mentioned before are being studied.

NEW YORE. N. Y.

[COMMUNICATION NO. 460 FROM THE KODAK RESEARCH LABORATORIES]

EFFECT OF NEUTRAL SALTS ON THE RATE OF HYDROLYSIS OF CELLULOSE ACETATE IN ACETIC ACID SOLUTIONS[1]

BY J. T. FUESS AND C. J. STAUD

RECEIVED MARCH 7, 1931 PUBLISHED MAY 6, 1931

Introduction

The effect of the presence of neutral salts of the alkali metals **on** the rate of chemical reactions has been the subject of the investigation of several workers in recent years. The published results appear to have been concerned mostly with crystalloids. L. E. Bowe[2] has investigated the effect of sodium chloride and sodium bromide on the rate of saponification of ethyl acetate by hydrochloric acid. Grube and Schmid[3] studied the hydrolysis of cyanamide to urea by nitric acid in the presence of nitrates, and the saponification of ethyl acetate by hydrochloric acid in the presence of alkali and alkaline earth chlorides. Hawkins[4] worked on the

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[15] Pregl, "Quantitative Organic Micro Analysis," Blakiston's Sons, Philadelphia, 1930.

[1] Study carried out under the direction of H. LeB. Gray, Superintendent of the Organic Research Laboratory.

[2] Bowe, J. Phys. Chem., 31, 298 (1927).

[3] H. Grube and G. Schmid, *Z. physik* Chem., 119, 19 (1926).

[4] J. E. Hawkins, University of Pennsylvania, "Thesis," 1927.

hydrolysis of ethyl acetate in dilute aqueous solutions; Kautz and Robinson[5] gave results of an investigation of the hydrolysis of sucrose by hydrochloric acid in the presence of alkali and alkaline earth chlorides. Sherman, Caldwell and Cleaveland[6] ascertained the effect of neutral salts on the rate of inversion of starch by amylase, and Roberts and Terry[7] investigated the velocity of saponification of ethyl formate by ammonium hydroxide in the presence of ammonium salts. In general, it has been observed that neutral salts increase the reaction velocity in rather widely different types of reactions.

As far as has been learned, however, no publication has been made of the effect of neutral salts on the rate of hydrolysis of cellulose esters. Since these compounds present a different aspect of the general problem in that their dispersions are colloidal in character, an investigation of the results obtained by the addition of neutral salts appeared of interest.

Experimental

Cellulose acetate was prepared by the esterification of cellulose in the form of cotton linters, through the action of a mixture consisting of acetic anhydride, acetic acid and a catalyst. A calculated amount of water more than sufficient to convert the excess acetic anhydride to acetic acid was added. In this way the difficulty of redissolving cellulose triacetate in acetic acid with possible lack of uniformity of the solution was overcome. The concentration of the various components of the solutions used in the hydrolysis experiments was as follows: cellulose triacetate, 89 g., acetyl content 43.5 to 44.2% (theoretical 44.8%); acetic acid, 563.5 g.; water, 22.9 g.; sulfuric acid, 0.9 g.; phosphoric acid, 2.7 g., and sodium bisulfate, 2.0 g.

Four groups of experiments were carried out. In each series fresh preparations of cellulose triacetate were made in sufficient quantity for all of the experiments in that group. The procedure employed in acetylation was the same in all cases.

Three 550-g. portions of cellulose triacetate solutions of the composition given above were taken for the first series of experiments. One contained in addition 17 g. of sodium nitrate, the second 20 g. of potassium nitrate, while the third contained no neutral salt, this portion serving as a control. The hydrolyses were carried out in glass-stoppered bottles, maintained at 53 ± 1° in a constant-temperature air-bath. After various intervals throughout the saponification approximately 100-g. samples were removed and these, after dilution with an equal volume of acetone to assist in obtaining fluffy precipitates which could be easily washed, were precipitated by pouring slowly into warm water (approximately 60°) with vigorous stirring. The precipitated cellulose acetates were then washed with water until the residual acid had been removed, as indicated by testing the precipitates with brom thymol blue. They were then air-dried.

The acetyl content of each sample was determined using a modification of the Knoevenagel method as given below.

Approximately one-half gram of the material after air-drying is placed in a small glass weighing bottle and further dried at 105° for sixteen to eighteen hours. After cooling in a desiccator over anhydrous calcium chloride, the bottle and contents are weighed. The cellulose acetate is transferred to a 250-cc. Erlenmeyer flask, the bottle again weighed and the weight of sample obtained by difference.

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[5] C. F. Kautz and A. L. Robinson, THIS JOURNAL, 50, 1022 (1928).

[6] H. C. Sherman, M. L. Caldwell and M. Cleaveland, *ibid.*, 52, 2436 (1930).

[7] E. N. Roberts and E. M. Terry, *ibid.*, 52, 2604 (1930).

Twenty cubic centimeters of 75% ethyl alcohol (by weight) are added and, after covering the flask, maintained at 56° in an air-bath for thirty minutes. At the end of this time 20 cc. of 0.5 N sodium hydroxide is pipetted into the flask. The flask is then stoppered and after heating at 56° for fifteen minutes it is permitted to stand at room temperature for approximately twenty-four hours. The excess alkali is back-titrated using 0.5 *N* hydrochloric acid. The acetyl content is calculated using the formula

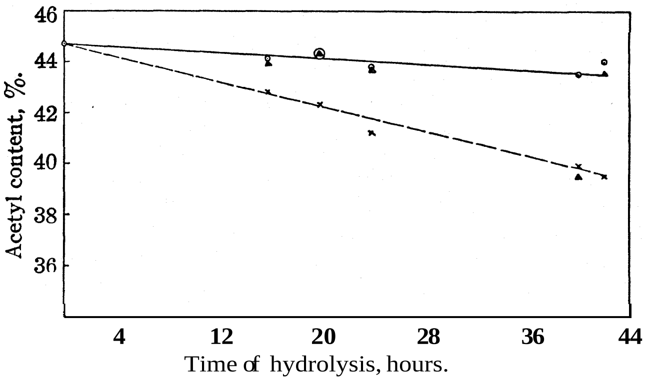
$$\% \ \mathrm{CH_3CO} = \frac{(\text{Cc. of NaOH taken} \times N - \text{cc. HCl used} \times N) \times 0.043)}{\text{Weight of sample}} \times 100$$

The results obtained in the first series are given in Table I and graphically in Fig. 1.

TABLE I

EXPERIMENTAL RESULTS

Time of hydrolysis. hours	Acetyl content		
	17 Grams of $NaNO_3$ present	20 Grams of KNO_3 present	Check, no salt present
0	44.7–44.7	44.7–44.7	44.7–44.7
16	44.2–44.0	44.1–43.8	42.7–42.9
20	44.3–44.4	44.5–44.1	42.3–42.3
24	44.1–43.5	44.0–43.5	41.2–41.0
40	43.5–43.5	39.4–39.6	40.2–39.6
42	44.3–43.7	43.7–43.4	39.7–39.3



⊙, $NaNO_3$; A, KNO_3; X, check.

Fig. 1.

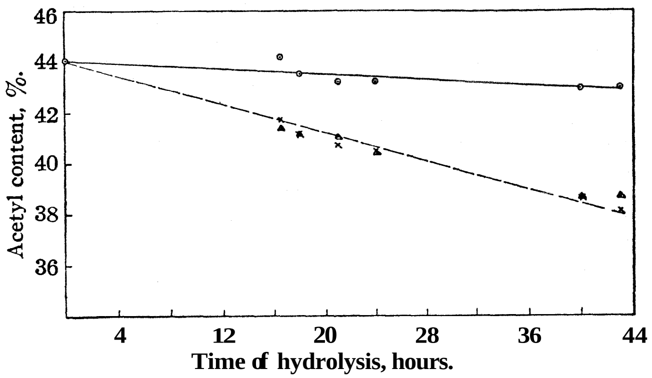
The sample from the hydrolysis in the presence of potassium nitrate after forty hours appears to have met with an accident during analysis.

A second series of experiments was carried out using solutions of the same composition as employed in the first group of experiments, but adding 10 *g.* of sodium nitrate to one of three samples, maintaining two as controls. This was done to confirm the results previously obtained. The hydrolysis procedure and method of determination of acetyl content were the same as those previously described. The results are given in Table II and graphically in Fig. 2.

TABLE II

EXPERIMENTAL RESULTS

Time of hydrolysis, hours	Acetyl content		
	10 Grams of $NaNO_3$ present	Check I, no salt present	Check II, no salt present
0	44.2–43.9	44.2–43.9	44.2–43.9
16.5	44.1–44.2	41.4–41.3	41.7–41.7
18	43.4–43.6	41.0–41.3	41.1–41.2
21	43.1–43.3	41.0–40.9	40.6–40.8
24	43.4–43.0	40.6–40.2	40.5–40.4
40	42.8–43.1	38.6–38.7	39.6–39.6
43	43.1–42.8	38.6–38.7	39.0–39.2



⊙, $NaNO_3$; A, check I; X, check II.

Fig. 2.

Since Hawkins found that the alkali sulfates exerted an effect on the saponification of ethyl acetate of approximate numerical equality but opposite in sign from that of the nitrates, it appeared of interest to ascertain the results of sodium and potassium sulfates in place of the corresponding nitrates in the hydrolysis of cellulose acetate.

The procedures employed were the same as those previously described. The amounts of sodium and potassium sulfates added were approximately molecular equivalents of the corresponding nitrates used in the first series of experiments, that is, 15 g. of potassium sulfate and 14 g. of sodium sulfate, both being in the anhydrous form.

The results of the third series of experiments are given in Table III and graphically in Fig. 3.

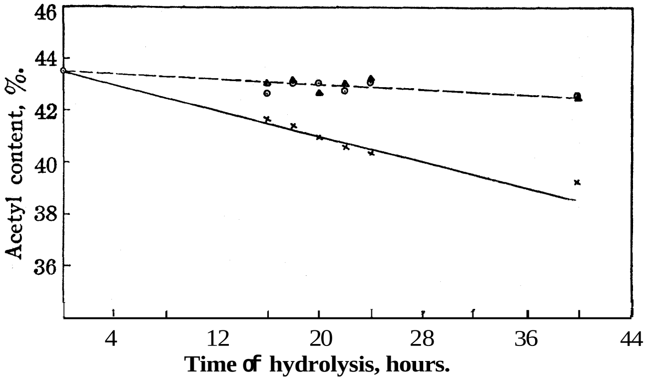
In the fourth series of experiments, the run was made using sodium chloride for comparison with the results obtained using sodium nitrate and sodium sulfate. Two experiments were made to determine whether the addition of the neutral salts after partial hydrolysis would exhibit the same effect as when added at the start of the reaction.

Five portions of cellulose triacetate solution were taken; to one was

TABLE III

EXPERIMENTAL RESULTS

Time of hydrolysis, hours	Acetyl content: 14 Grams of Na_2SO_4 present	Acetyl content: 15 Grams of K_2SO_4 present	Acetyl content: Check, no salt present
0	(43.5)	(43.5)	(43.5)
16	42.6-42.7	43.2-43.1	41.6-41.7
18	43.1-43.2	43.3-42.9	41.6-41 2
20	42.9-43.2	42.6-42.8	41.0-40.9
22	43.0-42.5	42.9-43.2	40.2-40.9
24	43.4-42.8	42.8-43.6	40.4-40.2
40	42.7-42.5	42.5-42.6	39.2-39.2



⊙, Na_2SO_4; A, K_2SO_4; ×, check.

Fig. 3.

added 10 g. of sodium nitrate and to the second 7 g. of sodium chloride, an approximately molecular equivalent of the sodium nitrate. The remaining three portions were hydrolyzed without the addition of salts. All five samples were maintained at 53 ± 1°. After forty-two hours' hydrolysis, two of the samples to which no salt had been added were removed from the air-bath for sufficient time to permit the addition of 10 g. of sodium nitrate to one and 7 g. of sodium chloride to the other, each of the salts being dis-

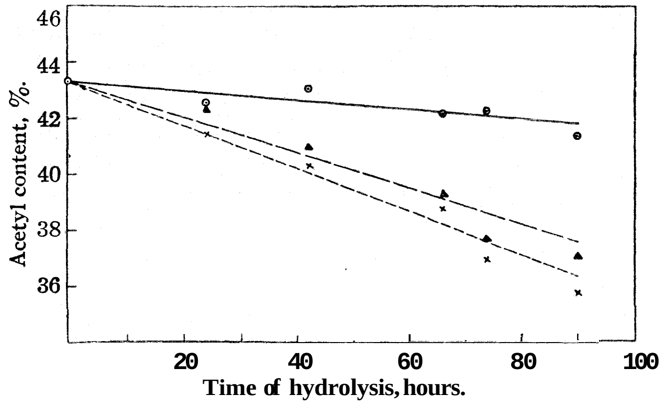
TABLE IV

EXPERIMENTAL RESULTS

Time of hydrolysis, hours	Acetyl Content: 10 Grams of $NaNO_3$ present	Acetyl Content: 7 Grams of NaCl present	Acetyl Content: Check. no salt present	Acetyl Content: No salt present at start	Acetyl Content: No salt present at start
0	43.3	43.3	43.3	43.3	43.3
24	42.4-42.7	42.1-42.6	41.6-41.2	41.2-41.2	41.1-40.8
42	43.2-42.9	40.9-41.0	40.4-40.2	40.0-40.4	40.5-40.7
				10 Grams of $NaNO_3$ added	7 Grams of NaCl added
66	42.1-42.2	39.1-39.5	38.6-38.9	39.6-39.5	37.9-37.9
74	42.2-42.3	37.5-37.9	36.9-37.0	38.9-38.7	37.6-37.8
90	41.2-41.5	37.2-36.9	35.7-35.8	39.2-39.5	37.4-37.7

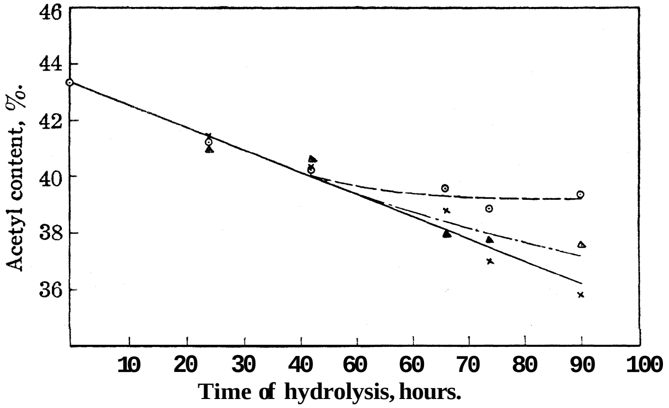
solved in 50 cc. of glacial acetic acid before addition. This required from three to five minutes, after which they were replaced in the air-bath at 53°.

The procedure from this point was as previously described. The results are given in Table IV and graphically in Fig. 4 for the experiments in which the salts were added at the start of the hydrolysis, and in Fig. 5 where the salts were added after partial saponification.



⊙, NaNO$_3$; A, NaCl; ×, check.

Fig. 4.



⊙, NaNO$_3$; △, NaCl; ×, check.

Fig. 5.

Discussion

From an examination of the data there appear several points of interest to be considered. It is seen that in all cases the presence of the neutral salts of the alkali metals tried, resulted in a retardation of the rate of saponification. The factors influencing this saponification in colloidal solution and in media in which activity coefficients do not appear to have been accurately determined, make this reaction too complex and the data too meager to permit of calculation of the reaction constants. It is thought, however, that the qualitative results of this problem are of sufficient interest to warrant brief discussion.

From the first series of experiments (Table I, Fig. 1) in which sodium nitrate and potassium nitrate were present at the beginning of the saponification in approximately molecular equivalents, it appears that the retarding effect is not influenced by the difference in atomic weight between sodium and potassium, but that the controlling influence is dependent upon the presence of the nitrate radical. When sodium or potassium nitrate is used, the decrease in acetyl content in forty-two hours is approximately 1%, whereas the saponification in the absence of salt had resulted in a reduction of the acetyl content of 5%. This corresponds to the removal of 2.2% of the available acetyl in the case of saponification in the presence of sodium and potassium nitrate and 11.2% in the absence of neutral salts. The data given in Table II and Fig. 2 confirm the results of the first group of experiments as regards the effect of sodium nitrate and indicate the degree of reproducibility of such saponification.

When sodium and potassium sulfates were employed in approximately molecular equivalents of the corresponding nitrates, retardation was again observed (Table III, Fig. 3). In this case the neutral salts permitted saponification of but 2.3% of the available acetyl as compared to 9.9% for the control. It therefore appears that the effect of the sulfate radical is approximately equal to that of the nitrates previously mentioned. The effect noted in these experiments is different from that observed by Hawkins in the saponification of ethyl acetate in which it was found that the sulfates and nitrates had opposite effects upon the saponification rate.

In the fourth series of experiments (Table IV, Fig. 4) a comparison of the first two experiments, in which sodium nitrate and sodium chloride were used, indicates that during forty-two hours of saponification the effect of the former is almost double that of the latter, the percentage of available acetyl removed in the case of sodium nitrate being 2.7% and for sodium chloride 5.3%. During the same period the control decreased 7.0%. All of the hydrolyses to which no salts were added during the first forty-two hours show the same acetyl content, within experimental error, being 40.3, 40.2 and 40.6%. A comparison of the results when sodium nitrate and sodium chloride were added after forty-two hours of saponification shows the following at the end of forty-eight hours' subsequent hydrolysis. The experiment in which sodium nitrate was used showed a decrease of 2.5% of the remaining available acetyl content, the sodium chloride experiment 7.4%, while the control to which no salt had been added decreased 8.7%. The curves indicate that the effect of the addition of neutral salts after saponification has proceeded for some time is not instantaneous.

In general, it is noted that the effect of the presence of neutral salts of the alkali metals in a reaction involving the saponification of cellulose acetate in colloidal dispersion in acetic acid, is opposite to that recorded by investigators of similar reactions involving crystalloids.

The subject matter of this paper is covered by a pending patent application of Eastman Kodak Company and the publication of this paper is not to be taken in any way as suggesting or permitting the commercial use of this development.

Summary

The effect of the presence of the nitrates, sulfates and chlorides of sodium and potassium on the rate of saponification of cellulose acetate dispersed in acetic acid has been studied.

It has been found that all of these salts appear to exert a retarding influence on the reaction rate. A greater effect was observed when nitrates and sulfates were used than when chloride was employed.

Addition of neutral salts after the reaction had proceeded for forty-two hours showed an effect similar to that noted when they were present at the beginning of the saponification.

ROCHESTER, NEW YORK

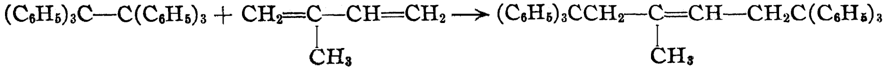
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ADDITION OF FREE RADICALS TO UNSATURATED COMPOUNDS (PRELIMINARY PAPER)

BY J. B. CONANT AND H. W. SCHERP

RECEIVED MARCH 10, 1931 PUBLISHED MAY 6, 1931

Free radicals containing trivalent carbon such as triphenylmethyl are known to combine with quinones (forming a di-ether) and with free radicals containing divalent nitrogen. Aside from these reactions there seems to be no published account of the addition of a free radical to an unsaturated organic compound. We have now found that triphenylmethyl (hexaphenylethane) combines with isoprene and dimethylbutadiene; the addition takes place in the 1,4 position.



$$(C_6H_5)_3C—C(C_6H_5)_3 + CH_2{=}\underset{\substack{|\\ CH_3}}{C}—CH{=}CH_2 \longrightarrow (C_6H_5)_3CCH_2—\underset{\substack{|\\ CH_3}}{C}{=}CH—CH_2C(C_6H_5)_3$$

The structure of the product obtained from isoprene was established by ozonization. Triphenylpropionic acid and 1,1,1-triphenylbutanone-3 were obtained from the ozonide by decomposition and oxidation with silver oxide. The identity of these compounds was proved by mixed melting point determinations with synthetic material. The ketone is new and was synthesized from triphenylpropionic acid by converting the latter into the acid chloride and treating with methyl zinc chloride in ether.

The nature of the product obtained with dimethylbutadiene was shown by the fact that on ozonization the same triphenylbutanone was obtained. The two new hydrocarbons obtained from isoprene and dimethylbutadiene, respectively, melted at 166 and 240°, respectively. Both combined with bromine in chloroform solution but considerable substitution takes place as evidenced by the copious evolution of hydrogen bromide.

It is a matter of considerable interest to see how far the type of addition reaction we have discovered can be extended. There seems no reason to believe that it is limited to dienes or to ethanes as highly dissociated as hexaphenylethane. Such reactive linkages as those in maleic anhydride or acrolein might well be expected to combine with free carbon radicals. Indeed, we have evidence that a reaction does take place between each of these compounds and triphenylmethyl but the nature of the product has not been as yet determined. We have been unable to bring about the addition of hexaphenylethane to 1,4-diphenylbutadiene, cinnamalacetophenone, or cinnamalmalonic acid, A study of the application of this reaction to the polyenes (including the carotinoid pigments) is now in progress.

Experimental Part

Reaction of Hexaphenylethane with Isoprene.—Three grams of hexaphenylethane (prepared from triphenylmethyl chloride and molecular silver) was treated with 40 cc. of isoprene in an atmosphere of nitrogen. After standing for two days, all the solid had dissolved and the orange-red color of the solution had changed to pale yellow. The excess isoprene was removed by distillation, the sirupy residue finally being heated on the steam-bath. On treatment with a mixture of ether and petroleum ether, 1.3 g. of slightly yellowish crystals was obtained which melted at 160–161°. On recrystallization from ether 0.6 g. of product melting at 164–165° was obtained. A more convenient method of obtaining crude hexaphenylethane in quantity is by the reduction of triphenylmethyl chloride. This crude material can be used directly in the addition reactions; an example of this procedure is as follows. The chloride (10 g.) was dissolved in 200 cc. of acetone in a 2-liter flask and 15 cc. of concentrated hydrochloric acid was added. A strong current of carbon dioxide was passed into the flask and 100 cc. of approximately 1 *N* vanadous chloride was run into the solution. On adding a liter of water, the product precipitated in granular form. It was filtered off, thoroughly washed with water and transferred without drying to a 200-cc. flask fitted with a two-holed stopper carrying a dropping funnel and connection to a nitrogen–vacuum pump apparatus. The flask was swept out three times with nitrogen, about 40 cc. of isoprene run in and finally the flask was left under a pressure of 1–2 cm. of mercury for three days with occasional shaking. The excess isoprene was then distilled off and the residue taken up in about 300 cc. of ether. The solution was filtered, evaporated to a small volume and on standing overnight at 0°, 6.3 g. of large glassy crystals formed, which melted at 162–163°. On recrystallization from ether, 4.5 g. melting at 164–164.5° was obtained; yield, 45% of the theoretical calculated from the triphenylmethyl chloride.

Another equally convenient procedure for preparing the addition product of isoprene and hexaphenylethane is to employ benzene as a solvent and form the free radical from the chloride and metallic mercury in the presence of the unsaturated compound. The following is a typical procedure: **15** g. of triphenylmethyl chloride, **3.6** g. of isoprene, **50** cc. of thiophene-free benzene and **50** g. of mercury were sealed in a nitrogen filled capsule and shaken for seventeen hours. After ten days' standing, the reaction mixture was worked up in the same fashion as the previous preparation; yield, after one recrystallization from benzene and ether, **10.8** g. or **72%;** melting point, 163–164°.

1,4-(Triphenylmethyl)-2-methylbutene-2.—A portion of this substance was carefully crystallized from ether for analysis; melting point, 166°.

Anal. Calcd. for $C_{43}H_{38}$: C, 93.1; H, 6.9. Found: C, 92.7, 92.8, 92.6, 92.6, 93.0; H, 7.07, 7.04, 6.91, 6.98, 7.0.

Molecular weight (neglecting the first increment) in benzene, cryoscopic. Benzene, 25.47, 25.47 g.; substance, 0.1799, 0.1928 g.; At, 0.076, 0.079°. Molecular weight, 475,490. Calcd. for $C_{43}H_{38}$: 554.

Ozonization.—Two grams of the hydrocarbon was dissolved in about 200 cc. of carbon tetrachloride and ozonized oxygen prepared by means of an electric discharge apparatus was bubbled through for three hours, when the solution was very turbid. The solution was cooled with ice during the reaction. On shaking with water and zinc dust, and filtering, a clear solution was obtained. The carbon tetrachloride was evaporated off under reduced pressure and the yellow gummy residue was taken up in ether. This solution was shaken for one-half hour with saturated sodium bisulfite solution, and the aqueous layer was acidified with hydrochloric acid. A small amount of oily material separated, but not enough to indicate that any appreciable extraction had occurred.

The ether was then boiled off and the residue dissolved in methyl alcohol. About one gram of sodium hydroxide and the freshly precipitated silver oxide from 3 g. of silver nitrate were added. After three hours' boiling, during which a characteristic "silver mirror" appeared, the hot solution was filtered, acidified with hydrochloric acid and evaporated to a small volume under reduced pressure. There was no precipitate of silver chloride. The mixture was dissolved in ether and extracted with sodium carbonate solution. The aqueous layer was acidified with hydrochloric acid, extracted with ether, and the acid removed once more with sodium carbonate solution. The acid was then reprecipitated by hydrochloric acid, extracted with ether, and crystallized from ether and petroleum ether; yield, 0.6 g. melting at 177.5–178.5°. Calculated as β-triphenylpropionic acid, the yield was 55%.

A duplicate experiment was carried out, but no sodium hydroxide was used in the silver oxide oxidation. At the end of the oxidation, 10 cc. of concentrated hydrochloric acid was added and boiling continued for one-half hour to liberate the acid from the silver salt; yield, 0.4 g. (37%) melting at 179°. The combined acids were recrystallized from 50% alcohol, the product being in the form of fine needles and melting at 180.5°. A mixed melting point with synthetic β-triphenylpropionic acid showed no depression.[1]

The non-acid fractions from the ozonizations were concentrated and treated with petroleum ether to the point of cloudiness. On standing overnight at 0°, a total of 0.85 g. of crystalline material melting at 135–137° was obtained; yield calculated as 1,1,1-triphenylbutanone-3, 39%. After two recrystallizations from ether, the substance melted at 140.5–141°. A mixed melting point with the synthetic material (see below) gave no depression.

1,1,1-Triphenylbutanone-3 was prepared by the reaction of β-triphenylpropionyl chloride and zinc methyl chloride.[2] Methylmagnesium iodide was prepared in the usual

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[1] Fosse, *Compt. rend.*, 145, 197 (1907); Kellerman, THIS JOURNAL, 49, 1737 (1927).

[2] This method was developed by W. D. Peterson in this Laboratory.

fashion from 0.45 g. of magnesium turnings, 2.7 g. of methyl iodide and 40 cc. of absolute ether. Four grams of stick zinc chloride was fused under reduced pressure until bubbling ceased. It was then taken up in 25 cc. of absolute ether and added to the Grignard reagent, cooling the latter meanwhile with an ice-salt mixture. The solution was then warmed to room temperature and stirred for fifteen minutes. β-Triphenylpropionyl chloride was prepared by treating β-triphenylpropionic acid with three times the calculated amount of thionyl chloride. The excess thionyl chloride was boiled off and the product heated under reduced pressure until odorless. A solution of 4 g. of this material in absolute ether was added to the zinc methyl chloride. After one hour's stirring with gentle boiling, the mixture was allowed to stand overnight. It was then decomposed with water and hydrochloric acid. The ether solution was washed with sodium hydroxide to remove any β-triphenylpropionic acid, dried with calcium chloride and evaporated to a small volume. On standing for some time, a crystalline product formed, which had a low indefinite melting point and was obviously impure. A portion was recrystallized twice from ether, and 0.33 g. of material melting sharply at 140.5–141° was obtained. In addition, 1.0 g. of another substance melting at 120–124° was obtained. (This was not further investigated.) The substance yielded iodoform on treatment with iodine and sodium hydroxide in methyl alcohol solution.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 88.2, 88.0; H, 6.9, 6.7.

Reaction of Hexaphenylethane with Dimethylbutadiene.—2,3-Dimethylbutadiene was prepared by the catalytic dehydration of pinacol with iodine, following the directions of Hibbert.[3] Five grams of triphenylmethyl chloride, 1.5 g. of dimethylbutadiene, 10 cc. of thiophene-free benzene and 15 g. of mercury were sealed in a nitrogen filled capsule and shaken on a machine for twelve hours. After one week's standing the contents of the capsule were shaken for some time with air to oxidize any hexaphenylethane, filtered, and concentrated. A slightly yellow crystalline material was precipitated by petroleum ether. This was recrystallized from benzene and petroleum ether, 1 g. melting at 227–231° being obtained. This was recrystallized twice from benzene and ether for analysis. It then melted at 240° under nitrogen with some decomposition.

Anal.[4] Calcd. for $C_{44}H_{40}$: C, 92.9; H, 7.1. Found: C, 92.6, 92.6; H, 7.36, 7.38.

Ozonization.—Ozonized oxygen was bubbled for five hours through a solution of 0.8 g. of the hydrocarbon in 50 cc. of carbon tetrachloride chilled with ice. After shaking with water and zinc dust and filtering, the solution was evaporated to dryness under reduced pressure. The gummy residue was dissolved in 5 cc. of ether, and a sandy precipitate formed weighing about 0.025 g. and melting above 150". The mother liquor was allowed to evaporate slowly at room temperature and the crystals which formed were washed with ether and recrystallized from the same solvent. The yield was 0.16 g. or 19%. The melting point was 140.5–141°. A mixed melting point with synthetic $(C_6H_5)_3CCH_2COCH_3$ showed no depression.

Summary

Triphenylmethyl combines with isoprene and dimethylbutadiene, addition taking place in the 1,4-position.

CAMBRIDGE, MASSACHUSETTS

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[3] Hibbert, THIS JOURNAL, 37, 1747 (1915).

[4] We are indebted to Miss H. F. Hawes for these microanalyses.

[Contribution from the Chemical Laboratory of Iowa State College]

CYCLOHEXYLMAGNESIUM CHLORIDE AND BROMIDE

By Henry Gilman and E. A. Zoellner

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Introduction

Grignard reagents are alike in the sense that they can be represented by the general formula RMgX. Strictly speaking, the resemblance ends here because of differences in rate of formation,[1] differences in yields,[2] differences in conditions for obtaining optimal yields,[3] differences in rates of reaction[4] and yields and kind of products with other reactants,[5] and differences in the degree of dissociation[6] and the extent of the equilibrium with $R_2Mg + MgX_2$ compounds.[6,7]

There are essential differences in the optimal conditions for the preparation of various RMgX compounds. Fortunately, these are not of a kind to warrant special procedures for every possible Grignard reagent. Actually it is possible to arrange roughly the methods for the preparation of RMgX compounds after the relative reactivities of the halogen in definite groups of RX compounds like R_3CX, RCH=CHX, RCH=CH-CH_2X, etc.

Cyclohexyl halides have properties which serve to set them apart from other RX compounds. This is reflected in some of the results reported in the present study. The relatively low and erratic yields and the troublesome by-products of cyclohexylmagnesium chloride and bromide, as reported very recently by different investigators,[8] can be avoided. It is possible to prepare cyclohexylmagnesium bromide in yields of about 92%, and cyclohexylmagnesium chloride in yields of about 96.5%.

The decrease in yield when cyclohexyl bromide is added very rapidly to magnesium in ether is one of the largest so far observed for RMgX

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[1] Gilman and Zoellner, This Journal, 50, 2520 (1928).

[2] Gilman and McCracken, *ibid.*, 45, 2462 (1923), and *Rec. trav. chim.*, 46, 463 (1927); Marvel, Blomquist and Vaughn, This Journal, 50, 2810 (1928); Gilman, Zoellner and Dickey, *ibid.*, 51, 1576 (1929).

[3] Gilman and McGlumphy, *Bull. soc. chim.*, 43, 1322 (1928); Gilman and Zoellner, This Journal, 50, 425 (1928); 51, 3493 (1929); 52, 3984 (1930).

[4] Gilman, Heck and St. John, *Rec. trav. chim.*, 49, 212 (1930); Gilman and St. John, *ibid.*, 49, 222 (1930).

[5] A leading recent reference is that of Conant and Blatt. This Journal, 51, 1227 (1929).

[6] Gilman and Fothergill, *ibid.*, 51, 3149 (1929).

[7] Schlenk and Schlenk, *Ber.*, 62, 920 (1929); Gomberg and Bachmann, This Journal, 52, 2455 (1930); Bachmann, *ibid.*, 52, 4412 (1930); Noller, *ibid.*, 53, 635 (1931).

[8] Palmer and Kipping, *J. Chem. Soc.*, 1020 (1930); Zelinsky and Titz, *Ber.*, 64, 183 (1931).

compounds, and is the largest decrease now known for a secondary bromide. On the other hand, the corresponding chloride shows but a small decrease in yield when the RCl compound is added rapidly. Very generally, a significant drop in yield of RMgX compound with a rapid addition of halide can be correlated with low and erratic results unless special conditions are observed. Partly for this reason it is recommended that cyclohexylmagnesium chloride instead of the bromide be used whenever possible. Not only does the chloride give higher yields of RMgX compound, but it gives higher yields with an astonishing abuse or lack of care in addition. Furthermore, RMgCl compounds enjoy other advantages over RMgBr and RMgI compounds: (1) they frequently undergo more ready reaction with another compound; (2) they generally give higher yields of products with a given reactant, and on the basis of an equal content of RMgX compound; and (3) there is probably a general lesser opportunity for side reactions because the binary system ($MgCl_2$ + Mg) is less active[g] than the corresponding systems with magnesium bromide and magnesium iodide. Over and against these general advantages, they are formed with slightly greater difficulty than the corresponding bromides or iodides; but the difference in time of starting, when a catalyst like iodine or the activated magnesium-copper alloy is used, is very small.

Experimental Part

The apparatus and general procedure were those used in related studies.[10] The quantity of RX compound was 0.05 mole, and the yields so obtained were duplicated in larger runs (0.2 and 0.5 mole). Additional confirmation of the essential correctness of the results obtained by titration was had in the very high yield of cyclohexanecarboxylic acid isolated subsequent to carbonation.

TABLE I

YIELDS OF CYCLOHEXYLMAGNESIUM CHLORIDE AND BROMIDE IN 0.05 MOLE EXPERIMENTS

RMgX (0.05 mole)	Magnesium (atom) Turnings	80-80 mesh	Av. % yield of RMgX
$C_6H_{11}MgCl$	0.055	..	91.1[a]
$C_6H_{11}MgCl$	...	0.055	94.4[b]
$C_6H_{11}MgCl$	...	.15	96.6[c]
$C_6H_{11}MgBr$	.055	..	80.1[d]
$C_6H_{11}MgBr$	...	.055	84.0[b]
$C_6H_{11}MgBr$	...	.15	92.0[e]

[a] About a 10% solution of chlorocyclohexane in ether was used to start the reaction with magnesium. In all experiments a small crystal of iodine was used. When all of the chloride had been added, the apparent reaction (as indicated by gentle refluxing, with no application of external heat) was five to ten minutes. When this spontaneous reaction had ceased, the mixture was stirred and refluxed for ten to fifteen minutes be-

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[e] Gomberg and Bachmann, THIS JOURNAL, 49, 2584 (1927); Gilman and Brown, *ibid.*, 52, 1128 (1930).

[10] Gilman, Zoellner and Dickey, *ibid.*, 51, 1576, 1583 (1929).

fore removing aliquots for analysis. In an experiment where the chloride in ether was added at one time (instead of dropwise over a period of thirty minutes), the yield was 90%, and the spontaneous reaction continued for thirty-five minutes after all the halide had been added. This yield was decreased 5% when undistilled chloride was used.

[b] Reaction sets in immediately with the fine magnesium (30–80 mesh). These runs were made under the same conditions as those with commercial turnings, with the exception that 8 equivalents of ether were used. The time of addition of the halide in ether was thirty minutes.

[c] The time of addition in these experiments was one hour, and 0.425 mole of ether was used. A larger ratio of ether is used with fine magnesium in order to reduce the spattering of magnesium on the walls of the flask.

[d] The bromide reacts more readily than the chloride, and an initial concentration of **6–7%** in ether is sufficient to start the reaction. Spontaneous reaction continued for five minutes after adding all of the bromide over a period of thirty minutes, and the mixture was then stirred and refluxed for ten minutes before removing samples for analysis. When all of the bromide in ether is added at once (after starting the reaction with a part of the bromide), the spontaneous reaction continues for twelve minutes and the yield drops to 54%. The time during which the spontaneous reaction occurs subsequent to addition of all of the halide is apparently a qualitative measure of the relative reactivity of the halide toward magnesium. Undistilled bromide decreases the yield **3%.**

The halides were freshly distilled, and as such gave higher yields and started to react with magnesium more readily than undistilled material. The time, and with some RX compounds the yield, is influenced by the nature of commercially available magnesium turnings. It is not an easy matter to describe the physical condition of the turnings, but those which gave the best results in the present study were about 0.48 mm. in thickness, 4 mm. in breadth and 10–50 mm. in length, when the coils were unwound.

Recommended Procedure for Laboratory Preparation.—The magnesium turnings (1.1 atom equivalents) are barely covered with ether and sufficient pure halide is added to give an optimal initial concentration (6–7% with bromide and 15% or greater with the chloride). After adding a crystal of iodine heat is applied, without stirring, and these conditions are maintained for five to ten minutes after the iodine color has disappeared. Reaction having set in, sufficient ether is added to cover the magnesium while it is stirred, and then the remainder of the halide in ether[11] is added. The rate of addition varies with the halide. With the chloride, there is no appreciable harm in rapid addition. However, the bromide must be added more slowly, and generally at a rate that causes gentle refluxing.

When all of the halide has been added, stirring and refluxing are continued for fifteen to twenty minutes with the chloride, and for ten minutes with the bromide.

The yield of cyclohexylmagnesium chloride in 0.2 and 0.5 mole runs under the above conditions is 92–95%.

In carbonating the Grignard reagent prepared as above, it is recommended that provision be made to admit an inert gas like nitrogen during

[11] In all about 6 mole equivalents of ether are used. One-half of this ether can be added to the mixture after the reaction has started, and the remainder is used to dilute the halide.

the cooling which is preliminary to carbonation. By so doing, the yield is improved because otherwise oxygen from the atmosphere would be pulled in and react with the Grignard reagent. In a 0.2 mole run the yield of cyclohexanecarboxylic acid based on an 80% yield of cyclohexylmagnesium bromide was 83%; and the yield of acid based on a 92% yield of cyclohexylmagnesium chloride was **93%.** It is recommended that the solution be diluted with ether (300–500 cc. in a 0.2 mole run) prior to carbonation, because of the sparingly soluble salt (RCOOMgBr) which is formed.

Summary

Cyclohexylmagnesium chloride and bromide can be prepared in excellent yields. In its reaction with magnesium, bromocyclohexane differs significantly from other secondary bromides. General recommendations are given for the use of RCl in preference to RBr and RI compounds for the preparation of Grignard reagents.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

PHYSICAL PROPERTIES OF THE NORMAL PARAFFIN HYDROCARBONS, PENTANE TO DODECANE

BY A. F. SHEPARD, A. L. HENNE AND T. MIDGLEY, JR.

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This paper presents some physical constants of the normal paraffin hydrocarbons, from pentane to dodecane, inclusive. These compounds have been prepared from a common source, and have all been purified by the same method and to the same extent. Consequently, physical measurements obtained with such samples are more comparable among themselves than are the isolated results obtained by various workers who have used different methods of synthesis, purification and measurement.

Preparation of the Samples.—The starting material was a special gasoline with a normal paraffin hydrocarbon content of about 70%. It was obtained from The Standard Oil Company of Indiana through the courtesy of R. E. Wilson. It was roughly separated into its constituents by distillation. Each cut was then treated with chlorosulfonic acid until a one-week treatment no longer altered the density. The details of this treatment have been reported previously.[1] Further purification was accomplished by careful fractionation through a flat spiral fractionating column, equipped with an efficient dephlegmator. The progress of the purification was measured by the density variations of the distillates. The purification was regarded as having reached its practical limit when the over-all density differences of several successive distillate fractions did

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[1] Shepard and Henne, Ind. *Eng. Chem.*, **22, 356 (1930).**

not exceed a few units of the fifth decimal. Table I summarizes the experimental results.

TABLE I

PREPARATIVE DATA

n-Paraffin	Properties after preliminary fractionation d^{25}_4	Engler distillation range, °C. 0–100%	10–90%	ClSO$_3$H treatment Amount treated, cc.	Days required	Pure product Volume recovered, cc.	Recovered, %	Over-all density range of product
Pentane[a]						550		0.00003
Hexane	0.672	1.1	0.6	2000	20	490	24	.00001
Heptane	.695	1.0	0.6	2880	49	650	23	.00001
Octane	.710	2.2	1.1	2545	45	730	29	.00001
Nonane	.724	2.2	0.7	2500	55	665	27	.00002
Decane	,739	3.0		1700	37	640	38	.00001
Undecane	.746	2.4	1.0	1550	54	745	48	.00002
Dodecane	.759	2.6	1.1	585	37	192	33	.00007

[a] Chlorosulfonic acid treatment of pentane is unnecessary; *cf.* S. Young. J. Chem. *Soc.*, 71, 440 (1897); 75, 172 (1899).

Repeated fractional crystallizations of these compounds gave no further separation; the freezing ranges were smaller than 0.1°.

Purity Tests.—Two criteria have been relied upon to indicate the degree of purity obtained, namely, the total boiling range (distillation curve) and the total freezing range (freezing curve). Details of the measurements are as follows.

Boiling ranges were determined on large samples of the hydrocarbons, usually 250 cc. The specimens were slowly distilled from a tube of the dimensions specified for the determination of the boiling point of sulfur.[2] The tube was provided with a side arm 17 mm. in diameter and was heated directly only on a small area at the bottom. Temperature readings were made as in an Engler distillation and the barometer was read at the same time. Superheating occurred when the last 5–10% of the sample was being taken off. To minimize this, the

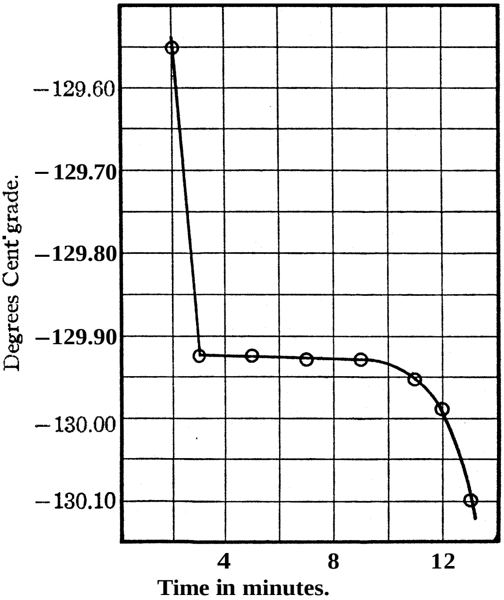

Fig. 1.—*n*-Pentane.

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[2] Mueller and Burgess, This Journal, 41, 745 (1919).

thermometer was covered with 0.5 g. of cotton,[3] which prevented superheating fairly effectively without changing the other distillation points or holding back much material. Where the substances boiled above 100°, a radiation shield of the type recommended by Mueller and Burgess[2] was used.[4] The boiling points were duplicated within ±0.01°.

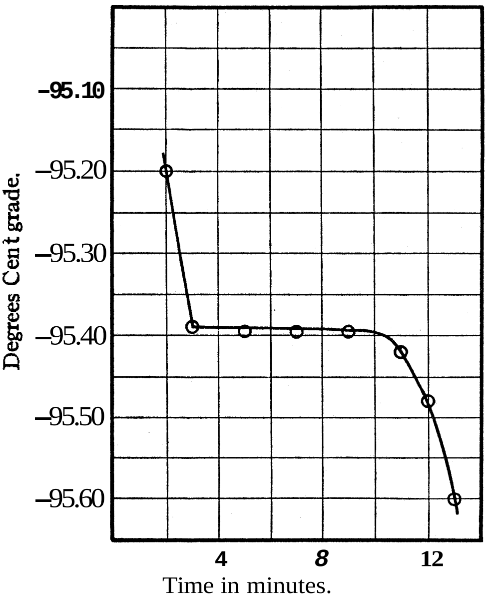

Fig. 2.—n-Hexane.

Since the accuracy of the absolute temperature measurements may have been less certain, the method of measuring is described. A platinum resistance thermometer (Leeds and Northrup No. 8162) was used. The Wheatstone bridge employed in the resistance measurements was of the Mueller type; the coils were checked among themselves and against primary standards, and corrections were made for temperature changes. A D'Arsonval galvanometer was used to determine the bridge balance; it was sufficiently sensitive to permit the measurements of less than 0.00001 ohm with the measuring current of 0.01 ampere which was used.

Calibration of the thermometer was made in the standard way at the ice, steam and sulfur points, taking the boiling point of sulfur as 444.60°.[5] The constants of the thermometer were as follows: R_0, 2.5079 ohms; R_{100}, 3.4882 ohms; $R_{443.22°}$, 6.62855 ohms. The fundamental coefficient calculated from these data is 0.003909 and A is 1.504, which constants indicate the platinum to be of the requisite purity. Checks on the calibration were obtained at the transition point of sodium sulfate decahydrate, and at several other temperatures between 0 and 100" against an instrument newly calibrated by the Bureau of Standards. All the instruments were frequently rechecked and agreement to ±0.01° was obtained in all cases.

A Fortin barometer was used in all the work; it was checked against the

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[3] An equivalent volume of glass wool was used when undecane and dodecane were distilled.

[4] The use of this shield made no change in the observed boiling points of water and of octane.

[5] Glazebrook "Dictionary of Applied Physics," Macmillan Co., London, 1922, Vol. I, p. 706.

local Weather Bureau instruments and the necessary corrections were made for temperature, elevation, latitude and capillarity. Boiling points were determined at several pressures near 760 mm. and were corrected to standard conditions with the aid of the dt/dp noted in Table II. The values thus obtained agreed in general to ±0.01°.

TABLE II

BOILING RANGES OF HYDROCARBONS

n-Paraffin dt/dp % Distd.	C_5H_{12} 0.039	C_6H_{14} 0.042	C_7H_{16} 0.045	C_8H_{18} 0.048	C_9H_{20} 0.050	$C_{10}H_{22}$ 0.052	$C_{11}H_{24}$ 0.054	$H_{12}C_{26}$ 0.056
0	35.99	68.70	98.37	125.57	150.69	174.04	195.80	216.16
10	36.00	68.70	98.38	125.58	150.70	174.05	195.81	216.19
20	36.00	68.71	98.38	125.58	150.70	174.06	195.81	216.20
30	36.00	68.71	98.38	125.59	150.71	174.06	195.82	216.21
40	36.00	68.71	98.38	125.59	150.71	174.06	195.83	216.22
50	36.00	68.71	98.38	125.59	150.71	174.06	195.84	216.23
60	36.01	68.71	98.38	125.59	150.72	174.06	195.84	216.24
70	36.01	68.71	98.38	125.60	150.73	174.07	195.85	216.25
80	36.02	68.72	98.39	125.60	150.73	174.07	195.86	216.27
90	36.03	68.72	98.39	125.60	150.74	174.08	195.87	216.30
95	36.03	68.72	98.39	115.61	150.74	174.09	195.89	216.35
Dry	36.05	68.73	98.40	125.61	150.74	174.10	195.92	216.42

NOTE.—Undecane and dodecane did not appear to be absolutely stable to distillation at atmospheric pressure. The distilled specimens gave a slight brown color to concd. sulfuric acid on shaking with it, and the acid on dilution had the odor of a higher alcohol. The pure materials gave no color on shaking with this acid, and no odor on dilution.

Freezing points were determined on 120-cc. samples. The resistance thermometer used had been calibrated for low temperature work by the Bureau of Standards. The constants of the thermometer were as follows: R_0, 25.575 ohm; R_{100}, 35.532; and A and β in the modified Callendar equation for use at low temperatures were 1.48 and 0.115. respectively. The freezing curves are given in Figs. 1–8.

Physical Properties.—The following properties have been measured.

Boiling Points and Freezing Points.—The experimental details are reported in the preceding paragraphs. For typographical reasons, only every fourth experimental point is reproduced on the freezing curves.

TABLE III

ROILING POINTS, MELTING POINTS AND DENSITIES

n-Paraffin	B. p , °C.	M. p., °C.	d_4^{20}	d_4^{25}
Pentane	36 00	−129.93	0 62632	
Hexane	68.71	− 95.39	.65945	0.65502
Heptane	98.38	− 90.65	.68378	.67963
Octane	125.59	− 56.90	.70279	,69882
Nonane	150.71	− 53.68	.71780	.71398
Decane	174.06	− 29.76	.73014	.72643
Undecane	195.84	− 25 65	.74025	.73667
Dodecane	216 23	− 9.73		.74542

Densities.—Densities have been taken at 20 and 25°. They were measured in 40-cc. pycnometers of the Sprengel type. The necessary temperature control was obtained with a thermostat held constant to ±0.01°, and the absolute accuracy of the temperature was checked against three Bureau of Standards thermometers. Weighings were made with standardized weights. All densities were reduced to vacuum and are accurate to *0.00003.

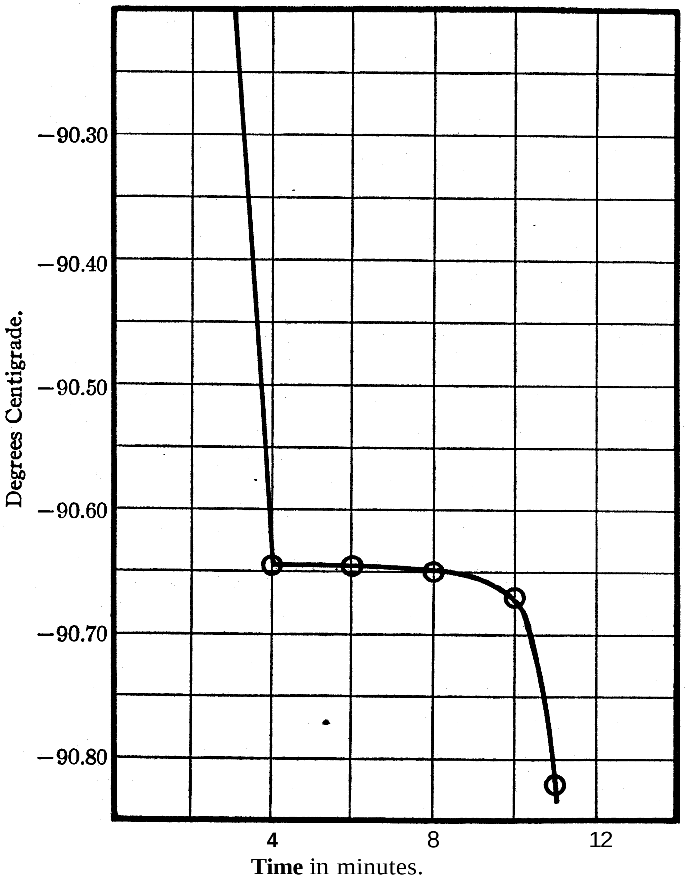

Fig. **3.—n-Heptane.**

Refractive Indices **and** Molecular Refractions.—Refractive indices relative to air were measured with a Pulfrich refractometer for the α, β and D lines. The refractometer was calibrated with pure water and the temperature desired was maintained by a current of water from a thermostat regulated to ±0.01°, the temperature of which had been checked with two Bureau of Standards thermometers. The refractometer prism was at the temperature indicated. Determinations were made at 20, 25 and 45.3° and are given in Table IV. Table V gives the molecular refractions and dispersions at 25°, calculated by the Lorentz–Lorenz formula, and by the more exact empirical formula of Eykman.[6]

TABLE IV

REFRACTIVE INDICES OF HYDROCARBONS

	Temp., °C.	20°	25°	45.3°
Pentane	n_α	1 35581	1.35309	
	n_D	1.35769	1.35495	
	n_β	1.36208	1.35930	
Hexane	n_α	1.37310	1,37043	1.35924
	n_D	1.37506	1.37230	1.36132
	n_β	1.37979	1.37695	1.36567
Heptane	n_α	1.38580	1.38345	1.37303
	n_D	1 38775	1.38553	1.37519
	n_β	1.39261	1.39035	1.37970
Octane	n_α	1.39557	1.39328	1.38334
	n_D	1 39760	1.39534	1.38561
	n_β	1.40255	1.40030	1.39037
Nonane		1.40356	1.40125	1.39181
		1.40563	1.40340	1.39389
	n_β	1.41077	1.40846	1.39883
Decane	n_α	1.40994	1.40771	1.39831
	n_D	1.41203	1.40986	1.40047
	n_β	1.41728	1.41492	1.40549
Undecane	n_α	1.41514	1.41300	1.40384
	n_D	1.41727	1.41516	1.40611
	n_β	1.42252	1.42036	1.41111
Dodecane	n_α	1.41965	1.41752	1.40852
	n_D	1.42188	1.41967	1.41081
	n_β	1.42720	1.42501	1.41588

TABLE V

MOLECULAR REFRACTIONS AND DISPERSIONS (FROM DATA AT 25°)

	Lorentz–Lorenz formula							
	MR_α		MR_D		MR_β		Dispersion $H_\beta - H_\alpha$	
n-paraffin	Obs.	Calcd.	Obs.	Calcd.	Obs	Calcd.	Obs.	Calcd.
C_5H_{12}[a]	25.14	25.17	25.26	25.29	25.54	25.57	0.40	0.40
C	29.77	29.77	29.90	29.91	30.23	30.24	.46	.47
C_7H_{16}	34.41	34.36	34.57	34.53	34.95	34.91	.54	.54
C_8H_{18}	39.01	38.96	39.19	39.14	39.62	39.57	.61	.61
C_9H_{20}	43.63	43.56	43.84	43.76	44.32	44.24	.69	.69
$C_{10}H_{22}$	48 25	48.15	48.48	48.38	49.01	48.91	.75	.76
$C_{11}H_{24}$	52.87	52.75	53.11	53 00	53.70	53.58	.83	.83
$C_{12}H_{26}$	57.49	57.35	57.75	57.62	58.39	58.25	.90	.90

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[6] J. P. Eykman, *Rec. trav. chim.*, 15, 52 (1896).

TABLE V (*Concluded*)

	Eykman formula			
	$MR\alpha$		$MR\beta$	
n-Paraffin	Obs.	Calcd.	Obs.	Calcd
C_5H_{12}[a]	54.95	54.99	55.88	55.86
C_6H_{14}	65.20	65.26	66.29	66.29
C_7H_{16}	75.50	75.51	76.78	76.73
C_8H_{18}	85.73	85.77	87.19	87.16
C_9H_{20}	96.02	96.03	97.64	97.59
$C_{10}H_{22}$	106.28	106.29	108.05	108.02
$C_{11}H_{24}$	116.54	116.55	118.50	118.45
$C_{12}H_{26}$	126.81	126.81	128.94	128.88

[a] From data at 20°.

Critical Temperature of Solution.—The critical temperature of solution of each hydrocarbon was measured in freshly distilled dry aniline having a boiling range <0.1°. Known amounts of aniline and the hydrocarbons were sealed in tubes and placed in a holder which was immersed in a large insulated water-bath. The bath was provided with an efficient stirrer and the tubes were continuously shaken while observations were being made. The Critical Temperature of Solution was observed on raising and lowering the temperature of the bath, and the rate of heating and cooling was such that the values obtained on heating and cooling checked to 0.1°. Temperatures were measured with a Beckmann thermometer which was frequently checked against two standard instruments. The results are believed to be reproducible to only ±0.1° because of the

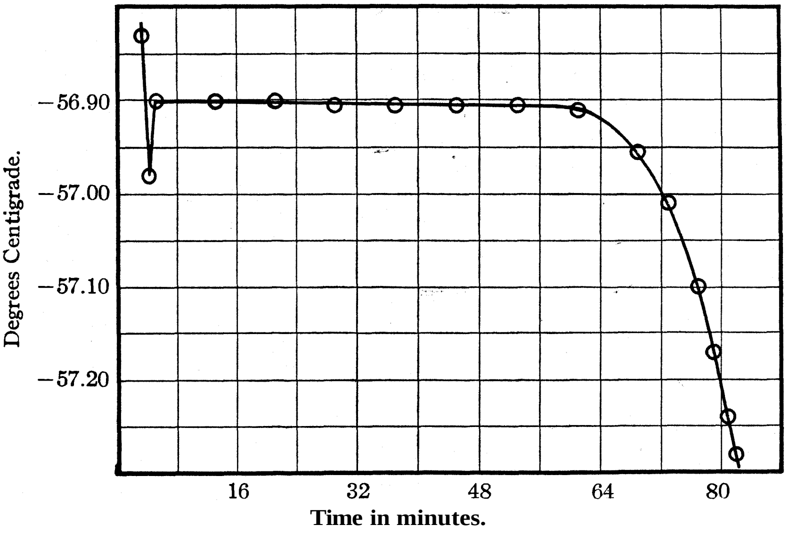

Fig. 4.----Octane.

personal factor involved in judging the exact temperature of complete solution. Fig. 9 shows the results obtained.

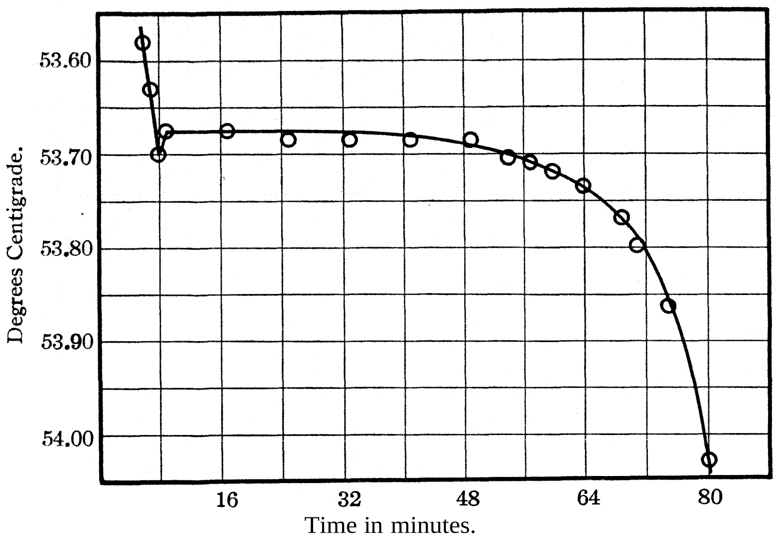

Fig. 5.—n-Nonane.

Viscosities.—Viscosities were measured in a pyrex viscometer of the type recommended by Washburn and Williams.[7] In view of the element of uncertainty attendant to the use of a kinetic energy correction,[8] the dimensions of the instrument were so adjusted that the kinetic energy correction amounted to less than 0.5% of the viscosity value in the case of n-pentane. The correction was neglected in computing the viscosities. The temperature was controlled to ±0.02° during the measurements; the values obtained are accurate to 0.5%.

Other Properties.—Several other properties have been

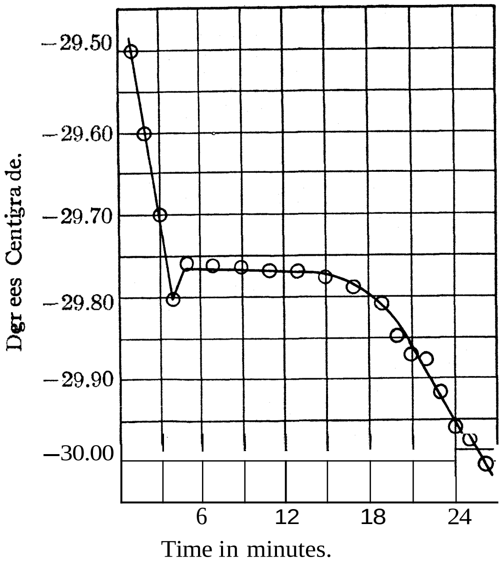

Fig. 6.—*n*-Decane.

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[7] Washburn and Williams, This Journal, 35, 737 (1913).

[8] F. Martin. *Bull. soc. chim. Belg.*, 34, 81 (1925).

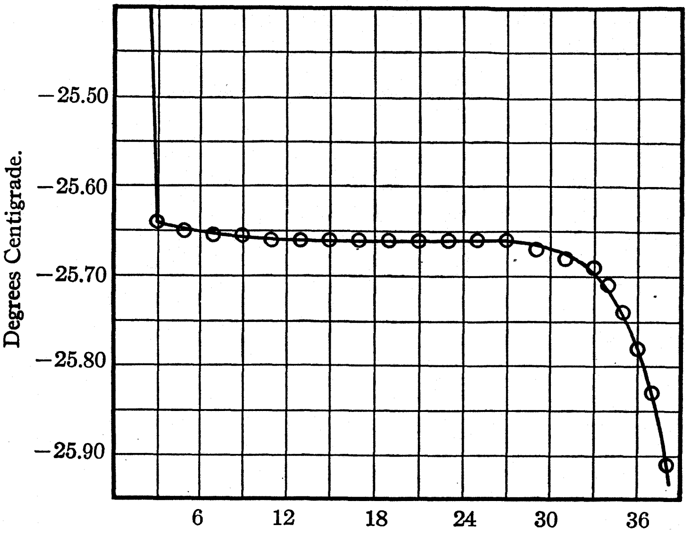

Fig. 7.—*n*-Undecane.

measured by other experimenters, to whom we here express our gratitude for measuring these properties and also for checking those already obtained in this Laboratory. The specific heats and heats of fusion have been measured by G. S. Parks of Stanford University, the dielectric constants and

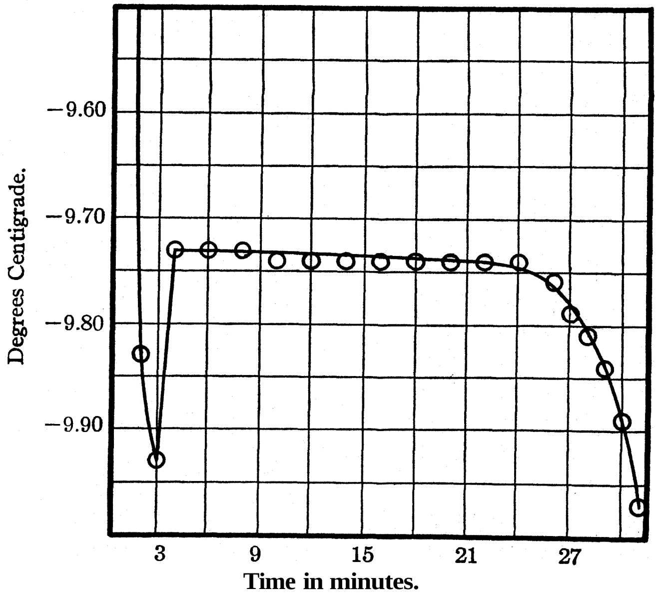

Fig. 8.—n-Dodecane.

densities by R. W. Dornte and C. P. Smyth,[9] the fluidity by E. C. Bingham and H. J. Fornwalt,[10] while at the present time the Bureau of Standards is measuring the heats of combustion and vapor pressure curves and the General Motors Research Laboratory is determining the Raman spectra.

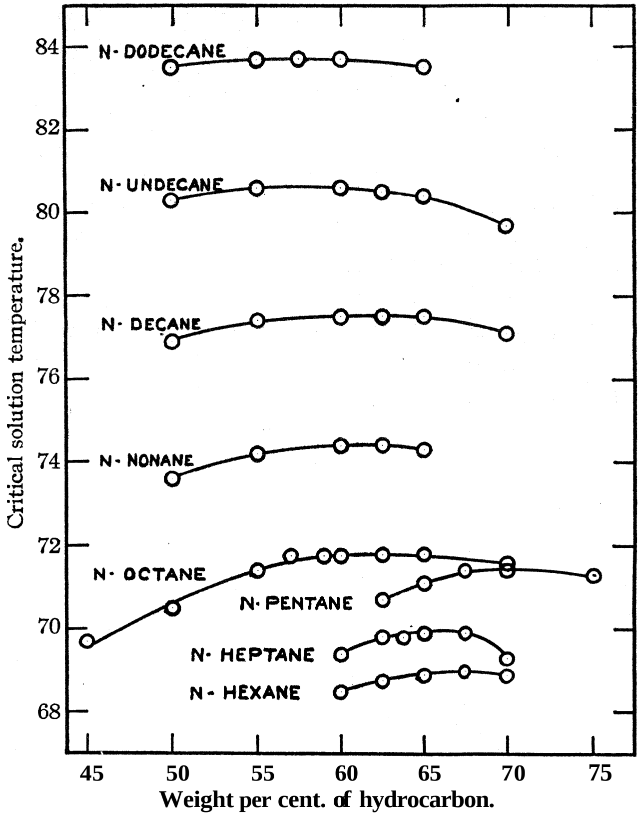

Fig. 9.

Empirical Relation Involving the Boiling Points, Molecular Weight, Refractive Indices and Densities.—Nekrasov[11] has proposed the relation $T\frac{\sqrt{MR}}{M-MR} = \text{constant}$, where T is the boiling point in °K., M is the molecular weight, and MR is the molecular refraction calculated by means of the Lorentz–Lorenz formula. He computed the constants of the normal paraffins by using data from the Landolt–Börnstein tables. They are reported in the second column of Table VII. They seem to exhibit a

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[9] R. W. Dornte and C. P. Smyth, THIS JOURNAL, 52, 3546 (1930).

[10] E. C. Bingham and J. H. Fornwalt, J. *Rheology*, 1, 372 (1930).

[11] B. Nekrasov, *Z. physik. Chem.*, *[A]* 140, 342 (1929).

TABLE VI

VISCOSITIES AND CRITICAL TEMPERATURES OF SOLUTION

n-Paraffin	Viscosity at 25° C. G. S. units × 10^5	Fluidity at 25° ÷ 10^5	C. T. S. in aniline
Pentane	216.6	461.6	71.4"
Hexane	293.7	340.4	69.0°
Heptane	385.9	259.1	69.9°
Octane	508.3	196.7	71.8"
Nonane	662.1	151.0	74.4"
Decane	852.7	117.3	77.5°
Undecane	1081	92.5	80.6"
Dodecane	1353	73.9	83.7"

functional variation, but when they are recomputed, to include the second decimal, this functional variation disappears. However, when the experimental data reported in this article were substituted for the Landolt values, a functional variation reappeared. The Nekrasov constants computed from densities and refractive indices measured at 25° are reported in the three last columns of Table VII; they were computed for the α, D and β lines, respectively.

TABLE VII

NEKRASOV'S CONSTANTS

	Nekrasov's computed values	Experimental values		
		K_{α}^{25}	K_{D}^{25}	K_{β}^{25}
Pentane	33.2	33.048	33.208	33.591
Hexane	33.3	33.105	33.259	33.640
Heptane	33.3	33.161	33.323	33.702
Octane	33.3	33.148	33.307	33.685
Nonane	33.1	33.127	33.286	33.662
Decane	33.1	33.076	33.233	33.604
Undecane	32.9	33.006	33.161	33.532
Dodecane	32.8	32.919	33.069	33.442

Summary

The normal paraffin hydrocarbons, from pentane to dodecane inclusive, have been prepared from a common source, by a single method, and in a comparable state of purity. Their boiling points, freezing points, densities, refractive indices, viscosities and critical temperature of solution in aniline have been determined. Evidence is presented to support the degree of accuracy claimed for the measurements. The boiling points and molecular refractions have been correlated by means of the Nekrasov equation.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS FROM THE STANDPOINT OF FREE RADICALS. I. SATURATED HYDROCARBONS

BY F. O. RICE

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When an organic compound decomposes, we may assume that it is broken up into two or more radicals depending on the number of bonds in the molecule. These radicals fly apart and the probability that they meet again and react is so small that we can neglect it. A radical produced in this way may do one of three things: first, it may react with one of the surrounding molecules; second, it may decompose into a compound and a smaller radical; or, third, it may diffuse to the wall and be absorbed there. In order to simplify our problem we will consider only a small fractional decomposition (a maximum of 5 to 10%) of the organic compound. Under these conditions the radicals produced can react only with the original substance and our problem is much less complicated. On the other hand, if we allow the organic compound to decompose to a considerable extent, the radicals react not only with the original compound but also with the products of the reaction, and the whole problem becomes hopelessly involved.

We can proceed with some confidence to examine the mechanism of the decomposition of organic compounds from this point of view because the actual existence of the simple alkyl radicals has now been demonstrated. Paneth and Hofeditz[1] heated lead tetramethyl in a rapid current of hydrogen and showed that the methyl groups were carried along the tube and could be made to react as far as 40 cm. from their point of origin. A later report by Paneth and Lautsch[2] stated that by means of similar experiments they had been successful in preparing the free ethyl radical. Less direct, although equally convincing, experiments have been made by Taylor and Jones,[3] in which they initiated the polymerization of ethylene by ethyl groups formed in the decomposition of lead or mercury alkyls.

The necessity for the use of free radicals in explaining the mechanism of organic decompositions becomes very evident even in the decompositions of fairly simple organic compounds. Propane decomposes into propylene and hydrogen, and it is conceivable that this occurs by the separation of a hydrogen molecule formed by two hydrogen atoms from adjacent carbon atoms; but it also breaks up into methane and ethylene, and for this to occur a hydrogen atom must jump from a 1 position to a 3 position, a

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[1] Paneth and Hofeditz, *Ber.*, 62, 1335 (1929).

[2] Paneth and Lautsch, *Nature*, 125, 564 (1930).

[3] Taylor and Jones, THIS JOURNAL, 52, 1111 (1930).

behavior which to say the least would be very remarkable.[4] Even more improbable mechanisms must be used to represent the decomposition of more complicated compounds.

When a paraffin hydrocarbon decomposes, we may assume that a C–C bond or a C–H bond breaks, and that this occurs in different ways depending on the complexity of the molecule. In order to determine the nature of the different fragments it is necessary to obtain an estimate of the strength of the different bonds present. From thermochemical measurements,[5] the heat of formation of methane from gaseous carbon and gaseous hydrogen atoms is

$$C_g + 4H_g \longrightarrow CH_{4g} + 373.2 \text{ kg. cal.}$$

which gives for the strength of the C–H bond in methane the value **93.3** kg. cal. A similar calculation for ethane gives

$$2C_g + 6H_g \longrightarrow C_2H_{6g} + 630.8 \text{ kg. cal.}$$

The strength of the C–H bonds in ethane will probably be slightly less than that of the C–H bonds in methane, but for the purpose of calculating the strength of the C–C bond we may assume that the C–H bond in methane and ethane has the same strength; there are six C–H bonds in ethane so that the strength of the C–C bond in ethane is $630.8-(6 \times 93.3)=71.0$ kg. cal.[6] It is obvious therefore that any breaking of a C–H bond is wholly negligible compared with that of a C–C bond. Paraffin hydrocarbons therefore decompose only through rupture of a C–C bond, thus producing two free radicals which fly apart and whose fate we will now consider.

A methyl group formed in this way probably undergoes only one reaction, namely, it takes a hydrogen atom from a molecule of the surrounding hydrocarbon to form methane and leave a free radical containing the same number of carbon atoms as the original hydrocarbon. It is true that this reaction will require some energy of activation, but even if it requires as much as 50,000 cal. it will go a great deal faster than the decomposition of the original hydrocarbon which requires a minimum activation energy of 71,000 cal. Furthermore, this process can occur even if the C–H bonds in methane and in the hydrocarbon have the same strength and it is

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[4] It is possible, of course, that one of the methyl groups might take one of the adjacent hydrogen atoms and the ethylidene radical then rearrange to ethylene; this mechanism, however, is not much better and could not occur in the reaction $CH_3COCH_3 \longrightarrow CH_4 + CH_2{=}CO$.

[5] The necessary data were taken from the "International Critical Tables," Volume V. Similar calculations have been made by Fajans, *Ber.*, 53, 643 (1920); 55, 2826 (1922); see also Weinberg, *ibid.*, 53, 1347, 1353, 1519 (1920); Hückel, *ibid.*, 55, 2839 (1922); Thiel, *ibid.*, 55, 2844 (1922).

[6] These figures will be used in the discussion and calculations but they are by no means certain, and will be discussed in greater detail in a separate communication: See Ellis, Phys. Rev., 33, 27 (1929); Mecke, *Nature*, 125, 527 (1930); Iredale and Mills, *ibid.*, 126, 604 (1930); Mecke, *Z.* physik. *Chem.*, [B] 7, 108 (1930); Hogness, paper presented at Indianapolis Meeting, American Chemical Society, April, 1930.

greatly favored by the condition which we have imposed, namely, a small percentage decomposition of the original hydrocarbon and therefore a small percentage of methane present. The methyl radical has a high chance of colliding with the hydrocarbon molecule and combining with one of its hydrogen atoms, but the hydrocarbon radical produced collides mainly with hydrocarbon molecules and only rarely with a methane molecule; furthermore, the process of methane formation from the free methyl group is also favored by the fact that the C–H bonds in methane are stronger than those in any other hydrocarbon. However, since heats of combustion are approximately additive, this difference is not great and can at most amount to 3 or 4 kg. cal. If we assume, for example, a difference of 2 kg. cal. in the C–H bonds of methane and the hydrocarbon under consideration, we can calculate the relative probability of loss of a hydrogen atom by a methane molecule or by a hydrocarbon molecule, when the two substances are present in equal concentrations. At 600° the process, CH_3 + hydrocarbon = CH_4 + hydrocarbon-radical, is $e^{2000/2 \times 873} = 3.2$ times more probable than the reverse reaction.

It is obvious that in the decomposition of hydrocarbons, radicals higher than methyl will be produced and we shall now discuss their possible behavior. Unlike the methyl group they can undergo two kinds of reactions; first, they may take a hydrogen atom from the surrounding hydrocarbon molecules and form a saturated hydrocarbon containing the same number of carbon atoms in the molecule; or, second, they may decompose either by giving off a hydrogen atom and forming a compound containing the same number of carbon atoms as the original hydrocarbon or they may break into a compound and a smaller free radical. This behavior may be best discussed with reference to a special example.

From the preceding discussion it will be seen that propane can decompose in one way only, namely, into a free methyl group and a free ethyl group. The resulting methyl group can undergo only one reaction, forming methane, but there are two possibilities for the ethyl group; it can take a hydrogen atom from one of the surrounding propane molecules to form ethane or it can decompose into ethylene and a hydrogen atom. It is now necessary to examine whether this last reaction can occur to an appreciable extent. The heat of formation of ethylene from gaseous carbon and gaseous hydrogen atoms is

$$2C_g + 4H \longrightarrow C_2H_{4g} + 497.0 \text{ kg. cal.}$$

The hydrogen atoms in ethylene are probably more strongly bound than those in methane, but as a first approximation we may assume that they are identical and we can thus calculate[5] the strength of the C=C bond to be $497.0 - (4 \times 93.3) = 123.8$ kg. cal. Therefore when a hydrogen atom flies off from the ethyl radical, a single bond becomes a double bond and thus $123.8 - 71.0 = 52.8$ kg. cal. becomes available. The energy necessary to break a C–H bond is 93.3 kg. cal., so that at least 93.3−52.8=40.5 kg. cal. of activation energy must be provided. Since the propane decomposition requires a heat of activation of at least 71.0 kg. cal., a rough estimate of the ratio of its decomposition to that of the decomposition of the ethyl radical into ethylene and hydrogen atoms is given by $e^{71000-40500/RT}$; for 600° and equal concentrations of propane and ethyl groups this ratio is $1:10^{7.5}$.

It is possible therefore, through a process of internal compensation, for a free radical to decompose into a hydrogen atom and a compound containing a double bond; the formation of the double bond contributes to the activation energy necessary to decompose the radical and thus permits the separation of a free hydrogen atom. An ethyl radical might also decompose into a methyl radical and the methylene radical, but this reaction would require a minimum activation energy of 71 kg. cal., and is therefore much less probable than the decomposition into ethylene and a hydrogen atom, which requires only 40.5 kg. cal.

It does not seem possible to calculate the relative probabilities of the two reactions

$$CH_3CH_2 + CH_3CH_2CH_3 \longrightarrow C_2H_6 + \text{propyl or isopropyl radical, and}$$
$$CH_3CH_2 \longrightarrow CH_2{=}CH_2 + H$$

but we can predict that dilution with an inert gas will diminish the bimolecular formation of ethane and leave the unimolecular decomposition unaffected; raising the temperature should also favor the ethylene reaction, since ethylene becomes relatively more stable than ethane at high temperatures.

When a hydrogen atom is removed from propane by a methyl or an ethyl group, either a free n-propyl or free isopropyl group results. The n-propyl radical can break up in a variety of ways, such as $CH_3CH_2CH_2 \longrightarrow CH_2{=}CH_2 + CH_3$, or $CH_3CH_2CH_2 \longrightarrow CH_3CH{=}CH_2 + H$, or $CH_3CH_2CH_2 \longrightarrow CH_3CH_2 + CH_2$. The first reaction is the most probable one since its minimum activation energy is only 18.2 kg. cal., as compared with 40.5 kg. cal. for the second and 71 kg. cal. for the third reaction. The isopropyl radical can also decompose in a variety of ways, but here again we find that the reaction

$$CH_3CHCH_3 \longrightarrow CH_2{=}CHCH_3 + H$$

is very much more probable than any other since it requires a minimum activation energy of 40.5 kg. cal. With hydrocarbons higher than propane we obtain the corresponding higher radicals and these can decompose in a great variety of ways; in every case, however, we can make calculations similar to those made for the propyl and isopropyl radicals and we find almost without exception that one decomposition is very much more probable than any other.

We see, therefore, that if any free radical R (except methyl) is introduced into a hydrocarbon it can decompose either into a hydrogen atom and a compound containing a double bond or into a smaller free radical and a compound containing a double bond. If a hydrogen atom is produced it will combine with one of the hydrogen atoms of the surrounding hydrocarbon to give a hydrogen molecule and the free radical R' corresponding to the hydrocarbon. This free radical, R', is also formed if the original free radical R combines with one of the hydrogen atoms of the hydrocarbon. The radical R' can only dissociate and will give a compound containing a double bond and either a smaller free radical or a hydrogen atom. Whichever is produced will then start a new cycle of reactions in which it is regenerated and this process presumably may go on for a great number of times.

Organic decompositions are therefore regarded as chain reactions in which certain atoms or radicals start a cycle of reactions at the end of which they are regenerated and start a new cycle. It follows, therefore, that the composition of the products is practically independent of the primary decomposition of the hydrocarbon and is determined almost exclusively by the chain cycle; this of course is only true if the chains are fairly long, *i. e.*, if they consist of 100 or more cycles. The atoms or groups which are regenerated are called carriers,[7] in order to distinguish them from other radicals which do not carry on the chain; the carriers are different for different reactions and are sometimes not produced in the primary decomposition but only at the end of the first chain cycle; since in the succeeding cycle the carrier is converted into a paraffin hydrocarbon, the carriers determine the saturated part of the products of the decomposition. The carriers may be destroyed in various ways, although combination through ternary collisions is probably the most important; recombination may also occur to some extent on the walls of the vessel but this effect cannot be very great because an increase of the surface to volume ratio does not appreciably affect the rate of decomposition.

Up to the present we have assumed that the C–H bond in all hydrocarbons and radicals is the same, and this is undoubtedly true in most cases to within 1 or 2%. However, before considering in detail the decomposition of the various hydrocarbons, it seems desirable to try to make an estimate of this small correction for the different C–H bonds. If we consider, for example, a free methyl group surrounded by molecules of propane, two side reactions can occur, according as the methyl group combines with a primary hydrogen atom or with a secondary hydrogen atom; and if all the hydrogen atoms of propane were exactly alike, the relative probabilities of the two reactions would be 6:2. The experimental results[8] for small fractional decompositions of propane show that

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[7] See Lewis, THIS JOURNAL, 52, 3120 (1930).

[8] Pease and Durgan, *ibid.*, 52, 1266 (1930).

the gases contain about 30% CH_4 and 20% H_2 and if we assume that all the hydrogen atoms are alike the calculated values are 37.5% CH_4 and 12.5% H_2; but undoubtedly the secondary hydrogen atoms are more loosely bound and if we assume that the strength of the secondary C–H bond is 1200 cal. less than the primary C–H bond, the calculated and the experimental values agree.

This value of 1200 cal. was therefore fixed arbitrarily and was assumed to be the same for all secondary C–H bonds; similarly, the strength of a tertiary C–H bond was taken arbitrarily as 4000 cal. less than the strength of a primary C–H bond. Table I was drawn up on the basis of these figures; a primary C–H bond is supposed always to have the same strength, a secondary C–H bond 1200 cal. less and a tertiary C–H bond 4000 cal. less. It is not true, of course, that all primary C–H bonds or all secondary C–H bonds have the same strength, but we can reasonably assume that the difference between two primary C–H bonds is small compared with the difference between primary and secondary C–H bonds. When measurements of the strengths of bonds can be made more precise it will no doubt be possible to assign slightly different values within the different classes of C–H bonds.

Column *2* gives the relative chance of loss of one particular hydrogen atom from a hydrocarbon, leaving a free radical, at 550° and columns 3 and 4 contain the same calculations for 600 and 650°; column 5 contains a statistical factor to take care of the number of hydrogen atoms of the particular kind available; multiplying by this factor we obtain columns 6, 7 and 8 which give the relative probabilities of radical formation by loss of any hydrogen atom of a particular kind from the different hydrocarbons at 550, 600 or 650°, respectively.

TABLE I

RELATIVE PROBABILITIES OF RADICAL FORMATION FROM DIFFERENT HYDROCARBONS

	1 ΔQ	2 $e^{-\Delta Q/1696}$ 550°	3 $e^{-\Delta Q/1746}$ 600°	4 $e^{-\Delta Q/1796}$ 650°	3 S	6 **P** 550°	P 600°	8 P 650°
$CH_3CH_2CH_2$–	0	1	1	1	6	6	6	6
$CH_3CH_2CH_2CH_2$–	0	1	1	1	6	6	6	6
$CH_3CH_2CH_2CH_2CH_2$–	0	1	1	1	6	6	6	6
$CH_3CH(CH_3)CH_2CH_2$–	0	1	1	1	3	3	3	3
$CH_3CH(CH_3)CH_2$–	0	1	1	1	9	9	9	9
$CH_3CH_2CH(CH_3)CH_2$–	0	1	1	1	6	6	6	6
CH_3CHCH_3	–1200	2.07	2	1.92	2	4.14	4	3.84
$CH_3CH_2CH(CH_3)$–	–1200	2.07	2	1.92	4	8.28	8	7.68
$CH_3CH_2CH_2CH(CH_3)$–	–1200	2.07	2	1.92	4	8.28	8	7.68
$CH_3CH_2CH(CH_2CH_3)$–	–1200	2.07	2	1.92	2	4.14	4	3.84
$CH_3CH(CH_3)CH_2CH_3$	–1200	2.07	2	1.92	2	4.14	4	3.84
$(CH_3)_3C$–	–4000	11.3	9.9	8.7	1	11.3	9.9	8.7
$(CH_3)_2C(CH_2CH_3)$–	–4000	11.3	9.9	8.7	1	11.3	9.9	8.7

The remaining part of this paper will be devoted to applying this concept to particular examples. In each case a series of equations will be given representing the course of the decomposition. The primary reactions are designated by the letter P and consist of the breaking of a C–C bond in different ways depending on the complexity of the molecule. Usually some of these radicals decompose or react with the surrounding hydrocarbon molecules in such a manner that they are not regenerated and these secondary reactions (S) are also given. However, the chain reactions designated by the letter A are the most important because they determine principally the composition of the products. An examination of these chain reactions will show that many of the radicals produced in the primary or secondary changes disappear in one chain cycle and the carriers formed determine the amount of saturated hydrocarbons and hydrogen in the products. The relative probabilities of the different chain reactions are given in Table I and determine the composition of the products; this has been calculated for different hydrocarbons and compared with such experimental data as are available.

Ethane.—The thermal decomposition of ethane may be represented as

P_1 $CH_3CH_3 \longrightarrow 2CH_3-$
S_1 $CH_3CH_3 + CH_3- \longrightarrow CH_4 + CH_3CH_2-$
S_2 $CH_3CH_2- \longrightarrow CH_2{=}CH_2 + H$
A $CH_3CH_3 + H \longrightarrow H_2 + CH_3CH_2- \longrightarrow H_2 + CH_2{=}CH_2 + H$

The decomposition of ethane is particularly simple because there is only one kind of chain cycle and one carrier, namely, the hydrogen atom. The decomposition should produce, therefore, ethylene and hydrogen in equal proportions providing the chains are fairly long, consisting of perhaps one hundred or more cycles. If the chain is very short and consists of only three or four cycles, there should be a considerable amount of methane present in the gases. The amount of methane present is of very great importance in connection with this proposed mechanism, because it enables us to calculate the number of chain cycles per hydrogen atom produced from a primary and secondary reaction or, in other words, the length of the chain. One molecule of methane is formed for every atom of hydrogen produced from the primary decomposition, and one molecule of hydrogen is produced in each chain cycle; consequently the ratio of H_2 to CH_4 should be the length of the chain.

Propane.—The mechanism for the decomposition of propane may be represented as

P_1 $CH_3CH_2CH_3 \longrightarrow CH_3CH_2- + CH_3-$
S_1 $CH_3CH_2- \longrightarrow CH_2{=}CH_2 + H$
S_2 $CH_3CH_2- + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH_2CH_2- \longrightarrow C_2H_6 + CH_2{=}CH_2 + CH_3-$
S_3 $CH_3CH_2- + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH(CH_3)- \longrightarrow C_2H_6 + CH_3CH{=}CH_2 + H$

$$A_1\quad CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH_2CH_2- \longrightarrow RH + CH_2{=}CH_2 + CH_3-$$
$$A_2\quad CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH(CH_3)- \longrightarrow RH + CH_3CH{=}CH_2 + H$$
$$R = CH_3-,\ H$$

The decomposition is somewhat more complicated than that of ethane since two alternative chain mechanisms A_1 and A_2 can occur depending on whether the carrier group reacts with the primary or secondary hydrogen atom of propane. Assuming the chains to be fairly long, the products must be mainly determined by Equations A_1 and A_2, and must consist of $50\%(CH_4 + H_2) + 50\%(CH_2{=}CH_2 + CH_3CH{=}CH_2)$. The ratio of methane to hydrogen and of ethylene to propylene should vary with the temperature and is given by the relative probabilities of reactions A_1 and A_2. Using the relative probabilities given in Table I, the analysis of the products has been calculated, and is given in Table II together with some experimental results taken from a paper by Pease and Durgan.[8] Since reactions S_2 and S_3 produce ethane, we should find a small percentage of this substance in the products, the amount depending upon the length of the chain; this will be given by the ratio $(CH_4 + H_2) : C_2H_6$.

TABLE II

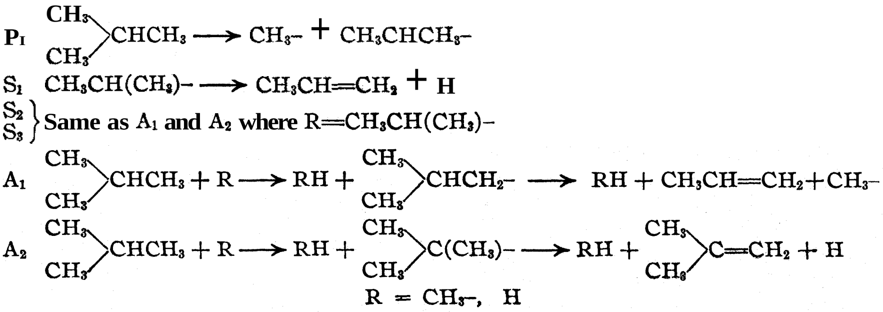
DECOMPOSITION OF PROPANE

Upper Part: Pease and Durgan's results
Lower Part: Values calculated from Table I

Temp., °C.	Decomp., %	H_2, %	CH_4, %	C_2H_4, %	C_2H_6, %
625	17	21	31	48	
625	26	18.5	34.5	47	
650	15	22	28	50	
650	21	21.5	31	47.5	
550	5-10	21.4	29.6	29.6	20.4
600	5-10	20.0	30.0	30.0	20.0
650	5-10	19.6	30.5	30.5	19.5

Some C_2H_6 will be present, since it is formed in reactions S_2 and S_3.

Isobutane.—The decomposition of isobutane may be represented as



$$P_1\quad \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>CHCH_3 \longrightarrow CH_3- + CH_3CHCH_3-$$
$$S_1\quad CH_3CH(CH_3)- \longrightarrow CH_3CH{=}CH_2 + H$$
$$\left.\begin{matrix}S_2\\ S_3\end{matrix}\right\}\text{Same as } A_1 \text{ and } A_2 \text{ where } R{=}CH_3CH(CH_3)-$$
$$A_1\quad \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>CHCH_3 + R \longrightarrow RH + \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>CHCH_2- \longrightarrow RH + CH_3CH{=}CH_2 + CH_3-$$
$$A_2\quad \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>CHCH_3 + R \longrightarrow RH + \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C(CH_3)- \longrightarrow RH + \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C{=}CH_2 + H$$
$$R = CH_3-,\ H$$

The chain mechanism is given by Equations A_1 and A_2, from which it will be seen that the only carriers are CH_3^- and H. The decomposition products should consist therefore of 50% (H_2 + CH_4) + 50% (CH_2=$CHCH_3$ + $(CH_3)_2C$=CH_2) and the ratio of methane to hydrogen should be the same as the ratio of propylene to isobutylene. Table III contains some experimental results taken from a paper by Pease and Durgan and also the calculated results. Pease and Durgan find small quantities of ethane in the products but there does not seem to be any way of accounting for this on the basis of the proposed mechanism; methane together with a small quantity of propane produced by reactions S_2 and S_3 should be the only paraffin hydrocarbons present.

TABLE III

DECOMPOSITION OF ISOBUTANE

Upper Part: Pease and Durgan's results
Lower Part: Calculated using Table I

Temp., °C.	Decomp., %	H_2, %	CH_4, %	C_2H_6, %	C_2H_4, %	C_3H_8, %	C_4H_{10}, %
600	18	25	22	3		50	
625	15	25	24	1		50	
650	18.5	24.5	24.5	1.5		49.5	
550	5–10	27.8	22.2	0	0	27.8	22.2
600	5–10	26.2	23.8	0	0	26.2	23.8
650	5–10	24.5	25.5	0	0	24.5	25.5

n-Butane.—The decomposition may be represented as

P_1 $CH_3CH_2CH_2CH_3 \longrightarrow CH_3{-} + CH_3CH_2CH_2{-}$
P_2 $CH_3CH_2CH_2CH_3 \longrightarrow 2CH_3CH_2{-}$
S_1 $CH_3CH_2CH_2{-} \longrightarrow CH_2{=}CH_2 + CH_3{-}$
$\left.\begin{matrix}S_2\\S_3\end{matrix}\right\}$ Same as A_1 and A, where $R{=}CH_3CH_2CH_2{-}$

$$A_1\quad CH_3CH_2CH_2CH_3 + R{-} \longrightarrow RH + CH_3CH_2CH_2CH_2{-} \longrightarrow$$
$$RH + CH_2{=}CH_2 + CH_3CH_2{-} \begin{cases} \nearrow CH_3CH_2{-} & A_1' \\ \searrow CH_2{=}CH_2 + H & A_1'' \end{cases}$$
$$A_2\quad CH_3CH_2CH_2CH_3 + R \longrightarrow RH + CH_3CH(CH_2CH_3){-} \longrightarrow$$
$$RH + CH_3CH{=}CH_2 + CH_3{-}$$
$$R = CH_3{-},\quad CH_3CH_2{-},\quad H$$

Equations A_1 and A_2 give the chain mechanism in which the carrier groups are methyl and ethyl groups and hydrogen atoms. A complication is introduced into reaction A_1 because the carrier group may react with the surrounding butane molecules or may decompose into ethylene and hydrogen atoms. If none of the ethyl groups produced in the chain mechanism decomposes, the products would consist of 50% (CH_4 + C_2H_6) + 50% (CH_2=CH_2 + CH_3CH=CH_2). On the other hand, if all of the ethyl groups produced in the chain mechanism decomposed, the products would consist of 40% (H_2 + CH_4) + 60% (CH_2=CH_2 + CH_3CH=CH_2). Table IV contains some experimental results obtained by Pease and Durgan on the decomposition of n-butane and also the calculated results using Table I. Since we do not know the relative probabilities of reactions

A_1' and A_1'', we cannot calculate the relative amounts of ethane and hydrogen; however, it is clear that raising the temperature should favor the production of hydrogen because ethylene becomes relatively more stable than ethane at higher temperatures: dilution with an inert gas would have the same effect because the bimolecular formation of ethane would be retarded and the unimolecular formation of hydrogen atoms would not be affected. The products should contain a small amount of propane produced by reactions S_2 and S_3 and this amount will be determined by the length of the chain.

TABLE IV

DECOMPOSITION OF *n*-BUTANE

Upper Part: Pease and Durgan's results
Lower Part: Calculated using Table I

Temp., °C.	Decomp.. %	CH_4, %	H_2, %	C_2H_6, %	C_2H_4, %	C_3H_6, %
600	18.5	33.5	4.5	11	51	
625	22.0	31.0	5.0	13	51	
650	26.0	30.0	6.0	12	52	
550	5–10	29.0	21.0		21.0	29.0
600	5–10	28.5	21.5		21.6	28.5
650	5–10	28.0	22.0		22.0	28.0

The relative amounts of H_2 and C_2H_6 cannot be predicted, but increase in temperature or dilution with an inert gas would increase the ratio of H_2 to C_2H_6. The figures for C_2H_4 and C_3H_6 have been calculated assuming that reaction A_1 is negligible. The products will contain a small amount of propane produced by S_2 and S_3.

***n*-Pentane.**—The decomposition may be represented as

P_1 $\mathrm{CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2{-} + CH_3{-}}$

P_2 $\mathrm{CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2{-} + CH_3CH_2{-}}$

S_1 $\mathrm{CH_3CH_2CH_2CH_2{-} \longrightarrow CH_2{=}CH_2 + CH_3CH_2{-}}$

S_2 $\mathrm{CH_3CH_2CH_2{-} \longrightarrow CH_2{=}CH_2 + CH_3{-}}$

$\left.\begin{array}{l} S_3 \\ S_4 \\ S_5 \end{array}\right\}$ Same as A_1, A_2 and A_3 where $\mathrm{R{=}CH_3CH_2CH_2CH_2{-}}$

A_1 $\mathrm{CH_3CH_2CH_2CH_2CH_3 + R{-} \longrightarrow RH + CH_3CH_2CH_2CH_2CH_2{-} \longrightarrow}$

$$\mathrm{RH + CH_2{=}CH_2 + CH_3CH_2CH_2{-}} \begin{array}{ll} \nearrow \mathrm{CH_3CH_2CH_2{-}} & A_1' \\ \searrow \mathrm{CH_2{=}CH_2 + CH_3{-}} & A_1'' \end{array}$$

A_2 $\mathrm{CH_3CH_2CH_2CH_2CH_3 + R{-} \longrightarrow RH + CH_3CH_2CH_2CH(CH_3){-} \longrightarrow}$

$$\mathrm{RH + CH_3CH{=}CH_2 + CH_3CH_2} \begin{array}{ll} \nearrow \mathrm{CH_3CH_2{-}} & A_2' \\ \searrow \mathrm{CH_2{=}CH_2 + H} & A'; \end{array}$$

A3 $\mathrm{CH_3CH_2CH_2CH_2CH_3 + R{-} \longrightarrow RH + CH_3CH_2CH(CH_2CH_3){-} \longrightarrow}$
$\mathrm{RH + CH_3CH_2CH{=}CH_2 + CH_3{-}}$

$\mathrm{RC = H_3{-},\quad CH_3CH_2{-},\quad CH_3CH_2CH_2{-},\quad H}$

We have now a considerably more complicated reaction and it seems desirable to discuss in some detail the reactions that the different radicals can undergo. The methyl group probably does not decompose, and therefore reacts only with the surrounding pentane molecules according to reactions A_1, A_2 and A_3. The ethyl group can either decompose into an ethylene molecule and a hydrogen atom or it can take a hydrogen from the surrounding pentane molecules. We do not know the relative probability of these two reactions and in the calculations I have neglected the decomposition into ethylene and hydrogen atoms. The normal propyl group can react with the surrounding pentane molecules to form propane or it can decompose into propylene and hydrogen atoms; probably both of these reactions occur but here also I have neglected the decomposition into propylene and hydrogen atoms. High temperatures will favor reactions A_1 and A_2 since ethylene becomes relatively more stable at higher temperatures; furthermore, dilution with an inert gas will have the same effect, since it does not affect the unimolecular formation of ethylene but retards the reaction between the radicals and the surrounding hydrocarbon. If we wish to avoid the production of methane and hydrogen the best conditions, so far as reactions A_1 and A_2 are concerned, would be low temperatures and high pressures.

All three amyl radicals produced can decompose through scission of a C—C bond and it is probable that they decompose practically completely in this way. Thus the n-amyl radical would decompose into ethylene and the *n*-propyl radical, and only to a very small percentage into 1-pentene and a hydrogen atom; the first reaction requires a minimum activation energy of 71.0 − (123.8 − 71.0) = 18.2 kg. cal., whereas the second reaction requires 93.3 − (123.8 − 71.0) = 45 kg. cal.; similar considerations govern the decomposition of the other two amyl radicals, so that pentenes should be entirely absent from the reaction products in the early stages of the decomposition.

The chain mechanism gives the following composition for the products: 50% ($CH_4 + C_2H_6 + C_3H_8 + H_2$) + 50% ($CH_2{=}CH_2 + CH_3CH{=}CH_2 + CH_3CH_2CH{=}CH_2$). We have neglected reactions A_1'' and A_2'' which produce ethylene, methane and hydrogen instead of ethane and propane. Table V contains some experimental results obtained by Calingaert[^]

TABLE V

DECOMPOSITION OF *n*-PENTANE

Upper Part: Calingaert's results
Lower Part: Calculated from Table I

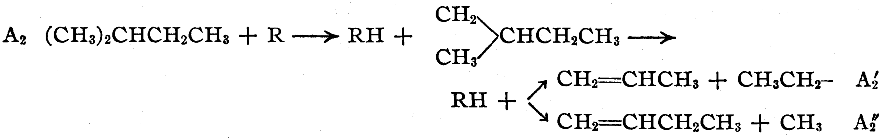
Temp., °C.	Decomp., %	H_2	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_4H_8	C_4H_6
	30	5	12	26	10	10	24	3	6
550	5–10	0"	11.2	22.5"	16.3^b	16.3"	22.5	11.2	0
600	5–10	0"	11.1	22.2"	16.7^b	16.7^c	22.2	11.1	0
650	5–10	0^a	11.0	21.9"	17.1^b	17.1^c	21.9	11.0	0

[a] The calculated % H_2 should be higher and the calculated % C_2H_6 should be lower, because reaction A_2 has been neglected. [b] The % C_3H_8 is too high and the % CH_4 ***too*** low because reaction A_1 has been neglected. [c] C_2H_4 is produced in reactions A_1 and A_2 which have been neglected; this would make the calculated % **still** higher.

aert,[9] who has made a careful study of the decomposition of n-pentane; for comparison the calculated results are also given using the probability values in Table I.

Isopentane.—The decomposition may be represented as

P_1 $(CH_3)_2CHCH_2CH_3 \longrightarrow (CH_3)_2CHCH_2- + CH_3-$
P_2 $(CH_3)_2CHCH_2CH_3 \longrightarrow CH_3CH(CH_2CH_3)- + CH_3-$
P_3 $(CH_3)_2CHCH_2CH_3 \longrightarrow CH_3CH(CH_3)- + CH_3CH_2-$
S_1 $(CH_3)_2CHCH_2- \longrightarrow CH_3CH{=}CH_2 + CH_3-$
S_2 $CH_3CH(CH_2CH_3)- \longrightarrow CH_3CH{=}CH_2 + CH_3-$
S_3 $CH_3CH(CH_3)- \longrightarrow CH_3CH{=}CH_2 + H$
A_1 $(CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + (CH_3)_2CHCH_2CH_2- \longrightarrow RH + CH_2{=}CH_2 + CH_3CH{=}CH_2 + H$



$$A_2 \quad (CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + \begin{matrix}CH_2\diagdown\\ CH_3\diagup\end{matrix}CHCH_2CH_3 \longrightarrow RH + \left\{\begin{matrix}\nearrow CH_2{=}CHCH_3 + CH_3CH_2- & A_2' \\ \searrow CH_2{=}CHCH_2CH_3 + CH_3 & A_2''\end{matrix}\right.$$

A_3 $(CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + (CH_3)_2CHCH(CH_3)- \longrightarrow RH + CH_3CH{=}CHCH_3 + CH_3-$
A_4 $(CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + (CH_3)_2C(CH_2CH_3)- \longrightarrow RH + (CH_3)_2C{=}CH_2 + CH_3-$
$R = H,\ CH_3-,\ CH_3CH_2-$

The chain mechanism is given by Equations A_1, A_2, A_3 and A_4, from which it will be seen that the carrier groups are H, CH_3 and CH_3CH_2. There is no difficulty in deciding how the amyl groups in Equations A_1, A_3 and A_4 will decompose because they can dissociate in only one way if a C–C bond is broken and a compound and a radical formed; on the other hand, the radical $—CH_2(CH_3)CHCH_2CH_3$ can dissociate according to Equations A_2' and A_2'' and in each case a C–C bond is broken and a compound and a free radical formed. As we do not know the relative probability of these two dissociations, reaction A_2'' has been neglected in the calculations. Table VI shows Calingaert's experimental results and the calculated results using the relative probabilities given in Table I.

TABLE VI

DECOMPOSITION OF ISOPENTANE

Upper Part: Calingaert's results
Lower Part: Calculated using Table I

Temp., °C.	Decomp., %	Ha	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8[a]	C_4H_8[b]	C_5H_{10}
600	30	6	30	24	..	15	20		4
550	5–10	6.1	31.6	12.3[c]	6.1	18.4	8.4	24.2	0
600	5–10	6.5	30.4	13.1[c]	6.5	19.6	8.7	21.7	0
650	5–10	7.0	29.1	13.9[c]	7.0	20.9	8.9	20.2	0

[a] $CH_3CH{=}CHCH_3$. [b] $(CH_3)_2C{=}CH_2$. [c] Since reaction A_2'' has been neglected, the % C_2H_6 is too high and the % CH_4 too low; this reaction also produces butene-1.

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[9] Calingaert, THIS JOURNAL, **45**, 130 (1923).

Neo-pentane.—The decomposition may be represented as

P_1 $(CH_3)_3CCH_3 \longrightarrow (CH_3)_3C- + CH_3-$

S_1 $(CH_3)_3C- \longrightarrow (CH_3)_2C{=}CH_2 + H$

S_2 $(CH_3)_4C + H \longrightarrow H_2 + (CH_3)_3CCH_2-$

S_3 $(CH_3)_3CCH_2- \longrightarrow (CH_3)_2C{=}CH_2 + CH_3-$

A_1 $(CH_3)_4C + R \longrightarrow RH + (CH_3)_3CCH_2- \longrightarrow RH + (CH_3)_2C{=}CH_2 + CH_3-$

$R = CH_3-$

Neo-pentane is of special interest because of the simplicity of the reaction, and it seems surprising that it has not been studied experimentally. There is only one primary reaction, namely, scission into a methyl and a *tert.*-butyl group; this can decompose in only one way, forming isobutylene and a hydrogen atom, which in turn forms a CH_3^- group according to Reactions S_2 and S_3.

Equation A_1 represents the chain mechanism, from which it will be seen that the methyl group is the only carrier and that the products of the reaction should be 50% methane and 50% isobutylene. The amount of hydrogen present is determined by the length of the chain.

Discussion

The application of the concept of chain reactions to the thermal decomposition of organic compounds gives a very satisfactory mechanism for these reactions and it becomes important therefore to consider whether organic compounds really decompose in this manner, especially in view of the fact that the experimental evidence supports the view that paraffin hydrocarbons undergo a simple unimolecular decomposition.[10] In this connection it may be pointed out that whenever two radicals collide, the reaction $2C_nH_{2n+1} = C_nH_{2n+2} + C_nH_{2n}$ can occur by transfer of a hydrogen atom and this reaction liberates a great deal of energy. Consequently we may assume that every collision[11] between two radicals is effective in forming hydrocarbons and, in this way, the chains are broken rather than by collision with the wall. The ordinary way to test for chain reactions is to increase the surface area per unit volume of the containing vessel and this method would fail if the chains are terminated chiefly by collisions between the alkyl radicals. The most promising method of verifying experimentally these proposed mechanisms would appear to be an attempt to prove the existence of the carriers and other fragments by conducting experiments similar to those of Paneth and his co-workers but using hydrocarbons instead of lead alkyls.

Summary

1. When a hydrocarbon decomposes, we may assume that it dissociates into two free radicals which fly apart. Comparison of the strength of a

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[10] Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., 1929, pp. 64-68.

[11] Probably a small correction would be necessary to take care of the steric factor.

C–H bond (93.3 kg. cal.) with that of a C–C bond (71.0 kg. cal.) shows that the dissociation occurs only through rupture of a C–C bond; any breaking of a C–H bond is wholly negligible compared with that of a C–C bond.[12]

2. The probability that the two radicals collide again is negligibly small and therefore free radicals produced in this way can only decompose or react with the surrounding hydrocarbon molecules. For example, a free methyl group can take a hydrogen atom from the surrounding hydrocarbon and form methane and a hydrocarbon radical. An ethyl group produced in this way can undergo two reactions; the first is similar to the methyl group and produces ethane and a hydrocarbon radical; the second is a dissociation into ethylene and hydrogen atoms. Radicals higher than ethyl can decompose in a similar manner into an ethylene hydrocarbon and either *a* hydrogen atom or a free radical.

3. This dissociation of free radicals is possible because, in the process, a single bond becomes a double bond; this process of internal compensation releases 52,800 cal. which can contribute to the minimum activation energy (93,000 cal.) necessary to break a C–H bond, or to the minimum activation energy (71,000 cal.) necessary to break a C–C bond.[12]

4. The decomposition of paraffin hydrocarbons is represented as a chain type of reaction in which free hydrogen atoms or free radicals combine with one of the hydrogen atoms of the surrounding hydrocarbon molecule. The hydrocarbon radical then decomposes into a compound and either a smaller free radical or a hydrogen atom. Thus we have a cycle of changes in which certain groups called carriers are regenerated and start a new cycle and this process presumably may go on for a great number of times.

5. The composition of the products is determined therefore almost exclusively by the chain cycle and is practically independent of the primary decomposition of the hydrocarbon. It is possible to calculate the composition of the products when a hydrocarbon is allowed to decompose to a small extent. In these calculations all primary C–H bonds are considered to have the same strength, all secondary C–H bonds 1200 cal less and all tertiary C–H bonds 4000 cal. less than a primary C–H bond. The only arbitrary assumption made in the calculations is the assignment of the relative strengths to the different classes of C–H bonds.

BALTIMORE, MARYLAND

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[12] The actual values given need not be accepted since it is only the relative strengths of the bonds which are important; it is only necessary that the C–H bond and the C=C bond are each at least 10,000 to 15,000 cal. stronger than the C–C bond.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE ACTION OF HYDROGEN PEROXIDE UPON SIMPLE CARBON COMPOUNDS. I. METHYL ALCOHOL, FORMALDEHYDE AND FORMIC ACID

BY H. SHIPLEY FRY AND JOHN H. PAYNE[1]

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Some perplexing anomalies are found in the reactions of hydrogen peroxide with simple carbon compounds. For instance, as naturally expected, formaldehyde is directly oxidized to formic acid and the latter in turn to carbonic acid, thus

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$$
$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O$$

but hydrogen peroxide may, on the one hand, *oxidize* formaldehyde to formic acid *with the liberation of hydrogen*

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2$$

while on the other hand it will *reduce* carbonic acid to formic acid *with the liberation of oxygen*

$$H_2CO_3 + H_2O_2 \longrightarrow HCOOH + H_2O + O_2$$

Since hydrogen peroxide may thus react either as an oxidizing agent or as a reducing agent, and in some instances in both capacities concurrently, it is not surprising to find in the literature many conflicting reports as to *the* exact character of its reactions; and, too frequently, few if any quantitative data are given to establish the nature of the reactions in question.

Therefore, an extended quantitative study of the action of hydrogen peroxide upon (A) formic acid, (B) formaldehyde and (C) methyl alcohol under a standardized method of procedure in a closed system was undertaken with the following objectives: (1) to determine the yields of all of the products formed, (2) to indicate the equations for all reactions occurring, successively or concurrently, or both, and (3) to check the respective yield of each product formed with the respective quantity of the hydrogen peroxide required in conformity with the equation for the reaction postulated for its formation.

Experimental

Each reaction investigated was run in duplicate with 0.25 mole of the pure carbon compound in a 250-cc. round-bottomed Pyrex flask and successively increasing amounts, from one-sixteenth to one mole, of 30–33% hydrogen peroxide free from organic preservatives. Sufficient water and dilute sulfuric acid were added to make the total volume of each reaction mixture equal to 125 cc. and 0.35 normality.

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[1] Summary of Doctorate Thesis of John H. Payne, read before the Organic Division of the American Chemical Society, Cincinnati, September 9, 1930.

The flask containing the standardized reaction mixture, submerged in a water-bath, was connected by way of a 30-cm. upright Liebig condenser to calcium chloride drying tubes and thence to a **28-cm.** U-tube filled with granular soda lime for absorption and subsequent weighing of evolved carbon dioxide. The soda lime tube was connected in train to another calcium chloride safety tube and thence to a gasometer for collection over water of the other evolved gases, hydrogen and oxygen, the yields of which were determined by standard methods of gas analysis.

Through the top of the condenser, a glass inlet tube with stopcock extended to the bottom of the reaction flask, thus making provision for the passing of a current of pure nitrogen through the train of apparatus to displace all air before the reaction began and to carry through all evolved gases after completion of the reaction.

After heating the reaction flask until cessation of evolution of any gases, pulverized silica (5 g.) was added to the reaction mixture to effect complete decomposition of any remaining hydrogen peroxide. From the difference between the initial amount of hydrogen peroxide used and the amount equivalent to the oxygen liberated through its direct decomposition, the total quantity of hydrogen peroxide actually engaged in reaction with the carbon compounds, *i. e.*, the *active* hydrogen peroxide, was determined.

The difference between the weights of the soda lime tubes before and after the runs gave the measure of the extent of the oxidation of the carbon compounds to carbonic acid. The yields of the other oxidation product, formic acid, were determined by the standard alkaline permanganate titration method.

Since the products of oxidation of methyl alcohol are successively formaldehyde and formic acid, the first experiments were with formic acid, the second with formaldehyde and the third with methyl alcohol.

A. Formic Acid.—The oxidation of formic to carbonic acid by hydrogen peroxide in acid solution has been studied by several investigators,[2] but in no instance was the amount of *active* hydrogen peroxide correlated quantitatively with the yield of carbonic acid to establish the following equation (a) for the assumed reaction

$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O \qquad (a)$$

To verify this equation, duplicate runs were made, as previously described, with pure formic acid (b. p. 100.5°). Five hours' heating of the reaction mixture at 100° were required for the apparent completion of the reaction. The reaction mixtures were diluted to 250 cc. and aliquot portions of 10 cc. were titrated for the unreacted formic acid content, which, subtracted from the initial quantity of formic acid used, gave the quantity

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[2] Kastle and Loevenhart, This Journal, 21, 262 (1899); *Am. Chem. J.*, *29*, *424* (1903); Batelli, *Compt. rend.*, 138, 651 (1904); Dakin, *J. Biol. Chem.*, *4*, *227* (1908); Holden and Hatcher, *Trans. Roy. Soc. Canada*, III, 18, *231* (1924).

oxidized to carbonic acid. Neither hydrogen nor carbon monoxide **was** obtained. The data are embodied in Table I.

TABLE I

FORMIC ACID

Run	I Initial H_2O_2, mole	II Initial HCOOH, mole	III H_2CO_3 found mole	IV % Oxidation $HCOOH \rightarrow H_2CO_3$	V $H_2O_2 \propto H_2CO_3$ (Eq. a), mole	VI $H_2O_2 \propto O_2$ (Eq. z), mole	VII Total H_2O_2 Eq. (a) + (z)
a	0.2500	0.2500	0.1896	76.20	0.1896	0.0670	0.2566
b	.2500	.2500	.1883	76.36	.1883	.0666	.2549

It will be noted that the total quantity of hydrogen peroxide used in the closed reaction system, Column VII, is distributed between only two reactions in conformity with the equations (a) and (z)

$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O \qquad (a)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (z)$$

and it is practically equal to the initial quantity of hydrogen peroxide employed, Column I. While only 76% of the initial formic acid was oxidized to carbonic acid, its oxidation conforms completely to Equation a. This confirmation necessarily precedes Parts B (Formaldehyde) and C (Methyl Alcohol) wherein the intermediate formation of formic acid occurs but with the concurrent liberation of hydrogen.

B. Formaldehyde.—Kastle and Loevenhart[2] reported the oxidation of formaldehyde to formic acid but did not mention the liberation of hydrogen, which reaction in basic solution according to Equation b

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 \qquad (b)$$

is commonly used for the quantitative determination of formaldehyde. On the other hand, Geisow[3] was unable to isolate any formic acid from either acid or alkaline reaction media, but, obtaining carbonic acid, he assumed the reaction to be represented by the equation *(c)*

$$HCHO + H_2O_2 \longrightarrow H_2CO_3 + H_2 \qquad (c)$$

A few years later, Lyford[4] disputed Geisow's results and postulated a primary reaction liberating hydrogen, Equation b above, to be followed by direct oxidation of formic to carbonic acid, Equation a above. He also assumed direct oxidation of formaldehyde to formic acid according to the equation (d)

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O \qquad (d)$$

Notwithstanding the above and other contradictory findings, it appears that the interaction of hydrogen peroxide and formaldehyde involves the reactions represented by Equations b and d, but no conclusions have been drawn previously as to the extent of their concurrence in acid media and in a closed system under standardized conditions.

To this end, six duplicate runs (I–VI) with formaldehyde in the readily

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[3] Geisow, *Ber.*, 37, 515 (1904).

[4] Lyford, THIS JOURNAL, 29, 1227 (1907).

weighable form of trioxymethylene were conducted with one-sixteenth, one-eighth, one-fourth, one-half, three-fourths and one mole, respectively, of hydrogen peroxide, thereby securing quantitative data indicating the effect of increasing concentrations of hydrogen peroxide upon one-fourth molar quantities of formaldehyde. All reactions proceeded smoothly, being completed after five hours' heating at 60°. In each run the reaction products were formic and carbonic acids, hydrogen and oxygen, and it was possible with the analytical data obtained (Tables II and III) to correlate all of the occurring reactions with the equations

$$\begin{array}{rlllr}
2HCHO + H_2O_2 & \longrightarrow & 2HCOOH & + H_2 & \text{(b)} \\
HCHO + H_2O_2 & \longrightarrow & HCOOH & + H_2O & \text{(d)} \\
HCOOH + H_2O_2 & \longrightarrow & H_2CO_3 & + \text{H20} & \text{(a)} \\
2H_2O_2 & \longrightarrow & 2H_2O & + O_2 & \text{(z)}
\end{array}$$

TABLE II

MOLAR QUANTITIES OF HYDROGEN PEROXIDE AND FORMALDEHYDE USED AND OF PRODUCTS FORMED

Run	1 Initial H_2O_2, mole	2 Initial HCHO, mole	3 HCOOH found, mole	4 H_2CO_3 found. mole	5 H_2 found, mole	6 O_2 found. mole
Ia	0.0625	0.2500	0.1184	0.0000	0.0563	0.0002
Ib	.0625	.2500	.1185	.0000	.0565	.0002
IIa	.1250	.2500	.2250	.0011	.1048	.0013
IIb	.1250	.2500	.2256	.0010	.1043	.0011
IIIa	.2500	.2500	.1911	.0597	.0854	.0091
IIIb	.2500	.2500	.1920	.0597	.0863	.0086
IVa	.5000	.2500	.0863	.1674	.0458	.0585
IVb	.5000	.2500	.0861	.1679	.0455	.0580
Va	.7500	.2500	.0335	.2214	.0308	.1472
Vb	.7500	.2500	.0327	.2230	.0307	.1460
VIa	1.0000	.2500	.0107	.2317	.0226	.2612
VIb	1.0000	.2500	.0117	.2326	.0227	.2596

Table II records the molar quantities of hydrogen peroxide and formaldehyde initially present in the reaction mixtures of the six sets of runs, in duplicate, with the molar quantities of the products formed. The complementary Table III gives the percentage yields of the products as calculated from the respective equations for the proposed reactions, thus facilitating comparison of the extents of the occurrence of the concurrent reactions as affected by the increasing concentrations of hydrogen peroxide. The quantities of hydrogen peroxide reacting according to the several equations are separately recorded in Table III, Columns 4, 5, 6 and 7, and are also totaled in Column 8 in order to check the sum of the ***active*** quantities and the ***inactive*** quantities with the ***initial*** quantity employed.

Table IV summarizes the average percentage extent to which each of the three principal reactions occurred in the presence of the increasing molar concentrations of the hydrogen peroxide employed.

TABLE 111

PERCENTAGE YIELDS OF PRODUCTS FORMED AND EQUIVALENT PERCENTAGE QUANTITIES OF HYDROGEN PEROXIDE USED

Run	1 % yield $H_2 \Leftrightarrow$ HCHO Eq. (b)	2 % yield HCOOH $\Leftrightarrow$ HCHO Eq. (d)	3 % yield $H_2CO_3 \Leftrightarrow$ HCOOH Eq. fa)	4 % H_2O_2 used $\Leftrightarrow$ H_2, Eq. (b)	5 % H_2O_2 used $\Leftrightarrow$ HCOOH. Eq. (d)	6 % H_2O_2 used $\Leftrightarrow$ H_2CO_3, Eq (a)	7 % H_2O_2 used $\Leftrightarrow$ O_2, Eq. (z)	8 Total % H_2O_2, used
la	95.10	4.90	0.00	90.08	9.28	0.00	0.64	100.00
Ib	95.36	4.64	.00	90.40	8.80	.00	.64	99.84
IIa	92.70	7.30	.48	8384	13.20	.88	2.08	100.00
IIb	92 06	7.94	.48	83.44	14.40	80	1 76	100.40
IIIa	68.10	31.90	23.81	34.16	32.00	23 88	7.28	97.32
IIIb	68.57	31.43	23.72	34.52	31.64	23 88	6 88	96.92
IVa	36.11	63.89	65.98	9.16	32.42	33 48	23 40	98.46
IVb	3583	64.17	66.10	9.10	32.68	3358	2320	98.48
Va	2417	75.83	86.86	4.11	25.79	2952	3925	98.67
Vb	24.01	75.99	87 21	4.10	24 91	29 73	38 93	98 67
VIa	18.64	81.36	95.59	2.26	19.72	23.17	52 24	97.39
VIb	18.59	81.41	9521	227	19.90	23.26	5192	9735

TABLE IV

FORMALDEHYDE: SUMMARY

Run	Mole of H_2O_2	Percentage HCOOH by Reaction (b)	Percentage HCOOH by Reaction (d)	Percentage H_2CO_3 bv Reaction (a)
I	$^1/_{16}$	95.23	4.77	0.00
II	$^1/_8$	92.38	7.62	0.46
111	$^1/_4$	68.33	31.67	23.76
IV	$^1/_2$	35.97	64.03	66.04
V	$^3/_4$	24.09	75.91	87.04
VI	1	18.62	81.38	95.40

The following conclusions may be drawn: (1) in all runs Reactions b and d were concurrent because the ratios of the moles of formic acid formed to the moles of hydrogen liberated were greater than 2:1, the ratio required by Equation b.

(2) Reaction a did not occur in Run I and only to a slight extent in Run II, but with increasing concentrations of hydrogen peroxide, the extent of the occurrence of Reactions a and d regularly increases while that of Reaction b regularly decreases. In other words, the liberation of hydrogen is apparently favored by the lower concentrations of hydrogen peroxide.

(3) In Column 8 of Table III, the sums of the *active* and *inactive* quantities of hydrogen peroxide as calculated in terms of the assumed equations (a), (b), (d) and (z) are equal, within the limits of experimental error, to the initial quantities of hydrogen peroxide employed. Thus these results serve to check the experimental procedure and data with the occurrence of the postulated reactions.

C. Methyl Alcohol.—A review of the literature pertaining to the action of hydrogen peroxide upon methyl alcohol[5] is disconcerting since reaction is both affirmed and denied; some do and others do not record the liberation of hydrogen; the formation of formaldehyde and formic acid is noted, and but few, if any, exact quantitative data and descriptions of experimental conditions have been recorded.

The oxidation of methyl alcohol should first yield formaldehyde according to the equation (f)

$$CH_3OH + H_2O_2 \longrightarrow HCHO + 2H_2O \qquad \text{(f)}$$

Formaldehyde would subsequently be oxidized to formic and carbonic acids in conformity with the previously recorded equations (b), (d), and (a), accompanied by some direct decomposition of hydrogen peroxide, equation (z), as described in the preceding Section B, formaldehyde. Thus, five reactions are involved.

Accordingly, a series of four runs in duplicate were made, as previously described, using one-fourth mole of methyl alcohol with one-eighth, one-fourth, one-half and three-fourths mole of hydrogen peroxide. Longer times were required for the completion of the successive runs at 100°, namely, twenty-four, thirty-six, forty-two and forty-eight hours, respectively. These periods would have been much longer had not the acidity of the reaction mixtures been reduced from 0.35 N to 0.05 N, since the higher acidity stabilizes the hydrogen peroxide and thus retards its oxidizing action.

Another difficulty, the intermediate formation of very volatile methyl formate ($HCOOH + CH_3OH \quad H_2O + HCOOCH_3$) and its possible absorption in the soda lime tubes, was overcome by inserting a Milligan wash-bottle containing concentrated sulfuric acid in the apparatus train between the condenser and first calcium chloride tube. The methyl formate thus was hydrolyzed and yielded carbon monoxide, which was collected in the gasometer, quantitatively determined in the subsequent gas analyses, and its formic acid equivalent added to the yield of formic acid. The yields of formaldehyde were determined by the method of Haywood and Smith.[6]

With the analytical data obtained, it was possible to correlate all of the reactions occurring in terms of the five previously described equations, (f), (b), (d), (a) and (z). The data, calculated equivalents and percentage yields are recorded in Tables V and VI, similarly to the method employed in Tables III and IV of the preceding Section B. For convenience in reference to data, the five reactions are retabulated

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[5] Renard, *Ann. chim. phys.*, 5, 335 (1879); Blank and Finkenbeiner, *Ber.*, 31, 2279 (1898); Frankforter and West, THIS JOURNAL, 27, 718 (1905); Heimrod and Levene, *Biochem. Z.*, 29, 31 (1900); Schmeidel, *Pharm. Zentralhalle*, 54, 709 (1913); Doroshevoskii and Bardt, *J. Russ. Phys.-Chem. Soc.*, 46, 754 (1914).

[6] Haywood and Smith, THIS JOURNAL, 27, 1183 (1905).

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\begin{array}{lll}
CH_3OH + H_2O_2 \longrightarrow HCHO + 2H_2O & & (f) \\
2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 & & (b) \\
HCHO + H_2O_2 \longrightarrow HCOOH + H_2O & & (d) \\
HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O & & (a) \\
2H_2O_2 \longrightarrow 2H_2O + O_2 & & (z)
\end{array}
$$

TABLE V

MOLAR QUANTITIES OF HYDROGEN PEROXIDE AND METHYL ALCOHOL USED AND OF PRODUCTS FORMED

Run	1 Initial H_2O_2, mole	2 Initial CH_3OH, mole	3 HCHO, found, mole	4 HCOOH found, mole	5 H_2CO_3 found, mole	6 H_2 found, mole	7 O_2 found, mole
Ia	0.1250	0.2500	0.0040	00379	0.0160	0.0117	0.0026
Ib	.1250	,2500	.0034	.0375	.0162	0125	.0026
IIa	.2500	.2500	0035	.0877	.0537	.0169	.0143
IIb	.2500	2500	0033	.0898	.0509	.0180	.0148
IIIa	.5000	,2500	0023	,0319	.1119	.0288	.0594
IIIb	.5000	.2500	0021	0381	1084	.0311	.0592
IVa	.7500	.2500	0008	0313	,1611	.0354	.1149
IVb	.7500	.2500	0001	0315	1598	0343	.1169

TABLE VI

PERCENTAGE YIELDS OF PRODUCTS FORMED AND EQUIVALENT PERCENTAGE QUANTITIES OF HYDROGEN PEROXIDE USED

Run	1 % yield HCHO $\Leftrightarrow$ CH_3OH, Eq. (f)	2 % yield H_2 $\Leftrightarrow$ HCHO, Eq (b)	3 % yield HCO_2H $\Leftrightarrow$ HCHO. Eq. (d)	4 % yield H_2CO_3 $\Leftrightarrow$ HCOOH, Eq. (a)	5 % H_2O_2 used $\Leftrightarrow$ HCHO, Eq. (f)	6 % H_2O_2 used $\Leftrightarrow$ Hz. Eq. (b)	7 % H_2O_2 used $\Leftrightarrow$ HCOOH, Eq. (d)	8 % H_2O_2 used $\Leftrightarrow$ H_2CO_3, Eq (a)	9 % H_2O_2 used $\Leftrightarrow$ O_2, Eq. (z)	10 Total % H_2O_2 used
Ia	6.89	43.41	56.59	29.69	46.32	9.36	24.40	12.80	4.16	97.04
Ib	5.95	46.56	53.44	30.17	45.68	10.00	22.96	12.96	4.16	95.76
IIa	3.99	38.54	61.46	61.23	36.48	6.76	21.56	21.48	11.44	97.72
IIb	3.67	40.09	59.91	56.68	37.24	7.20	21.52	20.36	11.84	98.16
IIIa	1.60	40.05	59.95	77.81	29.22	5.76	17.24	22.38	23.76	98.36
IIIb	1.43	42.45	57.55	74.00	29.72	6.22	16.86	21.68	23.68	98.16
IVa	0.42	36.80	63.20	83.73	25.65	4.72	16.31	21.48	30.64	98.80
IVb	0.05	35.86	64.14	83.54	25.51	4.57	16.38	21.31	31.17	98.94

The following conclusions are drawn from the above data. (1) The products of the oxidation of methyl alcohol are formaldehyde (equation f), formic acid (equations b and d), carbonic acid (equation a) and hydrogen (equation b).

(2) Here also, as in the formaldehyde runs of Part B, the reactions represented by Equations b and d decrease in extent while those represented by Equations a and z increase in extent with increasing concentrations of hydrogen peroxide. Reaction d, however, always occurs to a greater extent than Reaction b, again showing that the liberation of hydrogen is favored by the lower concentrations of hydrogen peroxide.

(3) Column 10 of Table VI affords data showing close agreement between the initial amounts of hydrogen peroxide employed in the several

runs and the sums of the amounts required for the several reactions as calculated on the basis of the proposed equations for the reactions involved.

Grateful acknowledgments are extended to Professor John Uri Lloyd, whose Fellowship in Chemistry made this study possible, and to Dr. H. P. Carveth, President of the Roessler–Hasslacher Chemical Co., who generously donated several shipments of the specially prepared hydrogen peroxide used in this study.

Summary

An extended study of the nature and extent of the action of increasing molar concentrations of hydrogen peroxide in acid media upon methyl alcohol, formaldehyde, and formic acid has confirmed the occurrence of a series of postulated reactions.

The equations for these reactions have been verified by the experimental data with respect not only to the yields of the several products obtained, but also to the quantities of hydrogen peroxide participating in the postulated reactions.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE ACTION OF HYDROGEN PEROXIDE UPON SIMPLE CARBON COMPOUNDS. II. THE MECHANISM OF THE REACTIONS[1]

BY H. SHIPLEY FRY AND JOHN H. PAYNE

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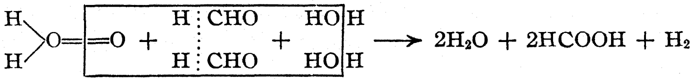
Two reaction mechanism schemes have been proposed previously to explain the apparently anomalous liberation of hydrogen when hydrogen peroxide and formaldehyde interact according to equation (b)

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 \qquad (b)$$

Briefly stated, Traube's explanation[2] postulates the liberation of hydrogen through the decomposition of water in conformity with the following scheme wherein the hydroxyl radicals of water combine with the aldehyde radicals of formaldehyde to produce formic acid



$$\begin{matrix}H\\ \\ H\end{matrix}\!\!>\!O=\boxed{\begin{matrix} & H\,\vdots\,CHO & & HO \\ =O\ + & \vdots & + & \\ & H\,\vdots\,CHO & & HO\end{matrix}}\begin{matrix}H\\ \\ H\end{matrix} \longrightarrow 2H_2O + 2HCOOH + H_2$$

This scheme also involves, as indicated by the dotted line, dissociation of the aldehyde hydrogen atoms, which combine with the peroxide oxygen atom to form water.

In the other reaction mechanism, Wieland[3] postulates, first, the con-

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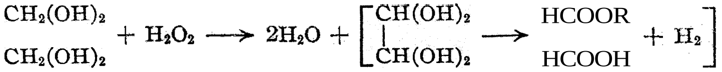
[1] Presented before the Organic Division of the American Chemical Society, Cincinnati, September 9, 1930.

[2] Traube, Ber., 16, 123 (1883).

[3] Wieland, *ibid.*, 45,484, 679, 2606 (1912); 46, 3327 (1913); 47, 2085 (1914); 54, 2353 (1921).

version of formaldehyde to formaldehyde hydrate, $CH_2O + H_2O \longrightarrow CH_2(OH)_2$, which then reacts with hydrogen peroxide according to the following scheme wherein the intermediately formed oxidation product, $[CH(OH)_2]_2$, decomposes yielding formic acid and hydrogen



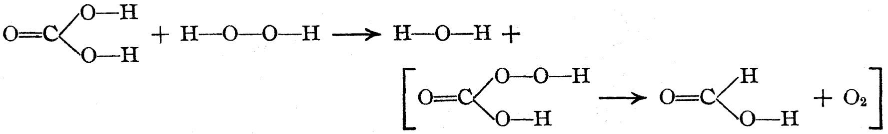
$$\begin{array}{c}CH_2(OH)_2\\ \\ CH_2(OH)_2\end{array} + H_2O_2 \longrightarrow 2H_2O + \left[\begin{array}{c}CH(OH)_2\\ | \\ CH(OH)_2\end{array} \longrightarrow \begin{array}{c}HCOOR\\ \\ HCOOH\end{array} + H_2\right]$$

The change noted within the brackets involves not only decomposition, but also rearrangement reactions.

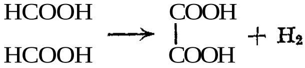
A third reaction mechanism scheme, less involved than the preceding schemes, is now proposed. It explains not only the liberation of hydrogen when formaldehyde is oxidized to formic acid, but also the liberation of oxygen when carbonic acid is reduced to formic acid, as well as other reactions wherein neither hydrogen nor oxygen is evolved. The latter, or the normal oxidation reactions, will be considered first.

It is here assumed that hydrogen peroxide displays a type of reaction which may be termed "*perhydrolysis*," that is, *a* double decomposition reaction involving *hydrogen peroxide* in precisely the same manner that *hydrolysis* is a double decomposition reaction involving *water*. Thus, for instance, the normal oxidation of formaldehyde to formic acid is a *perhydrolysis* reaction

The reduction of carbonic acid by hydrogen peroxide with the liberation of oxygen, $H_2CO_3 + H_2O_2 \longrightarrow HCOOH + H_2O + O_2$, may likewise involve *perhydrolysis*, forming percarbonic acid, which, in turn, yields formic acid through the liberation of oxygen, all in conformity with the reaction scheme

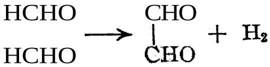


An explanation of the other apparently anomalous reactions, namely, the oxidation of formaldehyde to formic acid with the liberation of hydrogen (equation b), requires an additional assumption which is suggested by the well-known decomposition of sodium formate yielding sodium oxalate and hydrogen



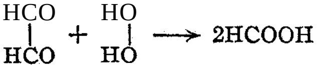
$$\begin{array}{c}HCOOH\\ \\ HCOOH\end{array} \longrightarrow \begin{array}{c}COOH\\ | \\ COOH\end{array} + H_2$$

The parallel reaction with formaldehyde would yield hydrogen and glyoxal



$$\begin{array}{c}HCHO\\ \\ HCHO\end{array} \longrightarrow \begin{array}{c}CHO\\ | \\ CHO\end{array} + H_2 \qquad (n)$$

to be followed immediately by the *perhydrolysis* of the intermediately formed glyoxal, yielding two molecules of formic acid



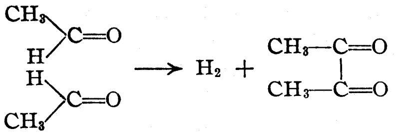
$$\begin{array}{c}\mathrm{HCO}\\|\\\mathrm{HCO}\end{array} + \begin{array}{c}\mathrm{HO}\\|\\\mathrm{HO}\end{array} \longrightarrow \mathrm{2HCOOH} \qquad \text{(o)}$$

The summation of the two equations (n) and (o) gives the complete equation (b)

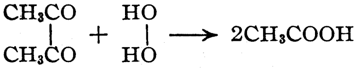
$$\mathrm{2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2} \qquad \text{(b)}$$

That no intermediately formed glyoxal was isolated is presumably due to the fact that the speed of the perhydrolysis reaction (o) is greater than that of the preceding reaction (n).

Now, if this proposed reaction mechanism has any validity, it should at least predict that the interaction of acetaldehyde and hydrogen peroxide would yield hydrogen or methane, or both hydrogen and methane, in conformity with the following completely parallel reaction mechanism schemes, wherein equations (n') and (n″), (o′) and (o″) and (b') and (b″) are exactly parallel to the above equations (n), (o) and (b), respectively.

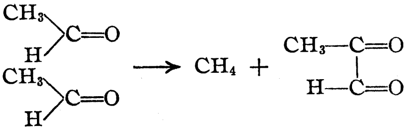


(n′)

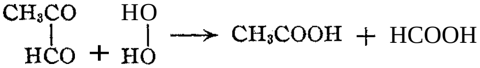


$$\begin{array}{c}\mathrm{CH_3CO}\\|\\\mathrm{CH_3CO}\end{array} + \begin{array}{c}\mathrm{HO}\\|\\\mathrm{HO}\end{array} \longrightarrow \mathrm{2CH_3COOH} \qquad \text{(o′)}$$

$$\text{(n′) + (o′)} \quad \mathrm{2CH_3CHO + H_2O_2 \longrightarrow 2CH_3COOH + H_2} \qquad \text{(b′)}$$



(n″)



$$\begin{array}{c}\mathrm{CH_3CO}\\|\\\mathrm{HCO}\end{array} + \begin{array}{c}\mathrm{HO}\\|\\\mathrm{HO}\end{array} \longrightarrow \mathrm{CH_3COOH + HCOOH} \qquad \text{(o″)}$$

$$(n'' + o'') \quad \mathrm{2CH_3CHO + H_2O_2 \longrightarrow CH_3COOH + HCOOH + CH_4} \qquad \text{(b″)}$$

The liberation of ethane, a third possibility, would necessitate a linkage of carbon atoms, which seems improbable, at least not so likely as the liberation of hydrogen and methane.

The predictions, with respect to the action of hydrogen peroxide upon acetaldehyde in conformity with the above equations (b′) and (b"), derived through the proposed reaction mechanism scheme, were confirmed by extending the experimental method, previously described in Part I, to acetaldehyde which gave the predicted products, hydrogen, methane, acetic acid and formic acid, thus indicating the concurrence of reactions (b') and (b'').

Before tabulating the confirmatory data, it should be noted that the literature affords only one observation[4] of the liberation of hydrogen when hydrogen peroxide interacts with acetaldehyde. No data were recorded.

Geisow[5] attempted to carry the analogy of the liberation of hydrogen according to the formaldehyde reaction, equation (b), to the liberation of methane from acetaldehyde but did not obtain any methane.

Other investigators[6] have severally recorded the formation of acetic, formic and carbonic acids, but none mentions the liberation of hydrogen or methane.

Experimental

Three sets of duplicate runs were conducted using one-fourth mole of pure paraldehyde in each case, varying the quantity of hydrogen peroxide from one-eighth to one-fourth, and one-half mole in solutions of 125 cc. volume containing 0.306 g. of sulfuric acid. In this acid solution the paraldehyde depolymerized to acetaldehyde and the time required for completion of the reaction varied from eighteen to twenty-four hours.

Some of the very volatile acetaldehyde escaped reaction with the hydrogen peroxide. To prevent its absorption in the soda lime tubes, two Milligan wash bottles were interposed as previously described in the runs with methyl alcohol (Part I, Section C). The first wash bottle contained ethyl alcohol, which collected the acetaldehyde vapor; the second contained sulfuric acid, which retained any traces of alcohol or acetaldehyde escaping from the first wash bottle.

The products of the reaction in each run were hydrogen, methane, formic and acetic acids, as predicted in equations (b') and (b''). The predominating reaction, however, was the direct oxidation of acetaldehyde to acetic acid

$$CH_3CHO + H_2O_2 \longrightarrow CH_3COOH + H_2O$$

Formic and carbonic acids were also formed in secondary reactions between acetic acid and hydrogen peroxide without the accompanying evolution of hydrogen or methane, as was confirmed in separately conducted runs with acetic acid.

Aliquot fractions of the reaction mixtures in all runs were analyzed for their combined formic acid and acetic acid contents by titration with standard alkali. The formic acid content was determined as previously noted by the mercuric chloride method; the acetic acid content was obtained by difference. All of the analytical data are embodied in Table I.

[4] Blank and Finkenbeiner, *Ber.*, 31, 2279 (1898).

[5] Geisow, *ibid.*, 37, 515 (1904).

[6] Dakin, *J. Biol. Chem.*, 4, 77 (1908); Heimrod and Levene, *Biochem. Z.*, 29, **31** (1910); Reiner, *Z. anorg. allgem. Chem.*, 141, 363 (1925).

TABLE I

MOLAR QUANTITIES OF HYDROGEN PEROXIDE AND ACETALDEHYDE USED AND OF PRODUCTS FORMED

Run	*Initial* H_2O_2	*Initial* CH_3CHO	CH_3COOH *found*	HCOOH *found*	H_2CO_3 *found*	H_2 *found*	CH_4 *found*
Ia	0.1250	0.2500	0.0670	0.0081	0.0183	0.0021	0.0032
Ib	.1250	2500	.0710	0099	.0172	.0017	.0023
IIa	2500	.2500	.1422	.0075	.0211	.0044	.0026
IIb	2500	.2500	.1422	.0078	.0231	.0038	.0022
IIIa	,5000	2500	.1870	.0082	.0444	.0035	.0007
IIIb	,5000	.2500	.1775	.0080	.0471	.0036	.0006

Summary

Without attempting to correlate, exactly quantitatively, the molar yields of the products obtained with the reactions involved in their formation, which is not possible because the extreme volatility of the acetaldehyde made its retention in the reaction mixtures impossible, the following conclusions may be drawn from the available data.

1. The yields of the two chief reaction products, *acetic* and *carbonic* acids, increase as increased quantities of hydrogen peroxide are used.

2. Since separately conducted runs with acetic acid and hydrogen peroxide gave formic and carbonic acids without the liberation of hydrogen or of methane, it follows that the hydrogen arises from the oxidation of acetaldehyde to acetic acid as indicated in the proposed equation

$$2CH_3CHO + H_2O_2 \longrightarrow 2CH_3COOH + H_2$$

3. While the maximum yields of hydrogen were obtained with equimolar concentrations of acetaldehyde and hydrogen peroxide, another striking parallel to the formaldehyde reaction (Part I, Section B) is found in the fact that the volumes of methane liberated according to the proposed equation, $2CH_3CHO + H_2O_2 \longrightarrow CH_3COOH + HCOOH + CH_4$, *decrease* with *increasing* concentrations of hydrogen peroxide.

In conclusion, the formation of acetic and formic acids with the concurrent liberation of both hydrogen and methane appears to be in conformity with the above equations for the reactions which were predicted by extending the proposed reaction mechanism scheme to acetaldehyde.

In proposing a new type of reaction mechanism, termed "perhydrolysis," to explain some of the normal and also apparently anomalous reactions of hydrogen peroxide, the authors would guard against the assumption that all reactions of hydrogen peroxide involve "perhydrolysis," for many do not.

Further confirmation of the perhydrolysis mechanism is under way in an extended study of the action of hydrogen peroxide upon other simple carbon compounds.

CINCINNATI, OHIO

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

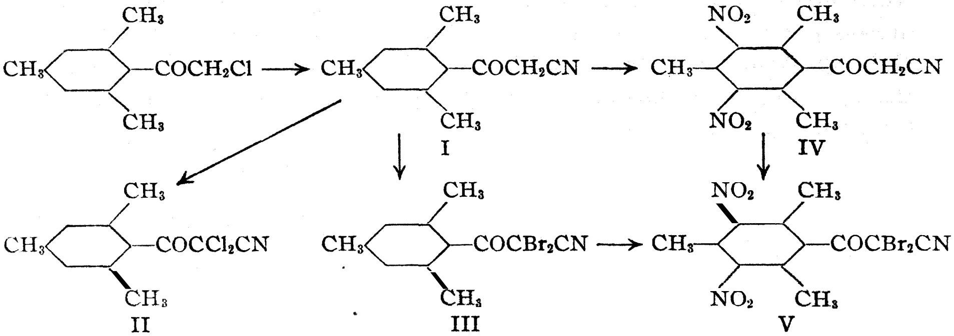
DIHALOCYANOACETYL DERIVATIVES OF MESITYLENE

BY REYNOLD C. FUSON AND REID G. BEVERIDGE

RECEIVED MARCH 16, 1931 PUBLISHED MAY 6, 1931

It has been shown that the halogenation of methyl phenyl ketones by solutions of hypohalites becomes possible when the action of the alkali on the carbonyl group is hindered by the presence of ortho substituents in the benzene ring. Thus when acetomesitylene is shaken for two days with an aqueous solution of sodium hypobromite, tribromoacetylmesitylene is formed.[1] Although the trihaloacetyl compounds so obtained are stable to cold alkali, they can be cleaved in the normal manner by long treatment with hot concentrated solutions of alkali. Work on the cleavage of these and similar trihalomethyl compounds will be reported elsewhere.[2]

A natural extension of this study of halogenation by solutions of hypohalites was its application to ketones having active methylene groups adjacent to the hindered carbonyl. Of these the cyanomethyl ketones offered particular interest because of the remarkable activity of the methylene group. In α-cyanoacetophenone, for example, the hydrogens of the methylene group enolize so readily as to render the compound soluble in alkali. It was to be expected from this that halogenation might proceed much more rapidly with this type of ketone than with those previously examined.



I II III IV V

Accordingly, cyanoacetylmesitylene (I) and di-(cyanoacetyl)-mesitylene (VI) have been prepared and their reaction with hypohalite solutions has been studied. When chloroacetylmesitylene, obtained from mesitylene and chloroacetyl chloride by the method of Collet,[3] is treated with potassium cyanide, cyanoacetylmesitylene (I) is obtained in good yield.

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[1] Fuson and Walker, THIS JOURNAL, 52, 3269 (1930).

[2] In a recent article Houben and Fischer, *Ber.*, **63B**, 2458 (1930), reported the cleavage of trichloroacetylmesitylene by boiling with a 40% sodium hydroxide solution for two hours.

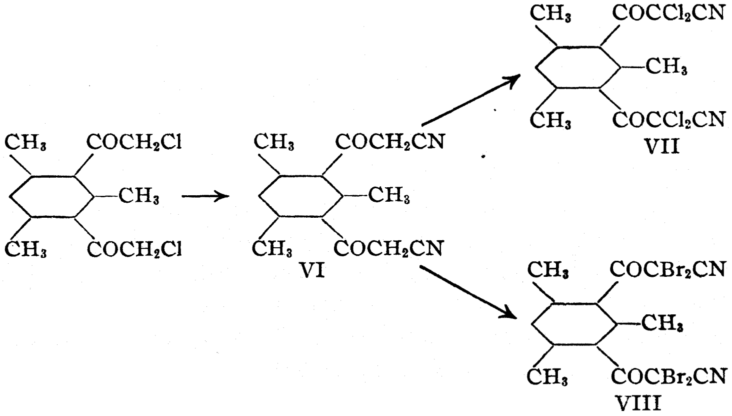
[3] Collet, *Bull. soc. chim.*, [3] 17, 510 (1897).

The cyano ketone is sufficiently acid to decompose potassium cyanide and for this reason it is necessary in the preparation to employ two molecular proportions of the salt for one of the chloro compound.

In an exactly similar fashion, di-(cyanoacetyl)-mesitylene (VI) is obtained from the corresponding dichloro compound.[4] Here, of course, four molecular proportions of potassium cyanide are necessary for every mole of di-(chloroacetyl)-mesitylene used. Both the cyano and the dicyano compounds are readily soluble in aqueous alkali and this property has been used in separating them from impurities such as the unchanged chloro compounds.

The action of hypohalite solutions on these cyano ketones is remarkable because of its rapidity. When the cyano ketone is added to a solution of sodium hypochlorite, for example, the crystals dissolve immediately but the material is almost at once reprecipitated in the form of the chlorinated derivative, dichlorocyanoacetylmesitylene (II). Both this compound and the dibromocyanoacetylmesitylene (111), obtained in an exactly similar manner, are stable to cold solutions of alkalies and are obtained in good yields even when the hypohalite solution is strongly alkaline.

The position of the two bromine atoms in dibromocyanoacetylmesitylene has been checked by the use of dinitrocyanoacetylmesitylene (IV). This compound, which was obtained from cyanoacetylmesitylene by direct nitration, was found to give dinitrodibromocyanoacetylmesitylene (V) when treated with a solution of sodium hypobromite. This same dinitrodibromo compound was obtained when dibromocyanoacetylmesitylene (III) was treated with fuming nitric acid. There can be no doubt then that the two bromine atoms in dibromocyanoacetylmesitylene are situated in the acetyl group.



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[4] The dichloro compound was prepared by the method of Breed (Bryn Mawr College Monographs, 1, No. 1, p. 7).

Di-(cyanoacetyl)-mesitylene (VI) when treated with solutions of sodium hypochlorite and sodium hypobromite yielded, respectively, di-(dichlorocyanoacetyl)-mesitylene (VII) and di-(dibromocyanoacetyl)-mesitylene (VIII). This process, however, presented a rather puzzling phenomenon. The crystals of the dicyano compound when added to a solution of a sodium hypohalite first dissolved completely. Then after a few seconds the solution became milky as though the neutral tetrahalo compound werd being precipitated. However, this precipitate redissolved rapidly and finally the expected tetrahalo compound separated and remained insoluble. This process is being studied.

Experimental

Cyanoacetylmesitylene[5] (I).—Ten grams of chloroacetylmesitylene was dissolved in 300 cc. of alcohol by boiling under a reflux condenser Four and a half grams of potassium cyanide was dissolved in a small amount of water and the solution was added through the condenser. After the solution had boiled for four hours, the alcohol was evaporated and the residue dissolved in 200 cc. of water. The crude material was precipitated by adding hydrochloric acid. After filtering, the material was dissolved in methyl alcohol and clarified by boiling with bone black. It was recrystallized from dilute methyl alcohol. The compound melted at 108–109° and the yield was 50 to 60% of the theoretical.

Anal. Calcd. for $C_{12}H_{13}ON$: C, 77.0; H, 7.0. Found: C, 76.8; H, 6.8.

Dibromocyanoacetylmesitylene (III).—A solution of sodium hypobromite was made by slowly adding 15 g. of bromine to a cold solution of 15 g. of sodium hydroxide in 150 cc. of water. To this solution 1 g. of cyanoacetylmesitylenewas added. A white crystalline substance formed and after being filtered it was recrystallized from dilute methyl alcohol. The substance melted at 81–82' and the yield was 50 to 60% of the theoretical.

Anal. Calcd. for $C_{12}H_{11}ONBr_2$: Br, 46.4. Found: Br. 46.3.

Dichlorocyanoacetylmesitylene (XI).—A solution of sodium hypochlorite was prepared by bubbling chlorine through a cold solution of 15 g. of sodium hydroxide dissolved in 150 cc. of water. One gram of cyanoacetylmesitylene was added to this solution. A white crystalline substance formed which went into solution on shaking. The solution was allowed to stand for twenty-four hours and was then filtered. The material was recrystallized from dilute methyl alcohol, The substance melted at 38–39° and the yield was 45 to 50% of the theoretical.

Anal. Calcd. for $C_{12}H_{11}ONCl_2$: Cl, 27.7. Found: Cl, 27.6.

Dinitrodibromocyanoacetylmesitylene (V).—One gram of dibromocyanoacetylmesitylene was added to 20 cc. of cold fuming nitric acid (sp. gr. 1.49–1.50). After being allowed to stand for fifteen minutes, the solution was poured into ice water and filtered. The compound was recrystallized from dilute methyl alcohol; it melted at 97–98°. The yield was 85% of the theoretical.

Dinitrocyanoacetylmesitylene (IV).—One gram of cyanoacetylmesitylenewas added to 20 cc. of cold fuming nitric acid (sp. gr. 1.49–1.50). The mixture was allowed to stand for a few minutes, was poured into ice water and filtered. The compound was recrystallized from dilute methyl alcohol. It melted at 170.3 to 171.3° (corr.) and the yield was 35% of the theoretical.

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[5] This preparation was first carried out by Mr. A. E. Knauf.

Anal. Calcd. for $C_{12}H_{11}O_5N_3$: C, 52.0; H, 4.0. Found: C, 51.8; H, 3.7.

Dinitrodibromocyanoacetylmesitylene.—One gram of dinitrocyanoacetylmesitylene was added to a solution of sodium hypobromite. The solution was allowed to stand for twenty-four hours and then filtered. . The substance was recrystallized from aqueous methyl alcohol and melted at 94–95". The yield was 45% of the theoretical.

Anal. Calcd. for $C_{12}H_9O_5Br_2N_3$: Br, 36.8. Found: Br, 36.6.

Di-(cyanoacetyl)-mesitylene (VI).—Ten grams of di-(chloroacetyl)-mesitylene was dissolved in 300 cc. of alcohol by boiling under a reflux condenser. Five and a half grams of potassium cyanide dissolved in a small amount of water was added through the condenser. After boiling for four hours the alcohol was evaporated and the residue dissolved in 200 cc. of water. The substance was precipitated by adding hydrochloric acid. After filtering, the crude material was dissolved in alcohol and clarified by boiling with bone black. The substance was recrystallized from dilute alcohol and melted at 156–157° (corr.). The yield was 70 to 80% of the theoretical.

Anal. Calcd. for $C_{15}H_{14}O_2N_2$: C, 70.9; H, 5.5. Found: C, 70.6; H, 5.3.

Di-(dichlorocyanoacetyl)-mesitylene (VII).—A solution of sodium hypochlorite was prepared by bubbling chlorine through a cold solution of 15 g. of sodium hydroxide dissolved in 150 cc. of water until the solution became yellow. One gram of di-(cyanoacetyl)-mesitylene dissolved in sodium hydroxide was added to this solution. A white substance formed but went into solution on shaking The solution was allowed to stand for twenty-four hours and then filtered. The substance was recrystallized from dilute methyl alcohol. It melted at 52–53° and the yield was 50 to 60% of the theoretical

Anal. Calcd. for $C_{15}H_{10}O_2N_2Cl_4$: Cl, 36.2. Found: Cl, 36.0.

Di-(dibromocyanoacetyl)-mesitylene (VIII).—A solution of sodium hypobromite was prepared by slowly adding 15 g. of bromine to a cold solution of 15 g. of sodium hydroxide dissolved in 150 cc. of water. One gram of di-(cyanoacetyl)-mesitylene dissolved in sodium hydroxide was added to this solution. After being allowed to stand for a few minutes the substance was filtered and recrystallized from methyl alcohol. The compound melted at 121.2–122.2' (corr.). The yield was 30 to 35% of the theoretical.

Anal. Calcd. for $C_{15}H_{10}O_2N_2Br_4$: Br, 56.1. Found: Br, 55.9.

Summary

1. Cyanoacetylmesitylene and di-(cyanoacetyl)-mesitylene have been prepared from chloroacetylmesitylene and di-(chloroacetyl)-mesitylene, respectively, by treatment with potassium cyanide.

2. Cyanoacetylmesitylene when treated with solutions of sodium hypochlorite and sodium hypobromite has been found to yield, respectively, dichlorocyanoacetylmesitylene and dibromocyanoacetylmesitylene.

3. Dinitrodibromocyanoacetylmesitylene has been prepared, (a) by nitration of dibromocyanoacetylmesitylene and (b) by treating dinitrocyanoacetylmesitylene with a solution of sodium hypobromite.

4. Di-(dichlorocyanoacetyl)-mesitylene and di-(dibromocyanoacetyl)-mesitylene have been obtained from di-(cyanoacetyl)-mesitylene by treatment of the latter with solutions of sodium hypochlorite and sodium hypobromite, respectively.

5. All of these dihalocyanoacetyl compounds have been found to be stable to cold solutions of alkalies.

URBANA, ILLINOIS

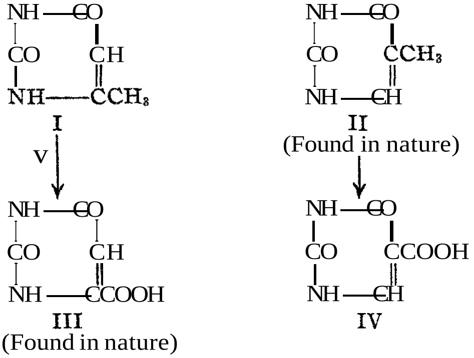
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXXII. IMPROVED METHODS FOR THE SYNTHESIS OF OROTIC ACID[1]

BY TREAT B. JOHNSON AND ELMER F. SCHROEDER[2]

RECEIVED MARCH 18, 1931 PUBLISHED MAY 6, 1931

Uracil-4-carboxylic acid (orotic acid) III is the only carboxylated derivative of the pyrimidine cycle which has thus far been shown to occur in nature. It was discovered in milk by Biscaro and Belloni[3] in 1905. Regarding its origin or its function in the animal organism we have at present no information. Chemically speaking, it is an oxidation product of 4-methyl-uracil I, bearing the same structural relationship to this pyrimidine as uracil-5-carboxylic[4] acid IV does to thymine II. Behrend showed in 1910 that 4-methyluracil can be oxidized to the amide of uracil-4-carboxylic acid by potassium ferricyanide, but no one has succeeded in oxidizing thymine to the corresponding uracil-5-carboxylic acid. Furthermore, no one has, thus far, been successful in showing that 4-methyluracil occurs in nature.



I

II

(Found in nature)

III

(Found in nature)

IV

The first investigator to prepare a derivative of uracil-4-carboxylic acid III was Müller,[5] who synthesized its ethyl ester by condensation of urea with diethyl oxaloacetate in acid solution. Müller did not prove, however, that he was dealing with a pyrimidine condensation product and it remained for Wheeler[6] of the Yale Laboratory to show, in 1907, that this ester of Müller's yields on saponification a true pyrimidine acid, namely, uracil-4-carboxylic acid III. Behrend and Struve[7] later found

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[1] This work was reviewed in a preliminary paper presented at the Spring Meeting of the American Chemical Society held in Indianapolis, Indiana, in April, 1931.

[2] Sterling Research Fellow in Chemistry, 1930–1931.

[3] Biscaro and Belloni, *Estratto Annuario Soc. Chimica di Milano*, **11**, 1 (1905); *Chem. Zentr.*, **II**, 63 (1905).

[4] Wheeler, Johnson and Johns, *Am. Chem. J.*, **37**, 392 (1907).

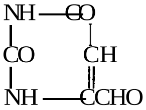
[5] Müller, *J. prakt. Chem.*, **56**, 488 (1897)

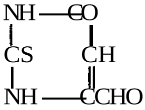
[6] Wheeler, *Am. Chem. J.*, **38**, 358 (1907)

[7] Behrend and Struve, *Ann.*, **378**, 153 (1910).

that the amide of this pyrimidine acid is formed by oxidation of 4-methyluracil with potassium ferricyanide in ammoniacal solution, and showed that this is converted into the acid III by the action of alkali. The last investigator to describe the synthesis of uracil-4-carboxylic acid III was Bachstez,[8] who first prepared the ester by Muller's method and then transformed this into its acid III according to the procedure of Wheeler. Bachstez was the first one to prove that this pyrimidine acid III is identical with orotic acid previously separated from milk by Biscaro and Belloni. Behrend and Struve's oxidation method is of no practical value for the synthesis of uracil-4-carboxylic acid and to obtain it in quantity by condensation according to the Müller reaction is difficult on account of the low yield of pyrimidine formed. This is only about 15 to 20% of the theoretical amount.

By reconsideration and extension of our researches on pyrimidine aldehydes, which were discontinued in 1915, we have now been successful in developing a procedure for synthesizing orotic acid which is a great improvement over the methods of preparation described above. Our method is based on the discovery that the 4-aldehydic derivatives of uracil and 2-thiouracil,[9] which can be derived easily from ethyl-γ,γ-diethoxyacetoacetate by condensation with thiourea, are oxidized smoothly to orotic acid by chromic acid without destruction of the pyrimidine ring. The methods of synthesizing 2-thiouracil-4-aldehyde VI and uracil-4-aldehyde V first described by Johnson and Cretcher have been so greatly improved for practical application that orotic acid III can now be made in quantity without any difficulty. Various modifications in technique have been introduced for preparing the acid from different derivatives and these will be discussed in the experimental part of this paper. In every case the pyrimidine acid obtained has been found to be identical with the natural orotic acid. We are greatly indebted to Dr. Bachstez for sending us a generous supply of natural orotic acid obtained from milk, and also its potassium salt, for comparison with our synthetical product.


V


VI

Experimental Part

Ethyl Diethoxyacetate, $(C_2H_5O)_2CHCOOC_2H_5$.—This ester was prepared by the method of Johnson and Cretcher.[9] The experience of former workers in this Laboratory

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[8] Bachstez, *Ber.*, 63, 1000 (1930); *Giornale di Chimica Industriale, Ed. Applicata*, 12, 174 (1930).

[9] Johnson and Cretcher, This Journal, 37, 2144 (1915); *J. Biol. Chem.*, 26, 99 (1916).

on the failure of commercial dichloroacetic acid to give satisfactory yields was verified. A very pure acid, best prepared from chloral hydrate according to the directions of Pucher,[10] is necessary. Attempts made to alkylate the moist silver salt of diethoxyacetic acid were not successful. The silver salt must be carefully dried before alkylation by spreading it out in thin layers and allowing it to stand in a vacuum desiccator over sulfuric acid in a dark place for several days. Due to the ease of decomposition, it cannot be dried by heating in a vacuum oven. Working in lots of 200 g. of dichloroacetic acid, 150 g. of the pure ester having a boiling point of 94–98" at 18 mm. pressure is easily obtained. This represents a yield of 55% of the theoretical.

Ethyl-γ,γ-diethoxyacetoacetate, $(C_2H_5O)_2CHCOCH_2COOC_2H_5$.—This β-ketone ester was prepared according to the directions of Johnson and Mikeska.[11] It was found very advantageous to wash the ethereal solution of the β-ketone ester with dilute sodium carbonate until free from acid, then to dry with sodium sulfate for ten to twelve hours. By this operation, a large part of the objectionable coloring matter is removed, resulting in a purer pyrimidine condensation product. One hundred and fifty grams of ethyl diethoxyacetate yield 150 g. of ethyl-γ,γ-diethoxyacetoacetate, or 80% of the theoretical amount.

Diethylacetal of 2-Thiouracil-4-aldehyde.—This pyrimidine was prepared by condensation of the above β-ketone ester with thiourea according to the method of Johnson and Cretcher[9] One hundred and fifty grams of the β-ketone ester gave 110 g. of the pyrimidine, corresponding to 70% of the theoretical. It was recrystallized from 95% alcohol, separating in the form of thick, rhombic blocks, colorless or slightly yellowish and sparingly soluble in water. It melted at 160°.

2-Thiouracil-4-aldehyde. VI.—Twenty-five grams of recrystallized diethylacetal of 2-thiouracil-4-aldehyde is dissolved in 500 cc. of dilute hydrochloric acid (1:1). The solution is then heated to boiling and rapidly filtered through glass wool. On cooling, this pyrimidine aldehyde separates in the form of golden-yellow plates containing one molecule of water of crystallization. The yield is 18.0 g. or practically quantitative, and it melts with decomposition at 250".

Diethylacetal of 2-Ethylmercaptouracil-4-aldehyde.—A solution of 2.5 g. of sodium in 250 cc. of absolute alcohol is prepared and cooled to room temperature. Twenty-five grams of the diethylacetal of 2-thiouracil-4-aldehyde is dissolved in the resulting solution and 15 g. of ethyl bromide is then added and the whole refluxed for two hours on the steam-bath. At the end of this period the reaction mixture is cooled, the precipitated sodium bromide filtered off and the filtrate evaporated to an oil on the steam-bath. On the addition of water, the oil solidifies to a white solid. It is recrystallized from a 40% alcohol–water solution and separates in the form of needles; yield, 24 g. or 85% of the theoretical. It melts at 128".

2-Ethylmercaptouracil-4-aldehyde (V).—This pyrimidine aldehyde was first obtained by Johnson and Cretcher[9] by hydrolysis of the diethylacetal of 2-ethylmercaptouracil-4-aldehyde in hydrochloric acid solution. A better yield is obtained by using dilute acetic acid. Ten grams of the diethylacetal of 2-ethylmercaptouracil-4-aldehyde is dissolved in 100 cc. of dilute acetic acid (1:1) and the solution evaporated to dryness on the steam-bath. The aldehyde remains as a yellowish residue, soluble in hot water and alcohol, slightly soluble in ether and benzene. It is recrystallized from hot water, separating in the form of colorless, elongated prisms. It melted at 148–149° and the yield was 5.3 g. or 75% of the theoretical.

Oxidation of 2-Thiouracil-4-aldehyde to Orotic Acid, III.—An oxidizing solution is prepared by dissolving 25 g. of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) and 30 g. of

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[10] Pucher, THIS JOURNAL, 42, 2251 (1920).

[11] Johnson and Mikeska, *ibid.*, 41, 810 (1919).

concentrated sulfuric acid in 115 cc. of water. The solution is cooled to room temperature. Five grams of 2-thiouracil-4-aldehyde is now added in small portions at such a rate that the temperature does not rise above 75°. The solution is constantly stirred during the addition. A vigorous reaction occurs, which is soon completed. When all the aldehyde has been added the solution is allowed to stand for ten minutes, after which it is heated to boiling for one minute. During this time the orotic acid partially separates. After cooling, the solution is filtered with suction, and the precipitate washed with water. The crude orotic acid (4.1 g.) is obtained in quite pure form as a slightly yellowish powder. It is purified by dissolving in 350 cc. of water, decolorizing with norite, filtering and cooling the filtrate rapidly. The acid is obtained as a white crystalline powder. The yield was 3.8 g. or 76% of the theoretical. The melting point was 345° (corr.).

The essential points in this technique are the portionwise addition of the aldehyde, and the short period of boiling. If the aldehyde is added all at once, yields are decreased to about 40%. Furthermore, since orotic acid is slowly attacked by boiling chromic acid solutions, prolongation of the boiling period beyond one minute also slowly decreases the yield.

Identification of the Product.—The synthetic acid was shown to be identical in every respect with natural orotic acid sent us by Dr. Bachstez. Its melting point is 345° (corr.); that of natural orotic acid is 345–347° (corr.); a mixed melting point shows no depression, melting at 345" (corr.). It crystallizes from hot water in rhombic prisms often exhibiting a characteristic twinning habit similar to that of the natural product. It is soluble in potassium hydroxide solution, from which acetic acid precipitates, not the free acid, but the potassium salt as a mass of fine needles. Similarly, acetic acid precipitates the ammonium salt from a solution of the synthetic acid in aqueous ammonium hydroxide. The acid is soluble in cold concentrated sulfuric acid, from which it is precipitated unchanged (m. p. 344°) on addition of water. It is tasteless. It reacts neither with Fehling's solution, nor with ammoniacal silver nitrate. Silver nitrate precipitates an amorphous white solid, soluble in nitric acid, from its aqueous solution. Similarly, barium chloride precipitates a crystalline barium salt. According to the methods of Bachstez, the bromine derivative, dibromobarbituric acid and the potassium salt of 5-nitro-orotic acid were prepared from the synthetic acid. The former melted at 235" (uncorr.) and the latter showed the characteristic color change to yellow accompanying its decomposition to potassium nitro-uracil when heated to 130°.

Heated at 130°, the synthetic orotic acid loses one molecule of crystal water. 0.2240 g of substance lost 0.0233 g. of H_2O: Calcd. for $C_5H_4O_4N_2 \cdot H_2O$: H_2O, 10.3 Found: H_2O, 10.4.

The acid was titrated in hot aqueous solution using phenolphthalein as an indicator. 0.3215 g. of substance required 18.7 cc. of 0.1295 *N* NaOH. Calcd. for $C_5H_4O_4N_2 \cdot H_2O$: 18.5 cc. 0.2582 g. required 14.9 cc. of 0.1295 *N* NaOH. Calcd., 14.8 cc.

Oxidation of 2-Thiouracil-4-aldehyde-diethylacetal, **2-Ethylmercaptouracil-4-aldehyde-diethylacetal** and 2-Ethylmercaptouracil-4-aldehyde to Orotic Acid.—The 2-ethylmercaptouradl-4-aldehyde was oxidized by the method previously described for the oxidation of 2-thiouracil-4-aldehyde. Three grams of the ethylmercapto-aldehyde gave 1.4 g. of pure orotic acid, corresponding to 55% of the theoretical. It was found that in the case of the acetals, portionwise addition of the solid acetal to the oxidation mixture gave very low yields. However, fairly good yields could be obtained by boiling the acetals for a few minutes in dilute sulfuric acid to effect hydrolysis of the acetal grouping, and then adding the oxidizing mixture to the resulting solution.

Three grams of 2-thiouracil-4-aldehyde-diethylacetalis suspended in a solution of 20 cc. of concentrated sulfuric acid in 50 cc. of water. The mixture is boiled for several minutes, when most of the acetal dissolves and the solution assumes the bright yellow color of the free aldehyde. The solution is now removed from the flame, allowed to cool somewhat, and a solution of 15 g. of sodium dichromate in 30 cc of water added at such a rate that the temperature remains between 80 and 90°. At the end of the addition, the solution is boiled for another minute. The orotic acid is recovered as previously described; yield, 1.5 g. or 68%.

Similarly, by the above procedure, 3 g. of 2-ethylmercaptouracil-4-aldehyde-diethylacetal gave 1.0 g. of pure orotic acid, corresponding to 53% of the theoretical.

Preparation of the Diethylacetal of Uracil-4-aldehyde from the Diethylacetal of **2-Thiouracil-4-aldehyde.**—Two grams of 2-thiouracil-4-aldehyde diethylacetal is covered with 60 cc. of 3% hydrogen peroxide and 15 cc. of 20% sodium hydroxide. The pyrimidine readily dissolves, yielding a colorless solution. Considerable heat is developed, the temperature rising to about 50°. The solution is now heated to a gentle boil for three minutes. It is then cooled in ice water and acidified with concentrated hydrochloric acid. Large amounts of sulfur dioxide are evolved, and separation of the sulfur-free acetal usually begins spontaneously. Occasionally vigorous scratching of the sides of the beaker with a glass rod is necessary to induce crystallization. The latter appears to be favored by a considerable excess of hydrochloric acid. The reaction mixture is allowed to stand at room temperature for several hours. The crude acetal is then filtered off, washed with cold water and recrystallized from a small amount of hot water. The diethylacetal of uracil-4-aldehyde separates in the form of colorless hexagonal prisms, melting sharply to a clear oil at 179°: yield, 1.8 g., or practically quantitative. The purified product gives no test for sulfur. It is easily soluble in the cold in methyl alcohol, ethyl alcohol, acetone and acetic acid, and insoluble in ether, benzene and ligroin. By oxidation with a $Na_2Cr_2O_7$–H_2SO_4 mixture as previously described, a good yield of orotic acid is obtained.

Anal. (Kjeldahl). Calcd. for $C_9H_{14}O_4N_2$: N, 13.08. Found: N, 13.05, 13.15.

Uracil-4-aldehyde, V.—A quantitative yield of this interesting pyrimidine aldehyde may be obtained by the careful hydrolysis of the corresponding uracil-4-aldehyde-diethylacetal. Two grams of the latter compound is dissolved in 25 cc. of dilute hydrochloric acid (one part concentrated acid and two parts water) and the solution finally heated to boiling for one minute. The solution assumes a pinkish color, which deepens on prolonged boiling. On cooling in ice water and scratching the beaker with a glass rod, the uracil-4-aldehyde separates out as a white solid. After standing for several hours, the reaction product is filtered off, washed with cold water and recrystallized from a small amount of hot water or dilute hydrochloric acid. The aldehyde separates in the form of colorless elongated prisms arranged in rosets; yield, 1.5 g. It does not possess a sharp melting point, but turns yellow when heated to about 260° and carbonizes without melting at 273–275°. This behavior is not changed by repeated crystallization from dilute hydrochloric acid. Uracil-4-aldehyde reduces Fehling's solution on warming, and ammoniacal silver nitrate in the cold. It gives a good Schiff's aldehyde reaction. With phenylhydrazine it yields a crystalline yellow hydrazone in the cold, decomposing at 330°. The aldehyde is very sensitive to the action of hot mineral acids. When boiled for a short time with concentrated hydrochloric acid its solution assumes a deep red color. It is much less soluble in the common organic solvents than the corresponding acetal, being insoluble in ether, benzene, ligroin and acetone, and moderately soluble in hot methyl and ethyl alcohol and hot acetic acid. By means of $Na_2Cr_2O_7$–H_2SO_4 mixture, it is easily oxidized to orotic acid. The aldehyde contains a molecule of water of crystallization, which it loses when heated to 120° for one hour.

Anal. (Kjeldahl). Calcd. for $C_5H_4O_3N_2\cdot H_2O$: N, 17.72. Found: N, 17.66, 17.80
0.4320 g. of substance lost 0.0497 g. of H_2O. Calcd.: 0.0492 g.

Summary

1. Uracil-4-carboxylic acid (orotic acid) known to occur in milk is most easily prepared in quantity by oxidation of 2-thiouracil-4-aldehyde or uracil-4-aldehyde with chromic acid.

2. The uracil-4-carboxylic acid thus obtained is identical with the natural orotic acid from milk furnished to us for comparison by Dr. Bachstez of Italy.

3. This is the only pyrimidine carboxylic acid thus far known to occur in nature.

NEW HAVEN, CONNECTICUT

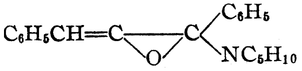
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ALPHA PIPERIDINO BENZALACETOPHENONE

BY E. P. KOHLER AND W. F. BRUCE

RECEIVED MARCH 19, 1931 PUBLISHED MAY 6, 1931

In a recent paper Kohler and Addinall[1] expressed the opinion that a peculiar red piperidine derivative which was first described by Watson[2] and later studied with care by Dufraisse and Moureu[3] is an unsaturated ethylene oxide (I). This view is erroneous; the substance is an unsaturated ketone and it has the structure assigned to it by Dufraisse and Moureu (II).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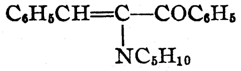
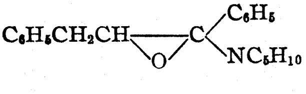


$$C_6H_5CH{=}\underset{NC_5H_{10}}{\underset{|}{C}}{-}COC_6H_5$$

II

As a means of discrimination between the two formulas all methods of degradation by oxidation proved useless, but fairly convincing evidence was obtained from a series of transformations based on hydrogenation. In the presence of platinum the red compound combines with two atoms of hydrogen and forms a yellow addition product which reacts with a mole of methyl magnesium iodide without liberating gas. This compound might, therefore, be either a saturated oxide or one of two saturated ketones.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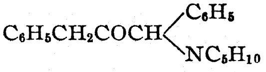
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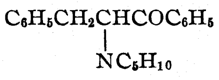

$$C_6H_5CH_2\underset{NC_5H_{10}}{\underset{|}{C}}HCOC_6H_5$$

V

The yellow reduction product can be made by the action of piperidine on *α*-bromo benzylacetophenone and it reacts with hydroxylamine like

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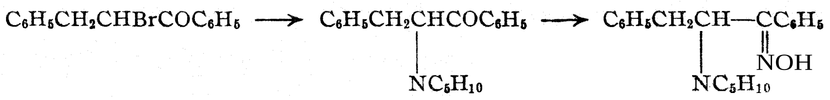
[1] Kohler and Addinall, THIS JOURNAL, 52, 3728 (1930).

[2] Watson, *J. Chem. Soc.*, 85, 1322 (1904).

[3] Dufraisse and Moureu, Bull. sac. *chim.*, [4] 41, 457 (1927).

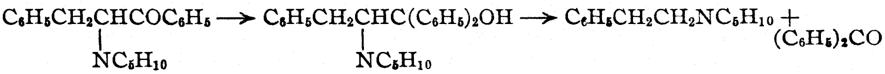
a ketone. Ordinarily this would be regarded as adequate evidence that the substance is the ketone V and the sequence of reactions would be represented as follows



$$C_6H_5CH_2CHBrCOC_6H_5 \longrightarrow C_6H_5CH_2\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}HCOC_6H_5 \longrightarrow C_6H_5CH_2\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}H{-}\underset{\displaystyle NOH}{\underset{\|}{C}}C_6H_5$$

VI VII VIII

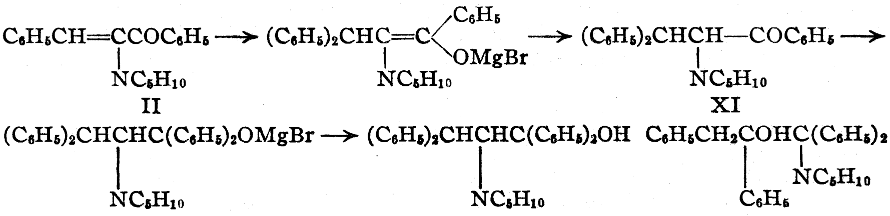
But unfortunately in this case the evidence is inconclusive, because the reaction between piperidine and the bromo compound might lead to the formation of the oxide III,[4] and it was not possible to regenerate the yellow compound from the product obtained in the reaction with hydroxylamine. Additional evidence as to the structure of the reduction product was obtained by treating it with phenyl magnesium bromide. It combined very readily with one equivalent of the reagent. The product of this reaction is colorless. It is stable to fairly high temperatures but above 280° it decomposes, giving mainly benzophenone and β-phenylethyl piperidine



$$C_6H_5CH_2\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}HCOC_6H_5 \longrightarrow C_6H_5CH_2\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}HC(C_6H_5)_2OH \longrightarrow C_6H_5CH_2CH_2NC_5H_{10} + (C_6H_5)_2CO$$

VII IX X

These transformations are difficult to reconcile with any formula other than VII; but since the final step involved the use of high temperatures and we were reluctant to accept this formula without the best of evidence, we decided to study another series of transformations. To this end we treated the red compound itself with excess of phenyl magnesium bromide. It combined with but one mole; but the yellow compound that was obtained by decomposing the resulting magnesium derivative was capable of combining with a second equivalent of the reagent. This is the characteristic behavior of α,β-unsaturated ketones with which organic magnesium compounds form 1,4-addition products



$$C_6H_5CH{=}\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}COC_6H_5 \longrightarrow (C_6H_5)_2CH\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}{=}C\begin{smallmatrix}C_6H_5\\ OMgBr\end{smallmatrix} \longrightarrow (C_6H_5)_2CH\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}H{-}COC_6H_5 \longrightarrow$$

II XI

$$(C_6H_5)_2CH\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}HC(C_6H_5)_2OMgBr \longrightarrow (C_6H_5)_2CH\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}HC(C_6H_5)_2OH \qquad C_6H_5CH_2\underset{\displaystyle C_6H_5}{\underset{|}{C}}OH\underset{\displaystyle NC_5H_{10}}{\underset{|}{C}}(C_6H_5)_2$$

XII XIII

Since ethylene oxides are capable of combining with organic magnesium derivatives, it is possible to imagine a similar series of reactions beginning with an oxide like I and ending with the carbinol XIII. Between these two possible carbinols it was easy to decide, because when the final product of the reaction was oxidized with chromic acid, it yielded two molecules

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[4] Ref. 1, p. 3730.

of benzophenone. It is therefore the carbinol XII, and **the** red piperidine derivative must be the unsaturated **ketone** II.

Experimental Part

On the assumption that the red piperidine derivative has the structure assigned to it by Dufraisse and Moureu, the simplest and best proof of its structure would be its synthesis by the condensation of benzaldehyde and w-piperidino acetophenone

$$C_6H_5CHO + \underset{\underset{NC_5H_{10}}{|}}{CH_2}COC_6H_5 \longrightarrow C_6H_5CHOH\underset{\underset{NC_5H_{10}}{|}}{CH}COC_6H_5 \longrightarrow C_6H_5CH{=}\underset{\underset{NC_5H_{10}}{|}}{C}{-}COC_6H$$

Since the red compound is readily hydrolyzed by acids, it was necessary to undertake the condensation in the presence of bases; all attempts to effect condensation under these conditions were unsuccessful.

Another relatively simple method of differentiating between the two possible formulas of the red compound might be ozonization. This also was tried; a solution of the substance in carbon tetrachloride absorbed ozone with avidity. After removing the solvent and manipulating the residue in the usual manner, the products were benzaldehyde, benzoic acid and an oil which could not be purified but which gave piperidine and phenyl glyoxylic acid when it was digested with alkali. Inasmuch as these products might be formed both from the ketone and from the oxide the results are inconclusive.

Hydrogenation.—The red compound was hydrogenated in methyl alcohol with Adams' platinum oxide as the catalyst. It absorbed hydrogen rapidly at first, but the rate gradually fell off and there was no sharp break in the rate curve at the point representing the addition of two hydrogen atoms. After some preliminary experiments it was found advantageous to interrupt the operation when one mole of hydrogen had been absorbed, even though not all of the substance had been hydrogenated. Thus, a solution of 10 g. of the red compound in about 300 cc. of methyl alcohol was shaken with 0.2 g. of platinum oxide and hydrogen until 840 cc. of the latter had been absorbed Most of the catalyst was then removed by filtration, the remainder with active charcoal. The clarified solution, on concentration, deposited a mixture which was partially separated by crystallization. It yielded 7.1 g. of pure saturated ketone and 1.5 g. of a mixture of the original substance and its reduction product that was difficult to separate.

a-Piperidino Benzylacetophenone, **VII.—The** hydrogenation product is readily soluble in ether, moderately soluble in methyl alcohol. It crystallizes in pale yellow needles and melts at 81°. It dissolves readily both in dilute and in concentrated hydrochloric acid. The solution in 6 N acid deposited a colorless solid in large hexagonal prisms—doubtless the hydrochloride—from which alkalies regenerated the yellow base.

Anal. Calcd. for $C_{20}H_{23}ON$: C, 81.8; H, 7.9. Found: C, 81.9; H, 7.9.

Preparation from **α-Bromobenzylacetophenone.**—One gram of the bromo compound was added to **3** cc. of piperidine; it dissolved with cooling but the temperature soon rose rapidly and the solution became yellow. After half an hour it was diluted with water, whereupon it deposited an oil that soon solidified. After recrystallization from methyl alcohol the product melted at 80–81° and a mixed melting point determination proved its identity with the substance obtained by hydrogenation.

Reaction with **Hydroxylamine.**—A solution of 0.5 g. of the substance. 0.8 g. of hydroxylamine hydrochloride and 2 g. of potassium hydroxide in 25 cc. of methyl alcohol was boiled for half an hour, then poured into water. The product was recrystallized from methyl alcohol, from which it separated in colorless needles melting at 141–142°.

Anal. Calcd. for $C_{20}H_{24}ON_2$: C, 77.9; H, 7.9; N, 9.1. Found: C, 77.9; H, 8.0; N, 9.1.

The substance is, doubtless, the oxime VIII, which might be expected to resist hydrolysis. It is slightly soluble in 30% potassium hydroxide, and soluble in both dilute and concentrated acids—as would be expected in view of its piperidine group. In an attempt at hydrolysis it was heated overnight at 100° with 6 N hydrochloric acid. The result was a white solid melting at 240° which was not attacked by sodium bicarbonate but from which potassium hydroxide regenerated the oxime. With concentrated hydrochloric acid the result was the same.

Attempts to effect a Beckmann rearrangement were equally unsuccessful. Phosphorus pentachloride in cold ether immediately produced a white precipitate—doubtless the chloride—and when the solution was heated the result was a mixture of decomposition products among which benzonitrile was recognized by the odor. Hot formic acid merely transformed the substance into a salt—the formate—from which bases regenerated the oxime. After recrystallization from 5% aqueous formic acid the salt melted at 177–178".

Anal. Calcd. for $C_{21}H_{26}O_3N_2$: C, 71.2; H, 7.4. Found: C, 71.1; H, 7.4.

Action of Phenyl Magnesium Bromide, **α,α,γ-Triphenyl-β-piperidinopropanol, IX.**—An ethereal solution of 2.9 g. of the reduction product was added to a solution of the reagent that had been prepared from 0.96 g. of magnesium. Reaction occurred readily at 10° but the mixture was boiled for half an hour after all of the ketone had been added. The magnesium derivative was decomposed with ammonium chloride in the usual manner. The ethereal layer on evaporation left a solid and a small quantity of yellow oil. By recrystallization from methyl alcohol the solid carbinol was obtained in colorless plates melting at 148–149°.

Areal. Calcd. for $C_{26}H_{29}ON$: C, 84.1; H, 7.9. Found: C, 84.2; H, 7.8

Pyrolysis of the **Carbinol.**—A tube containing 1.6 g. of the carbinol was exhausted to 11 mm., then scaled and heated at 260–280° for seven hours in a Carius furnace. It was thus converted into a slightly discolored oil which was almost completely volatile with steam. In order to separate basic and non-basic constituents, the ethereal extract of the distillate was shaken with dilute hydrochloric acid The non-basic residue (0.82 g.) was identified as benzophenone by a mixed melting point. The acid solution, on treatment with alkali, yielded 0.50 g. of an oily base. The base formed a hydrochloride which crystallized in pearly plates, melting at 223° when crude and at 228° after recrystallization from methyl alcohol and ether. In the literature the melting point of β-phenylethyl piperidine hydrochloride is reported as 223°.[5]

Anal. Calcd. for $C_{13}H_{20}NCl$: C, 69.2; H, 8.9. Found: C, 69.1; H, 8.7.

Action of Phenyl Magnesium Bromide on the Unsaturated **Ketone.—α-Piperidino-β,β-diphenylpropiophenone,** XI.—A solution of 11 g. of the red ketone in 85 cc. of ether was added slowly to a solution of the reagent which had been made from 2.5 g. of magnesium. A deep blood-red coloration appeared where the solution met the reagent. At 0° this color persisted, but at the boiling point of the mixture it disappeared almost immediately. The mixture was boiled for an hour, then decomposed with ice and ammonium chloride. The ethereal layer was washed, dried and evaporated. It left a yellow solid and an oil. The oil was removed with methyl alcohol, and the solid was recrystallized from benzene and methyl alcohol. The ketone crystallized in yellow needles melting at 163°; yield, 61%.

Anal. Calcd. for $C_{26}H_{27}ON$: C, 84.5; H, 7.4. Found: C, 84.6; H, 7.3.

Action of Phenyl Magnesium Bromide, **α,α-Diphenyl-β-piperidino-γ,γ-diphenyl-**propanol, XU.—No perceptible reaction occurred when a benzene solution of one gram

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[5] **Kindler,** *Arch. Phurm.*. 265, 405 (1927).

of the yellow ketone was added to a solution of the reagent containing 0.2 g. of magnesium, but when the solution was boiled the yellow color gradually disappeared. After an hour's boiling, the solution was treated with ammonium chloride in the usual manner. The ethereal layer, on evaporation, left an oil which could not be induced to crystallize.

In the hope of securing a solid, an ethereal solution of the oil was treated with hydrogen chloride gas. The acid converted it into a product which likewise had a tendency to separate from solutions as an oil but which was finally obtained as a solid by the addition of petroleum ether to its solution in chloroform. An analysis of this solid, which melted at 162–164°, indicated that it was not a simple hydrochloride of the piperidine compound but that the strong acid had also replaced the hydroxyl group of the carbinol with chlorine.

Anal. Calcd. for $C_{32}H_{33}NCl_2$: C, 76.5; H, 6.6. Found: C, 75.5; H, 6.8.

From the chloro compound the carbinol was regenerated by shaking a suspension of the substance in ether with 10% sodium hydroxide. The ethereal layer, on evaporation, left an oil, but this was finally converted into a solid by dissolving it in benzene, concentrating and adding petroleum ether to the solution. The solid separated gradually in large and well-defined crystals melting at 136–137°.

Anal. Calcd. for $C_{32}H_{33}ON$: C, 85.9; H, 7.4. Found: C, 85.6; H, 7.8.

Oxidation of the Carbinol.—To a solution of 0.45 g. of the carbinol was added 1.1 g. of powdered sodium bichromate; the solution was kept at 44–45° for an hour, then diluted with 100 cc. of water, made alkaline with sodium hydroxide and distilled with steam. The distillate was thoroughly extracted with ether, and the dried extract evaporated. The oily residue was kept over potassium hydroxide in a vacuum desiccator until entirely dry. It solidified completely when touched with benzophenone and a mixed melting point showed that it was pure. The yield was 0.35 g. instead of 0.36 g. calculated on the assumption that one molecule of carbinol yields two molecules of benzophenone.

Summary

The brilliant red compound which is formed by the action of piperidine and bases on a-bromobenzalacetophenone is α-piperidino benzalacetophenone. It has the structure assigned to it by Dufraisse and Moureu.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PLANT PHYSIOLOGY, UNIVERSITY OF MARYLAND, AND THE AGRICULTURAL EXPERIMENT STATION]

DECARBOXYLATION STUDIES ON PECTINS AND CALCIUM PECTATES"

BY C. M. CONRAD

RECEIVED MARCH 24, 1931 PUBLISHED MAY 6, 1931

The acid hydrolysis of pectin and its various derivatives is accompanied by a certain amount of decarboxylation. With 12% hydrochloric acid the decarboxylation is complete and quantitative in five hours or less. However, the extent of decarboxylation in concentrations of mineral acids ordinarily used in hydrolysis of complex carbohydrates has not been reported except in a few isolated cases. Thus, Link and Niemann,[2] using lemon pectin, noted that **33.85%** of the galacturonic acid present was destroyed in fifteen hours by boiling 2% sulfuric acid and Link and Dickson,[3] with the same material and conditions except using 2.5% sulfuric acid, noted the same loss; again, Nelson and Cretcher,[4] noted a loss of carbon dioxide during the hydrolysis of algin.

In connection with certain studies it was desirable to know the extent of decarboxylation of pectins when boiled with different concentrations of hydrochloric and sulfuric acids. The data obtained are believed to be of sufficient interest to warrant publication.

Experimental Part

Materials.—Two samples of pectin were used. A purified apple pectin was kindly furnished by the Pectin Sales Company, since incorporated as General Food Sales Company of Fairport, N. Y. A rather pure lemon pectin was kindly supplied by Messrs. C. P. Wilson and H. W. Hall of the California Fruit Growers Exchange. These pectins gave the following analyses.

	Apple pectin	Lemon pectin
Moisture	11.55	10.50
Ash	7.80	7.85
Galacturonic acid (dry, ash-free)	74.30	85.70

Besides the pectins, several samples of calcium pectate were used. These were obtained in the course of *the* quantitative determination of pectin in fruit or vegetable tissues.

Apparatus and Method of Procedure

Figure 1 shows the apparatus employed to follow the decarboxylation. It was modeled somewhat after that described by Dickson, Otterson and Link,[5] differing es-

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[1] Published with the permission of the Director of the Maryland Agricultural Experiment Station.

[2] Link and Niemann, THIS JOURNAL, 52,2474 (1930).

[3] Link and Dickson, *J. Biol. Chem.*, **86**, 491 (1930).

[4] Nelson and Cretcher, THIS JOURNAL. 51, 1914 (1929).

[5] Dickson, Otterson and Link, *ibid.*, 52, 775 (1930).

sentially in the following features. Absorption of carbon dioxide occurs in an inclined 11-mm. glass tube without glass beads, platinum gauze, or other inclusions. Since the inclination of the tube from horizontal is only slight the bubbles travel up very slowly and absorption of carbon dioxide is complete. The reaction flask, usually a 300-cc. Erlenmeyer, rests on a 3-mm. sand-bath in a 20-cm. sand dish and is heated by a small carefully adjusted gas flame. A rubber stopper is used in the reaction flask. No appreciable error was found to result. It is renewed at intervals as it begins to show wear. All the bottles containing solutions used in the determination, together with burets, are permanently attached to the apparatus so that exposure to the air is avoided.

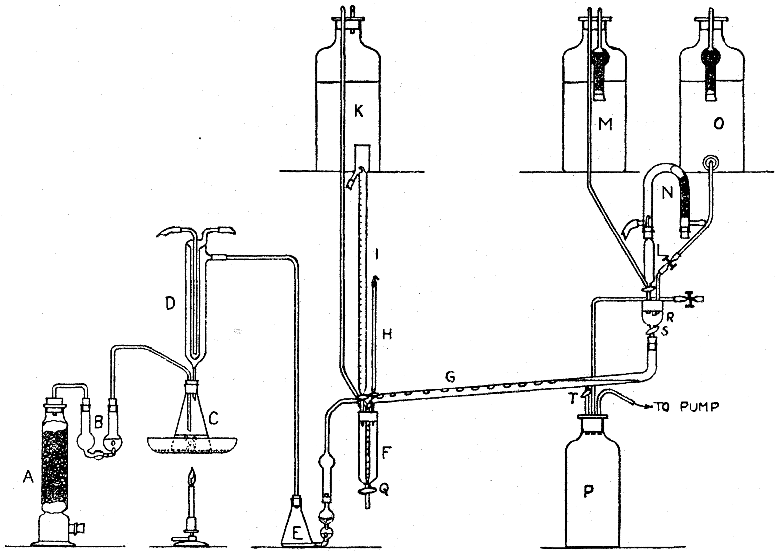

Fig. 1. –Apparatus used for decarboxylation studies: A, soda lime tower; B, trap with barium hydroxide solution; C, reaction flask; D, condenser; E, trap with 10% silver nitrate solution; F, titration chamber; G, absorption tube; H, buret for indicator; I, buret for standard hydrochloric acid; K, reservoir for standard hycrochloric acid; L, automatic pipet; M, reservoir for standard barium hydroxide; N, soda lime guard tube; O, reservoir for CO_2-free water; P, air chamber.

In determining the extent of decarboxylation the sample is placed in the reaction flask C and covered with 100 cc. of the acid solution desired. The flask is tightly fitted to its stopper and the sand-bath raised until the sand makes good contact with the bottom of the flask With stopcock Q closed and S open, 15 to 20 cc. of carbon dioxide-free water from reservoir O is allowed to flow through absorption tube G into the titration chamber F. Stopcock S is closed and the water pump turned on. T is almost closed, causing a partial vacuum in the trap P. S is now cautiously opened so that the distilled water is drawn from chamber F slowly up into tube *G*. As the last of the water passes into the tube, bubbles follow and the number and size of these are regulated by adjusting S. Carbon dioxide-free air is thus drawn through the system for fifteen minutes to sweep out all carbon dioxide. Stopcocks T and **Q** are then opened in the order named, allowing the distilled water to flow out. Stopcock **Q** is closed and a measured quantity of approximately 0.2 N barium hydroxide is allowed to flow from pipet I through chamber R into the absorption tube G. The stopcock of L is closed and the barium hydroxide is rinsed out of R with 4–5 cc. of water from O. Stopcock S is then closed and T again adjusted until only a small amount of air passes into P. Stopcock S is again cautiously opened and the barium hydroxide solution is drawn up into G, followed by a slow stream of bubbles. Cold water is passed through condenser D and the burner is lighted under the reaction flask. In actual runs boiling began in about twelve minutes. The flame was not changed after once having been adjusted.

When the reaction is finished, the flame is turned out and the stream of air drawn through the apparatus for about fifteen minutes longer. Stopcock T is then opened, followed by S, allowing the barium hydroxide carrying any carbonate to flow into the titration chamber. Buret I is filled with standard 0.2 *N* hydrochloric acid from the reservoir K A drop or two of phenolphthalein solution is introduced from H and the residual alkali in F is titrated. Frequently during the titration stopcock T is momentarily closed, thus drawing part of the titration mixture up into G. As T is opened, the mixture flows back into the chamber and mixing is readily accomplished. By proper manipulation of stopcock T in conjunction with stopcock S it is easy to control the movement of liquid in G. Especially near the end-point the liquid should be drawn entirely into *G* several times so that neutralization shall be complete. The end-point having been reached, the buret reading is taken and the titrated mixture discharged. The apparatus is then ready for another determination. The presence of a small amount of barium carbonate in *G* is not detrimental. However, this may be removed by means of water and acid from the reservoirs.

Repeated blank determinations with 100 cc. of 12% hydrochloric acid over the period used showed that barium hydroxide was neutralized equivalent to 0.0013 g. of carbon dioxide. All determinations were corrected for this amount.

Results

Decarboxylation of Pectins with Different Concentrations of Hydrochloric and Sulfuric Acids.—Samples of both apple and lemon pectins weighing from 0.3–1.0 g. were gently boiled with different concentrations of hydrochloric and sulfuric acids for sixteen hours in the apparatus previously described. The amounts of carbon dioxide produced, corrected for blank and calculated to one gram of dry ash-free pectin are shown in Tables I-III.

TABLE I

DECARBOXYLATION OF APPLE PECTIN BOILED WITH DIFFERENT CONCENTRATIONS OF HYDROCHLORIC ACID FOR SIXTEEN HOURS

Concn. of acid, %	CO_2 evolved, g	Galacturonic acid decomposed Actual, g.	Part of total. %
0.12	0.0149	0.0656	8.8
2.0	.0719	.3163	42.6
5.0	.1619	.7123	95.9
8.0	.1651	.7264	97.8
12.0	.1707	.7511	101.1
18.0	.1725	.7590	102.1

According to Ehrlich[6] and others pectins contain a complex consisting of four molecules of galacturonic acid joined in a ring. As the carboxyl groups are not concerned in the linkage, it is conceivable that decarboxyl-

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[6] Ehrlich and Schubert, *Ber.*, 62, 1974 (1929); Ehrlich and Kosmahly, *Biochem.* Z., 212, 162 (1929).

TABLE II

DECARBOXYLATION OF APPLE PECTIN BOILED WITH DIFFERENT CONCENTRATIONS OF SULFURIC ACID FOR SIXTEEN HOURS

Concn. of acid, %	CO_2 evolved, g.	Galacturonic acid decomposed	
		Actual, g.	Part of total, %
0.1	0.0070	0.0308	4.1
2.0	.0494	.2174	29.3
5.0	.0982	.4321	58.2
8.0	.1214	.5341	71.9
12.0	.1478	.6503	87.5
18.0	.1615	.7106	95.6

TABLE III

DECARBOXYLATION OF LEMON PECTIN BOILED WITH DIFFERENT CONCENTRATIONS OF SULFURIC ACID FOR SIXTEEN HOURS

Concn. of acid, %	CO_2 evolved, g.	Galacturonic acid decomposed	
		Actual, g.	Part of total, %
0.1	0.0102	0.0449	5.2
2.0	.0612	.2693	31.4
5.0	.1147	.5047	58 9
8.0	.1340	.5896	68 8
12.0	.1769	.7784	90.8

ation of pectin might take place entirely independent of the hydrolysis of pectin into galacturonic acid. However, it was observed that practically no carbon dioxide was formed until after some minutes of heating. Then if the acid was sufficiently strong it began to be evolved more rapidly, as was shown by the separation of barium carbonate in the absorption tube. This would suggest that hydrolysis precedes decarboxylation; however, it is not impossible that the hydrolytic products act catalytically.

It is seen from the tables that decarboxylation occurs already in very weak concentrations of hydrochloric and sulfuric acids and increases rapidly with increasing concentration of acid. Hydrochloric acid of a given percentage concentration is much more effective than sulfuric acid of the same percentage value but this is due principally to the greater hydrogen-ion concentration of the hydrochloric acid. Hydrochloric acid of 12% or more probably yields a little carbon dioxide from other sources than the carboxyl groups when the pectin is heated for sixteen hours. This is indicated by the high calculated values for galacturonic acid. In the case of sulfuric acid even as high as 18% fails to give the theoretical yields of carbon dioxide. It is therefore not appropriate for use in place of hydrochloric acid for determining uronic acids.

Decarboxylation of Calcium Pectate from Several Sources.—Pectins plant gums and similar complex polysaccharides are very generally hydrolyzed with 2% sulfuric acid.[7] Periods of heating vary from a few

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[7] Ehrlich and Sommerfeld, Biochem. Z, 168, 263 (1926); Butler and Cretcher, THIS JOURNAL, 51, 1519 (1929); Sands and Klass, ibid., 51, 3441 (1929); Bowman and McKinnis, *ibid.*, 52, 1209 (1930); Link and Niemann, *ibid.*, 52, 2474 (1930).

hours to as many as thirty, with a majority approximating sixteen hours. Inasmuch as the foregoing results showed so large a decarboxylation of apple and lemon pectin with this concentration of acid it was interesting to inquire whether this was a general property of the pectic substances from various sources. Therefore samples of calcium pectate which had been obtained in a rather pure condition in the course of other investigations were boiled with 2% sulfuric acid under the conditions previously described for pectins. The results are brought together in Table IV.

TABLE IV

DECARBOXYLATION OF CALCIUM PECTATE FROM VARIOUS SOURCES BY BOILING WITH 2% SULFURIC ACID FOR SIXTEEN HOURS

Calcium pectate from	Sample, g.	CO_2 obtained, g.	Galacturonic acid decomposed Weight, g.	Part of sample, %
Peach fruit	0.2665	0.0101	0 0444	16.7
Apple fruit	.3892	.0130	0572	14.7
Tomato fruit	.1528	0066	.0290	19.0
Strawberry fruit	.1999	.0075	.0330	16 5
Carrot root	.1674	.0053	.0233	13 9
Beet root	.1653	,0068	.0299	18.1

The results indicate that within the experimental error about the same percentage of galacturonic acid is decomposed in each case.

Summary and Conclusions

1. Decarboxylation of apple and lemon pectins with mineral acids occurs at low concentration of acid and is very appreciable with as weak as 0.1% sulfuric acid. The extent of decarboxylation of apple pectin in various concentrations of sulfuric and hydrochloric acids and of lemon pectin in various concentrations of sulfuric acid has been determined for a sixteen hour period of boiling.

2. **A** comparative study of the calcium pectate from several sources shows that the rate of decarboxylation with 2% sulfuric acid is approximately the same in each.

COLLEGE PARK, MARYLAND

COMMUNICATIONS TO THE EDITOR

OPTICAL ROTATION AND ATOMIC DIMENSION. IX. HALOGENO-TETRA-ACETYL DERIVATIVES OF MANNOSE. THEIR CONFIGURATIONAL PECULIARITIES

Sir:

In continuation of my investigations on Optical Rotation and Atomic Dimension [last publication, VIII, THIS JOURNAL, **51,** 1820 (1929)], there have been prepared the pure crystalline substances α-fluorotetraacetylmannose and a-iodotetraacetylmannose and their specific rotations measured. Further, we have revised the value for crystalline α-bromotetraacetylmannose as first measured by Micheel [Ber., **63,** 390 (1930)] and later by Levene and Tipson [*J. Biol.* Chem., 90, 93 (1931)]. As I prepared several years ago crystalline a-chlorotetraacetylmannose and measured its rotation, a series of values is available for comparison with the atomic dimension values.

It has been established in my former investigations on this subject that for all the investigated halogen derivatives of the monosaccharides (glucose, fructose, xylose and arabinose) the differences in specific rotation, Cl–F, Br–Cl and I–Br, are proportional to the corresponding differences in atomic diameters. These differences in the specific rotations have the same ratio to each other as the corresponding differences in the atomic diameters, namely, 41:17:21. By using the values for the neutral atomic diameters of Goldschmidt [see Wherry, Am. Mineralogist, **14,** 54 (1929)], the proportionality existing between the differences of specific rotation and atomic diameter values holds very accurately for the derivatives of these four monosaccharides. However, the values for the mannose derivatives give the ratio 41:25:35. These experimental results point to the explanation that for the mannose derivatives the halogens on the one hand and the atoms of the second carbon on the other influence each other, as will be discussed in detail in the forthcoming paper. The results of Freudenberg [*Naturwissenschaften,* **18,** 393 (1930)] and Haworth [J. Chem. *Soc.,* 1395 (1930)] are of interest in this connection. They found for the structure of some mannose derivatives that even ring formation occurs between the adjacent groups of the first and second carbon atoms. An explanation of the different behavior of the mannose derivatives in comparison with the other monosaccharide derivatives could be obtained by model studies (detailed in the forthcoming article) which show that for the α-halogen derivatives of mannose the acetyl group of the second carbon is directed through its CH_3 group to the halogens of the first carbon with a resulting influence; whereas for the a-halogen derivatives of glucose, arabinose and xylose, the acetyl group of the second carbon is directed through its CH_3 group to the ring or another oxygen atom and also that the detailed structure of the halogen derivatives of fructose (β-derivatives) does not show a similar influence on the halogen atoms.

If we consider the consequences of this explanation it is seen that for the α- and β-mannose pentaacetates the acetyl group of the second carbon atom has a different position for the α-compound in comparison with the @-derivative, as its CH_3 group is directed by the respective places of the oxygen atoms of the first carbon acetyl group, whereas such a difference does not exist (or is of another nature) for the other discussed monosaccharides. Hence the testing of the principle of optical superposition in the mannose and rhamnose series should be taken up with caution, taking into account these configurational peculiarities.

POLARIMETRY SECTION
BUREAU OF STANDARDS
WASHINGTON, D. C.
D. H. BRAUNS

RECEIVED APRIL 6, 1931
PUBLISHED MAY 6, 1931

THE VARIATION OF ELECTRIC MOMENT WITH TEMPERATURE

Sir:

Because of the uncertainty which has recently arisen in regard to the possible temperature variation of the moments of molecules in which two dipoles may rotate relative to one another, it has seemed of immediate importance to investigate this effect in such molecules. Ethyl acetate, the moment of which should depend, to a considerable extent, upon the position of the moment of the $O—C_2H_5$ bond relative to that of the C=O group, is found to show no significant variation of moment with temperature between -70 and $+30°$ when measured in dilute solution in heptane. The moment of ethylene chloride in solution in heptane is found to increase uniformly from 1.07×10^{-18} at $-70°$ to 1.41×10^{-18} at $+30°$ in satisfactory agreement with the measurements of Meyer [*Z. physik. Chem.*, [B] 8, 27 (1930)]. In similar fashion the moment of ethylene chlorobromide in heptane solution is found to increase from 0.92×10^{-18} at $-50°$ to 1.19×10^{-18} at $+30°$. This change is in accord with Meyer's idea that the mutual potential energies of the doublets in the two halves of the molecule cause these halves to occupy such positions relative to one another that the moments are partially canceled. The increase in rotational energy with rising temperature tends to overcome this effect of the mutual potential energies and so increase the moment.

Diethyl succinate which was found to have a moment lower than those of the other dicarboxylic acid esters and, apparently, increasing with temperature [Smyth and Walls, THIS JOURNAL, 53, 527 (1931)], has been measured over a wide range of temperature in solution in kerosene. The moment increases regularly from 2.01×10^{-18} at 0° to 2.47×10^{-18} at 180°, the latter value being practically identical with the moments of the higher members of the series. The tendency of the succinate molecule to bend in such a way that the doublets partially oppose and cancel one another at the lower temperatures is evidently overcome by the increased vibrational and rotational energy acquired within the molecule as the temperature rises.

FRICK CHEMICAL LABORATORY
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CHARLES P. SMYTH
RALPH W. DORNTE

RECEIVED APRIL 8, 1931
PUBLISHED MAY 6, 1931

THE ENTROPY OF POLYATOMIC MOLECULES

Sir:

The theoretical entropy of diatomic molecules has been calculated and discussed quite extensively,[1] but so far as I am aware, no one has as yet tackled the problem presented by the polyatomic molecule. I have recently computed the entropies (at 298.1°K.) of ammonia and of methane and find quite good agreement with the experimental thermochemical values. As such an agreement represents one of the few possibilities of actual check on the conclusions of band spectra as applied to chemistry, I am writing up the calculation in detail for publication, probably in the *Physical Review.*

The same formulas that were used for diatomic molecules[2] are applicable here but a double summation is necessary, corresponding to the two rotational quantum numbers, j and τ, in the symmetrical top type of rotator. When plausible assumptions are made for converting these summations to integrals, the absolute rotational entropy of each symmetry[3] modification (nuclear quartet and doublet forms in the ratio of 1:2, *respectively,* at high temperatures for ammonia and nuclear quintet, triplet and singlet forms in the ratio of 5:27:4, respectively, at high temperatures for methane) may be calculated. From this was subtracted the "zero point" entropy which is the correction term necessary on account of the experimental difficulties of reaching temperatures sufficiently near the absolute zero and in measuring the extremely small heat effects.

Using the moments of inertia of ammonia as given by Badger and Mecke,[4] the total effective entropy of ammonia is 44.0 E. U. and compares very favorably with the value derivable from the data in Lewis and Randall (p. 557), 43.5.

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[1] Fowler, *Proc. Roy. Soc.* (London), **A118**, 52 (1928); Giuque and Johnston, THIS JOURNAL, **50**, 3221 (1928); Rodebush, *Proc. Nat. Acad. Sci.*, **15**, 678 (1929); Villars, *ibid.*, **15**, 705 (1929); **16**, 396 (1930); Giauque and Johnston, *Phys. Rev.*, **36**, 1592 (1930); Giauque, THIS JOURNAL, **52**, 4816 (1930); Rodebush, *Phys. Rev.*, **37**, 221 (1931); Giauque, THIS JOURNAL, **53**, 507 (1931); MacGillavry, *Phys. Rev.*, **36**, 1398 (1930).

[2] Villars, *loc. cit.*, or Giauque, THIS JOURNAL, **52**, 4816 (1930).

[3] Cf. Hund, *Z. Physik*, **43**, 805 (1927), for NH_3; Elert, *ibid.*, **51**, 6 (1928), for CH_4.

[4] Badger and Mecke, *Z. physik. Chem.*, **B5**, 333 (1929).

For methane, three values were computed, depending on which line spacing one assumes to be representative of the moment of inertia. They are 44.1, 42.3 and 42.0; for $I = 10.2$, 5.66 and 5.17×10^{-40}. The last corresponds to the spacing most accurately measured (Raman effect)[5] and, for various reasons, is probably the correct one. In fact, the agreement with the observed entropy[6] 42.5 may be adduced as additional evidence for the reliability of this choice.

These results indicate that the actual calculation of thermodynamic equilibria[7] from band spectra data is not to be much longer limited to reactions between molecules having a maximum of two atoms.

STANDARD OIL CO. (INDIANA)
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D. S. VILLARS

RECEIVED APRIL 13, 1931
PUBLISHED MAY 6, 1931

2,4,5-TRIMETHOXYBENZOIC ACID: A DERIVATIVE OF DEHYDRODEGUELIN

Sir:

It has been shown by LaForge and Smith[1] that, through a series of reactions, the rotenone molecule may be ruptured in a manner which yields derric acid, $C_{12}H_{14}O_7$. Derric acid represents the half of the rotenone molecule which contains the methoxyl groups, but as yet the exact nature of the acid is unknown.

Recently three other insecticides of the same type as rotenone, namely, deguelin, tephrosin and toxicarol, have been described.[2] It has also been shown that structural relationships exist common to the entire molecule of rotenone, deguelin and tephrosin;[3] but the fact which is of immediate interest is that the derric acid portion of the molecule is common to all three substances.

It is desired at this time to report in a preliminary way the results of some experiments which clarify to a considerable degree the problem of the derric acid portion of rotenone and allied materials.

Permanganate oxidation of dehydrodeguelin in acetone solution yields two hydroxy acids, one of which contains the two methoxyl groups present in the starting material and thus represents the derric acid portion of the molecule. This acid crystallizes in plates which may be roughly described as rectangular with notched ends and with constrictions in the center of their long axis. It melts at 210° with decomposition and gives an intense blue color with ferric chloride.

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[5] Dickinson, Dillon and Rasetti, *Phys. Rev.*, 34, 582 (1929).

[6] Randall and Mohammad, *Ind. Eng. Chem.*, 21, 1048 (1929).

[7] Cf. Ludloff, Z. *Physik*, 57, 227 (1929), for a general discussion of this problem.

[1] LaForge and Smith, THIS JOURNAL, 52, 1091 (1930).

[2] Clark, *ibid.*, 52, 2461 (1930); 53, 313 (1931); 53, 729 (1931).

[3] Clark, *Science*, 73, 17 (1931); also a paper now being submitted to THIS JOURNAL for publication.

Analysis proved the material to be an hydroxydimethoxybenzoic acid. Methylation of the free hydroxyl group gave a trimethoxybenzoic acid which was shown by its melting point and derivatives obtained by bromination and nitration to be asaronic acid, 2,4,5-trimethoxybenzoic acid.

The hydroxydimethoxybenzoic acids which could give this acid are 2-hydroxy-4,5-dimethoxy-, 5-hydroxy-2,4-dimethoxy- or 4-hydroxy-2,5-dimethoxybenzoic acid. It is thought that because of the ferric chloride reaction given by the acid from dehydrodeguelin it is 2-hydroxy-4,5-dimethoxybenzoic acid. Work upon its synthesis is in progress, and it is hoped that a report upon its structure can be made shortly

INSECTICIDE DIVISION
BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.
E. P. CLARK

RECEIVED APRIL 18, 1931
PUBLISHED MAY 6, 1931

SYNTHESIS OF GAS–METAL COMPOUNDS BY SPUTTERING

Sir:

In connection with a somewhat extensive study of cathodic sputtering [see Phys. *Rev.*, 32, 649 (1928); 34, 972 (1929); Nature, 126, 204 (1930)], the writer has recently found that this process has remarkable possibilities as a method of chemical synthesis. This applies particularly to the formation of metal–gas compounds such as nickel and similar metals with hydrogen, nitrogen, etc. Nickel sputtered in nitrogen under rather special conditions of current, voltage and gas pressure gives a dark, somewhat metallic-looking film which shows on x-ray examination a crystal structure distinctly different from that of the pure metal. Heating to about 350° decomposes this compound, which gives off its gas and reduces to metallic nickel. Upon heating such a nitride film to 150° in hydrogen, ammonia is formed and in an amount which agrees reasonably well with the quantity of nitrogen absorbed in sputtering. Compounds of cobalt and iron with nitrogen have likewise been produced, as well as of nickel and hydrogen—this latter showing on crystal structure examination a lattice spacing some 6% larger than for pure nickel.

It seems certain then that we are dealing here with such unusual compounds as nitrides and hydrides of these metals. Moreover, they are formed, not at the expense of a difficult and special technique of synthesis [see A. C. Vournasos, Compt. rend., 168, 889 (1919)] but by a simple process of wide applicability, for the conditions encountered in sputtering, with the metal in the vapor state and the gas largely excited by the discharge, would seem to be ideal for the formation of a compound if this is chemically possible. Indeed one series of experiments yielded considerable evidence for the formation of compounds with even helium and argon, and, while this evidence was later vitiated by the discovery of impurities, the question is by no means as yet settled in the negative. Compounds with excited helium or argon are at least not unthinkable, and this is probably the most promising way of forming them.

A word of caution may not be out of place as to the use of this method of synthesis. Metals ordinarily contain a great deal of absorbed gas and while the usual baking (at say 500°) may remove the bulk of such impurity adsorbed on the surface, it will probably take little from the interior. Then as layer after layer of atoms is removed from the cathode in the sputtering process, fresh supplies of gaseous impurity are released, so when purity of product is a main factor some provision must be made to eliminate this source of trouble. It may be possible to secure nearly gas-free metal for the cathode, or to outgas it effectively by having it in the form of a thin strip which can be heated electrically to a high temperature, but probably the most feasible method is to dilute the impurity to a point where it becomes negligible by a continuous flow of fresh gas through the chamber during the sputtering.

DEPARTMENT OF PHYSICS
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
L. R. INGERSOLL

RECEIVED APRIL 23, 1931
PUBLISHED MAY 6, 1931

A RELATION CONCERNING ATOMIC NUCLEI

Sir:

An interesting numerical relation of known atomic species is to be found in the helium–thorium series. The atomic nuclei of this series have a composition represented by the general equation

$$a_{(Z/2+n/4)} + (e_2)_{n/4}$$

in which e is an electron, a represents a group of 4 protons and 2 electrons, Z is the atomic, and n, the isotopic number. For thorium Z is 90 and n is 26, so the specific formula is $a_{58}e_{26}$ In a recent paper Latimer develops a model for the nuclei of this series. He bases his model not only on the general hydrogen–helium theory[1] developed in 1915 by the writer, but he also makes use of the very specific features of this theory, such as the pairing of the nuclear electrons,[2] the introduction of the first pair of extra or cementing electrons in the argon nucleus[3] of mass 40, and the later addition of still other pairs of electrons as the atomic number increases.[4]

Latimer also uses the idea that the abundance of an atomic species is

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[1] Harkins and Wilson, THIS JOURNAL, 37, 1367–1396 (1915).

[2] Harkins, *ibid.*, 39, 859 (1917); 42, 1958, 1963–1964, 1991–1993 (1920).

[3] Harkins, *ibid.*, 39, 859, Table II (1917): *Phil.* Mag., 43, 305 (1921).

[4] Harkins, *Phil. Mag.*, 42, 1976 (1920).

related to its stability,[6] and considers that the stability is related to the intranuclear spins,[6] which are supposed to be due to the protons.

It is of interest to see if any known relations, other than those upon which the model is based, agree with the interesting tetrahedral model. Figure 1 gives a representation of the helium–thorium series, taken largely from an early paper," but extended to fit the most recent data of Aston.[8] It may be noted that this series is found only on levels 0, 4, 8, 12, etc., which correspond to 0, 1, 2, 3, etc., pairs of extra or cementing electrons. The length of the series at any level will be considered to be given by the number of places for members of the series beginning and ending with known species. The values are collected in Table I.

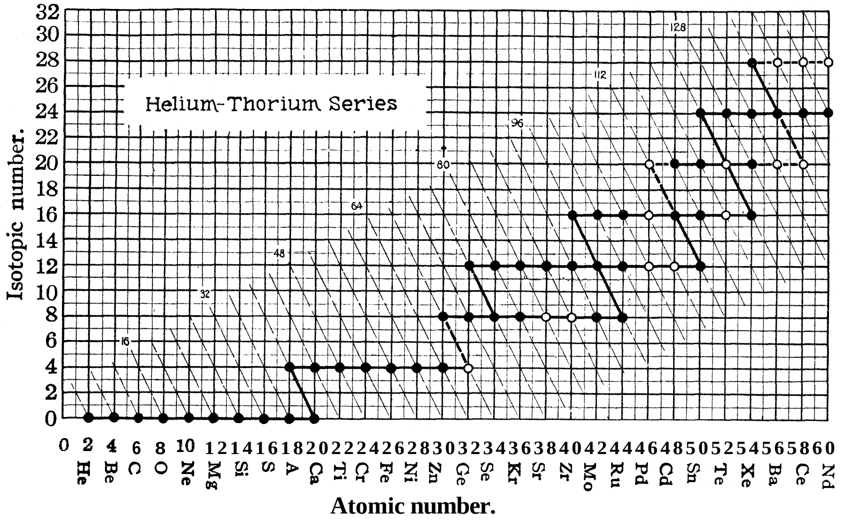

Fig. 1.—Open circles represent species as yet undiscovered.

Table I

1 Isotopic number, *n*	2 Number of cementing electrons, *n*/2	3 Number of species in known series	4 Number of species in Fig. 1
0	0	10	10
4	2	7	8
8	4	8	8
12	6	10	10
16	8	8	8

In explanation of Column 4 it may be said that Fig. 1 represents undiscovered species by open, and known species by black, circles.

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[5] Harkins, This Journal, 39, 856 (1917); Proc. *Nat. Acad. Sci.*, 2, 216 (1916).

[6] Harkins, *Phys. Rev.*, 35, 434 (1930).

[7] Harkins, J. Franklin *Inst.*, 195, 554 (1923).

[8] Aston, *Nature*, 127, 233 (1931).

Thus the number of species is **10** for either zero or three pairs of cementing electrons, and eight (possibly seven for one pair) for one, two, or four pairs. This agrees with the writer's early idea that the zero level should be a long one, and with Latimer's idea that the level for three pairs of cementing electrons should also be long. While later discoveries may change these limits, they will probably not destroy the validity of the general relations.

It may be noted that Latimer[9] makes no attempt to explain the most fundamental relation which concerns nuclear stability, the pairing of electrons in the nucleus. Also Dirac's principle of superposition, mentioned by Rodebush,[10] has not been developed to the extent necessary to explain this phenomenon. It is not improbable that the two electrons in an alpha particle move through the whole volume of the particle, but the distribution of electron density is entirely unknown. It is not intended to imply that the electron pairing cannot later be treated in terms of an overlapping of the eigenfunctions of the single electrons.

DEPARTMENT OF CHEMISTRY
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CHICAGO, ILLINOIS
WILLIAM D. HARKINS

RECEIVED APRIL 33, 1931
PUBLISHED MAY 6, 1931

THE STRUCTURE OF THE a-PARTICLE

Sir:

In the March number of THIS JOURNAL, W. M. Latimer has written an article in which he refers to a suggestion of mine. Inasmuch as one might infer therefrom that I considered the idea of the tetrahedral form of a-particle to be original with me, may I state that this was not the case. What I did suggest and discuss with Professor Latimer and others was the orientation of the spins of the proton, as used by Latimer, in which the spin of each proton was supposed to point out from the center of the tetrahedron. This was some time ago, and Professor Latimer writes me that our discussion was only recalled to him by our correspondence after this article was in manuscript form.

In view of this paper of Latimer's and recent discussions of nuclear spin [Bartlett, *Phys.* **Rev.,** 37, **327 (1931);** Gibbs and Kruger, *ibid* , 37, **656** (1931)], **a** word as to my reason for making this suggestion may not be out of place. I wished to have the resultant spin for one, two or three protons the same (and the same as that of the electron, equal to $^1/_2$ unit), and the spin for four protons equal to zero. This is a natural result of the tetrahedral structure though requiring some "distortion" of the angle (if such language has any meaning) between two protons in the case of two. This would explain the anomalous spin in the case of nitrogen (3 a-particles, 2 extra protons, 1 extra electron, resultant spin

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[9] Latimer, THIS JOURNAL, 53, 987 (1931).

[10] Rodebush, *ibid.*, 53, 1611 (1931).

2/2 units) and, in fact, accounts for the spin in all the cases considered by Bartlett. However, these cases will also fit into a scheme in which the electrons have no spin, and the proton spins behave like ordinary electron spins (Bartlett, *loc. cit.*). Both proposals will meet with difficulties in the case of Al (Gibbs and Kruger, *loc. cit.*). I think we must simply admit that we do not know how the spins in nuclei are produced. In the meantime, speculations regarding nuclear structure, such as Latimer's, which are based on other data, are of interest.

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O. K. RICE

RECEIVED APRIL 24, 1931
PUBLISHED MAY 6, 1931

THE PREPARATION OF COPPER–CHROMIUM OXIDE CATALYSTS FOR HYDROGENATION

Sir:

The new and very efficient catalyst for the hydrogenation of various organic compounds in the liquid phase [Adkins, Connor and Folkers, THIS JOURNAL, 53, 1091, 1095 (1931)] referred to as "copper chromite" suffers under the disadvantage that in the hydrogenation of certain compounds (ethyl phenylacetate to phenylethyl alcohol, for example), there occurs reduction of the catalyst to a red inactive compound. This undesirable feature is not present in a modified catalyst containing barium, for example, which was prepared by replacing 10% of the copper nitrate with a molecularly equivalent amount of barium nitrate using 750 ml. of water at 70° per mole of nitrate. The preparation of a copper-chromium catalyst: as originally described by us was based upon the method patented by Lazier for obtaining catalysts from certain chromates. Recently it has been found in this Laboratory that an equally if not more efficient copper-chromium catalyst may be prepared by a more convenient and simple method which is as follows. Seventy-one grams of ammonium carbonate monohydrate in 400 ml. of water was added to a solution containing 50 g. of copper nitrate trihydrate, 5.4 g. of barium nitrate and 77 g of chromium nitrate ($Cr_2(NO_3)_6 \cdot 15H_2O$) in 575 ml. of water. After thorough mixing of the reactants, the precipitate was filtered with suction on a Büchner funnel, and washed twice with 50-ml. portions of water. The solid was dried overnight at 100–110°, ground to a powder and heated to approximately 230° in order to expel ammonia, carbon dioxide, etc. The catalyst was then used as previously described.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON WISCONSIN
RALPH CONNOR
KARL FOLKERS
HOMER ADKINS

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NEW BOOKS

General Chemistry for Colleges. By B. SMITH HOPKINS, Professor of Inorganic Chemistry in the University of Illinois. D. C. Heath and Company, 285 Columbus Avenue, Boston, Massachusetts, 1930. x + 757 pp. 242 figs. 14.5 X 22 cm, Price, $3.72.

This is an excellent text for beginning classes in colleges and universities. While in arrangement it is like most American texts and therefore displays no marked originality, yet the writing has been well done and in some respects the book is an improvement over other texts. One of the main difficulties which the teacher of beginning chemistry encounters is to make his course adapt itself not only to the average student but also to the above average student. In the introduction attention is called to the cross references which encourage the student who is willing to do that sort of thing to make comparisons and to do independent thinking. The book also has references which call attention to the practical applications of chemistry. This arrangement enables the practical minded student to go out into the literature with a minimum of difficulty and initiates him, as it were, into the research attitude toward his work. The book proper is prefaced by two chapters of interesting historical matter. Following this we have the conventional arrangement of topics and of material which is carried throughout the rest of the text. The writer is to be congratulated upon the early introduction of the idea of equilibrium, which is perhaps the most important of the conceptions presented to the beginning student. It is questionable however whether atomic theory ought to be postponed to as late a point as is indicated by the position in the book. It has always seemed to the reviewer that a statement at least of atomic theory should be given early in the course and that this theory should be established by its application to the laws and phenomena which are discussed later.

The question may be raised whether or not the use of the term "plus and minus valence" in connection with the balancing of oxidation and reduction equations does not create a wrong impression regarding valence. If the word polar number should be substituted for plus and minus valence (as suggested by Bray), the objection to giving valence a minus value would be obviated. Dr. Hopkins has made some steps toward clearing up the inconsistencies of the old idea of partial dissociation which for an elementary class is still a very difficult task. He seems to have gone as far as is possible under the circumstances. The periodic arrangement suggested is simple and clear, and is to be commended as against some efforts which have been made to involve too many factors in the table.

The chapter on the structure of atoms, crystals, etc., might as well have been put anywhere else in the book as where it is. The information is apparently not made use of later; in fact what little use is made of the work on crystals comes earlier in the text. It is apparent however that any chapter of this type which is put into a book on freshman chemistry is put there largely for the purpose of including interesting material, not because of its direct value to the student. Inasmuch as practically every text written in recent years has contained this material either as a part of the text or in an appendix, its inclusion can hardly be criticized.

The book is well illustrated and contains many valuable diagrams. The chapters on the metals are exceptionally well done. All of the elements are included in the discussion at least by means of brief notes and the text is entirely up to date in this respect. It is to be noted that production figures are given for the various elements and important compounds, which always adds interest to the discussion of chemical substances. Taken as a whole the book is to be considered as one of the best of our modern American chemistries.

P. A. BOND

Leçons de chimie analytique. (Textbook of Analytical Chemistry.) By ALCIDE JOUNIAUX, Professor in the Faculty of Sciences of the University of Lille. Librairie Scientifique Hermann et Cie., 6 Rue de la Sorbonne, Paris, France, 1931. viii + 350 pp. Illustrated. 16 × 25 cm. Price, 60 fr.

The title of this book seems too general for its content. The author has presented only gravimetric and electrolytic analysis. A supplement on volumetric methods is perhaps planned, but there is no clear indication of this intent. Electrometric and other physicochemical methods are also passed over in silence.

The book is divided into four parts: (I) (100 pages) a general discussion of standard gravimetric operations; (II) (130 pages) a systematic review of methods for the various cations and anions; (III) (50 pages) gravimetric organic analysis; (IV) (30 pages) electrolytic analysis.

The first part includes a very interesting discussion of common ion effect and complex formation and of the physical state of precipitates, adsorption and colloidal phenomena. The treatment of the other general topics is less original. The discussion of errors and averaging is very brief and simple, and there is no mention of methods of sampling, of the properties of different types of laboratory ware, of the purity of reagents or of methods of preparing the solution for analysis.

The author's method of arrangement is as follows. Under "1st group metals" he treats successively Ag^+, Cl^-, Br^-, $I-$, CN^-, SCN^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, ClO_3^-, IO_3^-, IO_4^-, ClO_4^-, mixed halides, Hg^{++}, $PO_3^{\equiv}$, HCO_2^- and Pb^{++}. In other words, not only the cations but the anions which may be precipitated with their aid are included. In this first treatment of the analysis of lead, only the gravimetric sulfate method is given, apparently on the assumption that no interfering substances are present other than organic or mineral acids. Later, under the copper group, we find a brief mention of the separation of lead from the other metals, with no discussion of contamination by bismuth, alkaline earths or silica. Finally, in the last section, the electrolytic separation of lead from other metals and its determination by electrolysis are described. The treatment throughout is very brief, and seems insufficiently detailed and documented to be a safe guide even for the analyst who is interested only in gravimetric methods. Even for beginning students, working on carefully prepared solutions, the detail seems inadequate, as for example in the treatment of the gravimetric determination of copper as oxide (which seems to be the favorite method for copper), no mention is made of contamination by the alkali hydroxide used as precipitant, and no procedure is recommended which would reduce the error from this cause. Many of the newer organic reagents for the metals are discussed briefly. The section on electrolytic methods is relatively satisfactory.

In summary the reviewer feels that the omission of volumetric procedures and the inclusion of so much organic analysis constitute an undesirable choice of material for a beginner's text, while for such a text there is little advantage in the inclusion (without thorough discussion) of numerous methods for each ion. On the other hand, if the work is intended as a reference book for practical analysts, the omission of volumetric methods, the somewhat uncritical choice of gravimetric methods, and the lack of documentation and critical discussion, constitute serious defects.

NORRIS P. HALL

Lehrbuch der Thermodynamik für Studierende der Chemie und verwandter Wissenschaften. (Textbook of Thermodynamics for Students of Chemistry and Related Sciences.) By A. MAGNUS, Professor at the University of Frankfort-on-Main, Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany. 1929. xii + 288 pp. 23 figs. 16 X 24 cm. Price, unbound, RM. 16; bound, RM. 18.

This is an interesting and useful book. There is a brief and excellent mathematical introduction. After a discussion of the ideal gas and the van der Waals' equation, the first and second laws are developed in the classical manner and applied to chemical problems by the use of the usual thermodynamic functions. The explanations are full and seem to be the result of the author's own study; the student will doubtless find welcome help in the comprehension of details on which many books are silent.

There are sections on the van Laar–Richard Lorenz treatment of equilibrium in condensed systems, on entropy and probability, thermodynamics of radiation, and the specific heats of solids in relation to quantum theory.

There is a chapter on the Nernst heat theorem, developed in the Nernst manner (rather than the simpler manner of G. N. Lewis). Here the

Planck formulation ($S = 0$ at $T = 0$) is stated to go a step further than the Nernst formulation ($AS = 0$ at $T = 0$), in affirmation of Nernst's distinction, which the reviewer is unable to appreciate. Theodore W. Richards is not mentioned for his basic experimental contribution. The American work on supercooled liquids and the consequent limitation of the principle to pure crystalline solids are not discussed. In general, the author has drawn too much on German sources, and the book, at least to an American reader, seems to bear a very strong impress of nationality.

The author has not always been careful with regard to the historical inferences that would be drawn from his statements. Thus the Gibbs fundamental equation is discussed without reference to Gibbs, but (page 191) as "an equation, which Planck has called a canonical equation." Admirers of Gibbs will learn with surprise (page 200) that he devised an arrangement involving moving semipermeable membranes, for mixing gases reversibly, but will hardly regard this as compensation, if indeed they regard the statement as complimentary to Gibbs. The author discusses not only the thermodynamic potential $(U - TS + pV)$, but also the therefore superfluous function obtained by dividing this by minus the temperature, which he calls as usual the Planck function, although it is one of Massieu's characteristic functions, as noted by Gibbs, who preferred the function $U - TS + pV$.

L. J. GILLESPIE

Photo-electric Cells and their Applications. A Discussion at a Joint Meeting of the Physical and Optical Societies, June 4–5, 1930. Edited by JOHN S. ANDERSON, M.A., D.Sc., F.Inst.P. Published by The Physical and Optical Societies, 1 Lowther Gardens, Exhibition Road, South Kensington, London, S. W. 7, England, 1930. 236 pp. Illustrated. 18 X 26 cm. Price, 12 s./6 d. to non-members.

These thirty-one papers by experts from England, America and continental Europe will interest chiefly those who make and use photo-electric cells, including selenium cells. After an introductory lecture by Professor H. S. Allen, on the "Early History of Photo-Electric and Selenium Cells," there follows: one paper on a theory of selective photo-electric emission, ten papers on the manufacture, characteristics, testing and use for sound reproduction, eleven papers on various phases of photo-electric photometry, three papers on other applications including biology, four papers on the amplification of varying photo currents. The general discussion which concludes the volume is perhaps as interesting as any single paper. It would seem desirable to have included a greater number of papers by experts in the science of photo-electric action. It would also seem that the subject matter and price would warrant something better than a paper cover binding.

J. A. BECKER

Alcoholometry. An Account of the British Method of Alcoholic **Strength Determination.** By FRANCIS G. H. TATE, Government Laboratory, London. With historical introduction by the author in collaboration with George H. Gabb. Published by His Majesty's Stationery Office, Adastral House, Kingsway, London, W. C. **2,** England, 1930. xviii + **93** pp. Illustrated. **15.5** X **24 5** cm. Price, **5** s. net.

This work is largely an historical description of the development of the hydrometer as applied to the determination of alcohol in potable spirits. The historical portion of the work is very complete and is very interesting to those who may be doing work of this character. There are several very fine reproductions of early types of hydrostatic balance and several early hydrometers, some of which are 200 years old at present. The book contains an interesting chapter on the standardization of hydrometers. One chapter, two and one-half pages in length, is devoted to the use of the refractometer in connection with the hydrometer in order to obtain a correct alcohol percentage when the spirit is "obscured" with sugar or similar substances.

HERMANN C. LYTHGOE

Organic Syntheses. **An** annual publication of satisfactory methods for the preparation of organic chemicals. Vol. XI. Edited by CARL S. MARVEL, with ROGER ADAMS, W. H. CAROTHERS, H. T. CLARKE, J. B. CONANT, HENRY GILMAN, C. R. NOLLER and F. C. WHITMORE. John Wiley and Sons, Inc., **440** Fourth Ave., New York, 1931 vii + 106 pp. **15.5** X **23.5** em. Price, **$1.75.**

The eleventh annual volume of "Organic Syntheses" has appeared, as usual, in good time. The list of preparations which have been supplied by an unusually large number of contributors and checked by the self-sacrificing board of editors is as follows: acrolein acetal, a-aminoisobutyric acid, 1-amino-2-naphthol hydrochloride, 1,2-naphthol-4-sulfonic acid, azoxybenzene, a-bromoisovaleric acid, bromomesitylene, β-chloropropionaldehyde acetal, citraconic anhydride and citraconic acid, cyanogen bromide, 2,4-diaminotoluene, ethyl ethylenetetracarboxylate, ethyl phenylcyanopyruvate, ethyl pimelate, fumaric acid, dl-glyceric aldehyde, dl-glyceric aldehyde acetal, heptaldoxime, n-heptylamine, $-iodoaniline, isodurene, itaconic anhydride and itaconic acid, mesaconic acid, 3-methylpentanoic acid, a-naphthoic acid, n-pentane, symmetrical and unsymmetrical o-phthalyl chlorides, isopropyl thiocyanate, thiobenzophenone, o-toluic acid, triethylcarbinol.

E. P. KOHLER

Kleines Praktikum der Kolloidchemie. (Brief Laboratory **Manual** of Colloid Chemistry.) By PROF. DR. WOLFGANG OSTWALD, University of Leipzig, with the coöperation of Dr. P. Wolski and Dr. **A.** Kuhn. Seventh edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, **1930.** xii $ **174** pp. **21** figs. **15** X **23** cm. Price, unbound, RM. 3.60.

The first edition of this book was published in 1920. This **was** soon followed by the second and third editions, then after a limited revision and the addition of some fifteen experiments, a fourth edition appeared in 1922. This latter edition was translated into English by Kugelmass and Cleveland and was published by E. P. Dutton and Company, New York (1924) under the title "Practical Colloid Chemistry." Subsequent editions, including the present one, have appeared practically unchanged. The general topics covered come under the following heads: I, Preparation of Colloidal Solutions; II, Diffusion, Dialysis and Ultrafiltration; III, Surface Tension and Viscosity; IV, Optical Properties; V, Electrical Properties; VI, Experiments with Gels; VII, Adsorption; VIII, Coagulation, Peptization and Related Phenomena. All told, there are 183 individual experiments which are described in commendable detail and are well distributed over the above-mentioned general topics. In addition, a brief treatment is given of certain commercial colloids and of methods of capillary analysis.

The author has taken care to include only such experiments as can be carried out with comparatively simple apparatus, such as can be found in almost any chemical laboratory. This feature will be appreciated by those who are about to introduce a laboratory course in colloid chemistry. For use in well-established courses a greater number of strictly quantitative experiments would materially enhance the value of this book.

F. E. BARTELL

Jahrbuch der organischen Chemie. (Yearbook of Organic Chemistry.) By Professor DR. JULIUS SCHMIDT, Stuttgart. Vol. 15, 1928. Verlagsbuchhandlung von Franz Deuticke, Vienna, Austria, 1930. xvi + 245 pp. 17.5 X 25.5 cm. Price, unbound, M. 24; bound, M. 27.

The fifteenth volume of Schmidt's ***Jahrbuch,*** dealing with the developments in organic chemistry during 1928, is similar in character to its predecessors. Since this is the most extensive survey of its kind it is a great pity that it cannot be made more useful by bringing it more nearly up to date.

E. P. KOHLER

The Microbiology of Starch and Sugars. By A. C. THAYSEN and L. D. GALLOWAY, Oxford University Press, 114 Fifth Avenue, New York, 1930. viii + 336 pp. 14.5 X 22 cm. Price, $8.50.

This book is a companion volume of "The Microbiology of Cellulose, Hemicelluloses, Pectin and Gums" mitten by Thaysen and Bunker and published in 1927. As stated in the preface, the book has been written for the research worker. It is an excellent monograph, bringing together in compact, correlated form a great mass of valuable information appearing in botanical, bacteriological, chemical and technological journals. In reviewing this bulk of literature it is hardly possible to avoid omissions and errors, but those that have been noted were, for the most part, of minor importance.

The material in the book is divided into five parts: Part I deals with the constitution and microbiological hydrolysis of starch, glycogen, inulin, the tetra-, tri-, and disaccharides, and the glucosides. The discussion includes a consideration of the enzymes present in the hydrolyzing organisms. Brief descriptions of saké and soya manufacture are given, also the Amylo process for alcohol production, and the biological manufacture of indigo and gallic acid. In discussing the action of actinomycetes on saccharose, the authors state on p. 49 that "generally speaking, however, saccharose cannot be regarded as a carbohydrate favoring the growth of actinomycetes." No mention is made of the monograph on the actinomycetes by R. Lieske, Leipzig, 1921, in which the statement is found that "Sucrose is a good C source for all actinomycetes, but it appears to be assimilated without being inverted by an exoenzyme." In Chapter III the authors question the evidence for a direct fermentation of saccharose. Thus on p. 41 in criticizing the work of Gayon and Dubourg, who observed that certain mannitol-producing bacteria could ferment saccharose readily without producing mannitol, but yielded considerable quantities of this alcohol when acting on fructose, the authors advance the argument that fructose as liberated from saccharose might 'act differently *in* statu *nascendi* from the fructose from which the mannitol bacteria yielded mannitol. While Gayon and Dubourg present direct experimental evidence, the authors offer no data for their assumption. In the mind of the reviewer the burden of proof rests with the authors. In citing the papers on this subject, no reference is given to Miiller-Thurgau and Osterwalder [*Centr.* Bakt., 2 Abt., 48, 10 (1917–1918)] and Stiles, Peterson and Fred [*J. Biol.* Chem., 64, 649 (1925)], who substantiated Gayon and Dubourg's observations.

In Part II, consisting of nine chapters, the authors have adopted the Kluyver and Donker "working theory" of microbiological fermentation to explain the mechanism of the fermentation of monoses. It is unfortunate that the signs in the explanatory text, pp. 86–89, giving a method of constructing a balance sheet for the action of a particular organism on glucose, do not correspond with those of the accompanying table. On p. 133 the authors give an excellent classification of the lactic acid bacteria, namely, "The safest subdivision of the lactic acid bacteria remains at present the division based partly on their morphological characters and partly on their mode of action on fructose, whether they are capable of producing mannitol or not." In listing *Cl. acetobutylicum* as one of the names used to designate the commercial butyl alcohol organism, p. 147, the authors omit the paper on 'which the name is based [McCoy, Fred, Peterson and Hastings, *J.* Infect. *Dis.*, **39,** 457 (1926)]. In the list of products of a typical fermentation of starch by the acetone–butyl alcohol organism, p. 159, no mention is made of ethyl alcohol, although it is well known that this substance makes up 8–10% of the fermentation products.

Part III is a short section dealing with the microbiological synthesis of glycogen, starch, fat and mucus.

Part IV presents a discussion of the microbial flora and general microbiology of grain and flour, sizing materials, adhesive pastes, dough and bread. Part V similarly deals with sugar manufacture and storage.

Among the numerous fungi mentioned in the book, the ubiquitous *Penicillium glaucum* occupies a prominent place. It is unfortunate that the authors did not mention that this is an indeterminate species; a term which most investigators agree does not accurately describe any species of mold and which should be abandoned.

The book, as a whole, is well written and the Index of Authors and Subject Index facilitate easy reference to the original papers given at the ends of the various chapters. The book is a valuable addition to the reference shelf of every worker in the field of fermentation.

L. M. PRUESS

Entstehung, Veredlung und Verwertung der Kohle. (Origin, Processing and Utilization of Coal.) Edited by K. A. REDLICH, J. C. BREINL and H. TROPSCH. Verlag von Gebrüder Borntraeger, W 35 Schoneberger Ufer 12a, Berlin, Germany, 1930. vii + 359 pp. 86 figs. 16 X 25 cm. Price, unbound, M. 30; bound, M. 33.

This volume is based on a series of lectures given at the Deutsche Technische Hochschule at Prague, by leaders in different fields of coal technology and research. These lectures have been expanded and published in this book as the following separate papers: "Relation between Properties of Coal and its Geological History," by Dr. W. Petrascheck, Professor of Geology, Montanistischen Hochschule, Loeben, 21 pages. "The Representation of the Degree of Coalification (the Rank of Coal) by the Ternary Diagram and its Application to Coal Processing," by Dr. H. Apfelbeck, Director of Lanzer Kohlen-A.-G. Falkenau a.d.E., 40 pages. "The Present Status of our Knowledge of the Chemical Constitution and Origin of Coal," by Dr. H. Tropsch, Director of the Coal Research Institute, Prague, 20 pages. "The Drying and Carbonization of Brown Coal," by Dr. R. Heinze, Director, Kohlenverschwelungs-A.-G. Halle a.d.S., 357 pp. "The Synthesis of Organic Compounds Derived from Gases Obtained from Coal," by Dr. H. Tropsch, 53 pp. "The Economic and Energy-Economic Significance of Coal," by Dr. Kothny, Professor, Deutsche Technische Hochschule, Prague, 17 pp. "Combustion of Solid Fuels," by Dr. H. Löffler, Vienna, 11 pp. "The Szikla-Rozinek Process of Pulverized Coal Firing," by Dr. A. Rozinek, Budapest, 14 pp. "Theoretical Fundamentals of Mechanical Combustion Control," by Dr. J. C. Breinl, Professor, Deutsche Technische Hochschule, Prague, 17 pp.

From a chemical point of view, the outstanding contribution is the article by Tropsch on the Synthesis of Organic Compounds from Gases

Derived from Goal. This paper is the first well-digested review of the world literature on this important subject. It fills an urgent need. No one is more competent for this job than Tropsch, and it is hoped that it is a forerunner of a comprehensive monograph. The paper is replete with original refercnres to American, British and French, as well as German work and covers the purification of gases for synthetic purposes, the separation of the components of coke-oven gas by liquefaction and fractional distillation, the chemical utilization of ethylene, the pyrolysis of methane and higher hydrocarbons, the partial oxidation of methane, and the synthesis of hydrocarbons and alcohols from water gas. The chemist will also be interested in Apfelbeck's examples of the use of ternary diagrams in expressing the relation of the elementary composition of coal to its classification and properties, and in Tropsch's excellent review of the chemical constitution of coal, in particular the work of recent German investigators. The geologist's point of view on the origin and metamorphism of coal is well presented by Petrascheck in his paper on the Relation between Properties of Coal and its Geological History. The paper by Heinze on the Drying and Carbonization of Brown Coal contains a discussion of the colloidal nature of these high moisture coals that is of special interest in connection with the utilization of American lignites. However, the section on carbonization does not apply to American lignites because of their leanness with respect to oils and tars. The other papers in the volume are of an engineering nature.

A. C. FIELDNER

Alkylperoxyde und Ozonide. Studien uber peroxydischen Sauerstoff. (Alkyl Peroxides and Ozonides. Studies on Peroxide Oxygen.) By Dr. ALFRED RIECHE, Lecturer in Chemistry at the University of Erlangen. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1931. viii + 172 pp. 14 figs. 15 × 23 cm. Price, unbound, RM. 10.

A monograph that does not contain long lists of compounds which are treated as if they were museum specimens, that aims to be selective rather than comprehensive, critical rather than objective, is a refreshing novelty in modern chemical literature. And when it deals with subjects so actively under investigation as are peroxides, autoxidation and ozonides, it is certain to be useful to many who find it difficult to keep abreast of the numerous and widely scattered publications on these subjects.

Dr. Rieche explains that his little treatise naturally assumed its present form because it represents an expansion of his "habilitationsschrift." It begins with a survey on alkyl peroxides, the class which is most significant in biochemical oxidations and which has received the most attention in recent years. This section includes a discussion of the formula of hydrogen peroxide and an account of all peroxides that can be regarded as substitution products of hydrogen peroxide in which one or both of the hydrogen atoms have been replaced by alkyl, hydroxy alkyl and alkylidene groups. It also includes an interesting chapter on autoxidation—its role in biochemical oxidations, in the explosion of mixtures of oxygen and hydrocarbons, and in the chemistry of free radicals.

A second section deals with the investigation of peroxides by optical methods—refraction and absorption in the ultraviolet. Here the author adopts Fajans' interpretation of refraction and frequently employs electronic formulas "in order to be able to formulate matters that cannot well be represented in terms of the classical doctrine of valence."

A final section containing a chapter on ozonization as a source of peroxides and another devoted to general conclusions complete the volume. In this concluding chapter the author, with some reserve, expresses the opinion that there are two kinds of alkyl peroxide: the well-known type which is related to the common form of hydrogen peroxide, and another—"alkyl oxoxides"—of which no representative has been isolated but which can be inferred from the behavior of many substances toward activated oxygen.

This little treatise can be heartily recommended to all who are interested in these important subjects.

E. P, KOHLER

Bioassays. A Handbook of Quantitative Pharmacology. BY JAMES C. MUNCH, Director of Pharmacological Research, Sharp and Dohme; Pharmacologist, Bureau of Biological Survey, U. S. Department of Agriculture. The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Maryland, 1931. x + 958 pp. 15.5 X 23.5 cm. Price, $10.00.

Chemical knowledge of some of the most important drugs used in medicine has not advanced to a point where it is possible to determine by chemical analysis whether they are of suitable strength and purity to be used in the treatment of disease. This is the case, for example, with the most important drugs used in diseases of the heart and in child-birth, the various gland products and vitamins. In many cases, however, such information may be obtained by experiments upon lower animals and in some cases upon isolated organs (for example, the heart).

So important have some of these biological assay methods become that they are included in the U. S. Pharmacopoeia, the legal standard for medicines sold in the United States. The Health Committee of the League of Nations also has a committee on this subject in order to secure international uniformity in the case of a number of important drugs. Some of the methods are also indispensable in the detection of powerful poisons.

This volume of Dr. Munch is by far the most complete and authoritative work ox this subject which has appeared in any language. The enormous amount of work which has been done on this subject is evident from the fact that the author states that he bas consulted 17,000 references; 5000 of these are cited in the volume. The work is, however, much more than *a* compilation; the author concludes each chapter with a critical summary of the data presented and an expression of his own views based upon years of experience in this field.

Not only is the work remarkably complete and well illustrated but it seems to be peculiarly free of errors of any kind; the motto of the publishers, "Sans Tache" seems to be justified (although "Cod Liver Oil" dots not appear in the index).

It is safe to predict that this volume will for many years be the recognized authoritative work on this important subject.

REID HUNT

BOOKS RECEIVED

March 15, 1931—April 15, 1931

KASIMIR FAJANS. "Radioelements and Isotopes: Chemical Forces and Optical Properties of Substances." The George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University. McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York. 125 pp. $2.50.

WALTER FEITKNECHT. "Über topochemische Umsetzungen fester Stoffe in Flüssigkeiten." Fortschritte der Chemie, Physik und physikalischen Chemie, Band 21, Heft 2. Verlag von Gebriider Borntraeger, W 35 Schoneberger Ufer 12a, Berlin, Germany. 56 pp. Subscription, M. 5.20; separate, M. 7.

ALCIDE JOUNIAUX. "Leçons de Chimie Analytique." Librairie Scientifique Hermann et Cie., 6 Rue de la Sorbonne, Paris, France. 350 pp. 60 fr.

JAMES KENDALL. "Smith's Introductory College Chemistry." The Century Co., 353 Fourth Ave., New York. 555 pp. $3.25.

ICHIRO MIYAGAWA. "Pyritic Oxidation in Relation to Spontaneous Combustion of Coal." Reprinted from the ***Memoirs of the College of Engineering,*** Kyushai Imperial University (Vol. V, No. 5), Fukuoka, Japan. 103 pp.

OSCAR W. UNDERWOOD. "Drifting Sands of Party Politics." The Century Co., 353 Fourth Ave., New York. 411 pp. $3.50.

JOHN P. PETERS AND DONALD D. VAN SLYKE. "Quantitative Clinical Chemistry." Volume I, Interpretations. The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Maryland. 1264 pp. $12.00.

ERICH RABALD. "Werkstoffe. Physikalische Eigenschaften und Korrosion." Band I, Allgemeiner Teil. Metallische Werkstoffe. Band II, Nichtmetallische Werkstoffe. Verlag von Otto Spamer, Heinrichstrasse 9, Leipzig C 1, Germany. Part I, 976 pp. Part 11,392 pp. RMk. 128, unbound; RMk. 135, bound.

GÉZA SCHAY. "Hochverdiinnte Flammen." Fortschritte der Chemie, Physik und physikalischen Chemie, Band 21, Heft 1. Verlag von Gebrüder Borntraeger, W 35 Schoneberger Ufer 12a, Berlin, Germany. 68 pp. Subscription, M. 6.80; separate, M. 9.

A. Schoffner. "Enzyme und ihre Bedeutung zur Konstitutionsermittlung von Naturstoffen." Fortschritte der Chemie, Physik und physikalischen Chemie, Band 20, Heft 7. Verlag von Gebriider Bomtraeger, W 35 Schoneberger Ufer 12a, Berlin, Germany. 58 pp. Subscription, M. 6; separate, M. 8.

P. Schriftan. "Gasanalyse in der Technik." Verlag von S. Hirzel, Konigstrasse 2, Leipzig, Germany. 79 pp. RM. 5.

H. C. Sherman and S. L. Smith. "The Vitamins." Second edition. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Ave., New York. 575 pp. $6.00.

W. Tombrock. "Matter and Logic. An Attempt at a Logical Explanation of Material Properties and Natural Phenomena." Obtainable through Giro No. 72219 for the Dutch Post Office. 16 pp. 60 ct. (one shilling).

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THE OSMOTIC PRESSURE OF DILUTE BENZENE SOLUTIONS BY THE POROUS DISK METHOD[1]

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Introduction

An accurate method of measuring a colligative property (1) of very dilute solutions in order to test the Debye–Hückel theory of solutions at low concentrations and (2) of colloidal solutions is very desirable. Heretofore, none of the colligative properties could be investigated at sufficient dilutions for these purposes. Furthermore, a method is needed which is applicable over a range of temperature, concentration and kind of solvents. Osmotic pressure is one property which can be so studied.

Measurements of osmotic pressures of non-aqueous solutions have been very few, due mainly to the fact that no suitable membrane could be found. Usually the membrane either dissolved slightly in the solvent, or was nearly impermeable to it. A brief survey of the work with non-aqueous solvents is given by Bartell and Osterhof[2] and also by Murray.[3]

In order to overcome the difficulties of membranes in osmotic pressure measurements Townend,[4] working under the direction of Professors J. C. W. Frazer and W. A. Patrick, developed a new method of measuring these pressures in which the ideal membrane is used, that is, the vapor of the solvent itself. It is known as the "porous disk method" of measuring osmotic pressures and should be applicable to solutions of any volatile solvent and non-volatile solute. The method was improved by Martin and Schultz.[5] The apparatus used in the present series of measurements was designed after that used by the latter two workers, with the neces-

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[1] This is an abstract of the dissertation presented by the author to the Board of University Studies of the Johns Hopkins University, 1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] F. E. Bartell and H. J. Osterhof, *Coll. Sym.* Mon., *4*, 234 (1926).

[3] M. J. Murray, *J. Phys. Chem.*, 33, 896 (1929).

[4] R. V. Townend, THIS JOURNAL, 50, 2958 (1928).

[5] F. T. Martin and L. H. Schultz, *J. Phys. Chem.*, 35, 638 (1931).

sary modifications and improvements needed for use with non-aqueous solvents.

Temperature Regulation

In this method of measuring osmotic pressures it is very essential that the temperature of the osmometer (the instrument used to measure the osmotic pressure), including all parts having the vapor state in contact at any point with either the solution or the solvent, be kept very constant throughout the measurement of a tension (see Frazer and Patrick[6] and Martin.)[7]

For this purpose there was constructed a large thermostat 127 cm. high by 86 cm. in diameter, heavily insulated with hair-felt Instead of the usual type of toluene–mercury thermoregulator, which has presented a number of difficulties when attempts have been made to secure regulation better than 0.001°, a new method of temperature control, proposed by Dr. D. H. Andrews of this Laboratory, was tried. Using the principle of the Wheatstone bridge, a resistance thermometer was constructed of four 900-ohm coils, alternately nickel and constantan. No. 36 nickel wire was used and No. 30 constantan Each coil was wound on a sheet of asbestos board **15** X 15 × 0.32 cm. The four coils were mounted in a thin, water-tight copper shield filled with transformer oil. This was suspended in the thermostat in a location similar to that of the osmometer flask. The wires from the coils were led through a brass tube to the top of the thermostat. An e. m. f. of 12 volts was impressed across two sides of the bridge and a sensitive galvanometer was connected across the other two sides. A change in temperature unbalanced the bridge, causing the mirror of the galvanometer to move. Light was reflected from this mirror upon a photoelectric cell in such a manner as to move on the cell when the thermostat cooled down and to move off when it warmed up. The weak current of the cell was amplified by a vacuum tube and relays which cut on and off the current to the electric heater in the thermostat[8]

A stream of water, several degrees cooler than the main thermostat and held constant to ±0.02° by means of a small auxiliary thermostat, was circulated continuously through a coil in the center of the bottom of the main thermostat.

With this method of temperature control, regulation to ±0.002° was the best which could be secured. Applying the principle of the Gouy oscillating contact[9] for toluene–mercury thermoregulators, a "shutter," consisting of a metal strip 5.2 X 7.6 cm., was suspended in front of the photoelectric cell in the path of the beam of light. This shutter was connected to a crank on a reducing gear-box driven by an electric motor. Its amplitude was less than the operating width of the photoelectric cell and its frequency was about 45 cycles per minute. It operated in such a manner that, as the thermostat cooled down, the beam of light shone on the cell for larger fractions of each cycle; and as the thermostat warmed up, the light hit the cell for smaller fractions of each cycle When the temperature of the thermostat became very constant, the beam of light was practically stationary, shining on the position of the cell all the time and being cut off from the cell by the shutter at definite intervals. By this method it was possible to hold the temperature constant to ±0.0002°, or better, for several hours at a time.

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[6] J C. W. Frazer and W. A. Patrick, *Z. physik. Chem.*, 130,691 (1927).

[7] F. T. Martin, "Dissertation," Johns Hopkins University, 1929.

[8] Details of this method of temperature regulation have appeared in the literature since this work was done.

[9] Sligh, THIS JOURNAL, **42,** 60 (1920); also Gouy, *J. phys.*, 6,479 (1837).

A differential thermometer, consisting of a capillary of a 360" thermometer seated to a number of short, parallel tubes filled with an alcoholic solution of a dye, was used to read the temperature variations in the thermostat to 0.0002°.

Glass Apparatus.—The main change in the glass apparatus over that used by Martin and Schultz[5] with aqueous solutions was the elimination of all stopcocks where they might in any way come in contact with benzene, the solvent in the present experiments, because stopcock grease is soluble in benzene. This required an additional valve in the mercury traps. The osmometer was also changed slightly.

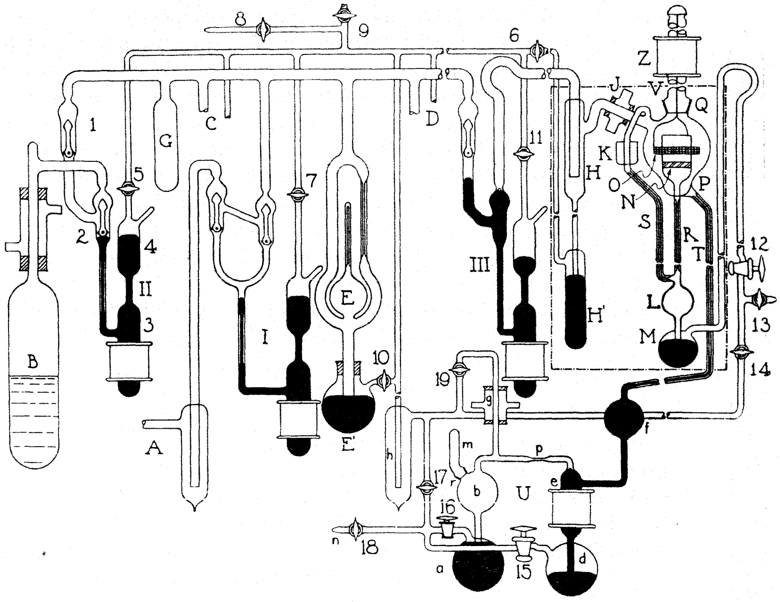

Fig. I.

A diagram of the apparatus is shown in Fig. I. The trap **A,** cooled with solid carbon dioxide, led to a two-stage mercury diffusion pump backed by a Cenco Hyvac oil pump. The mercury trap I connected the pumps to the main system. **A** bulb B of about 800-cc. capacity was a benzene reservoir. Another such bulb and trap were connected at D. At C was connected a mercury trap like trap I and a new type of deaerating apparatus. E was a McLeod gage. G was a 60-cc. bulb for condensing benzene vapor in the main system and as an approximate measure of benzene for diluting the solutions. Mercury trap III led to the apparatus in the thermostat H was a mercury cut-off in the thermostat for enclosing the vapor system entirely under water.

The main part of the apparatus, that used for the measurements, was the "osmometer." It consisted of a liter flask, P, inside of which was sealed a cup containing the porous disk, N. Near the top of the flask was a tube connecting it to the trap H. Over this tube was a small condenser, J, for distilling benzene into the solution. On the upper side of the tube, near the osmometer, was connected a small tube leading to the capillary S and around which was another condenser, K, which was used to distil benzene under the disk. Into the top of the osmometer was fitted a ground-glass, mercury-scaled stopper, Q, sealed to a tube, V, shown in detail in Fig. 2. In V was mounted the mechanism for operating the stirrer, O, in the solution. O was a platinum gauze bent in a circle around the cup containing the disk. Platinum wires supporting the gauze were welded together above the cup and hooked over F, a tungsten wire sealed into a glass rod, Y.

Martin and Schultz[5] observed during their measurements that liquid condensed in the tube containing the stirrer mechanism, at the point where the tube came through the water of the thermostat, and which caused an erroneous rate of distillation. Hence, a mercury seal had to be placed inside this tube. The detail of V, Fig. 2, shows the inverted glass cup at W fitted over a small tube. The cup was sealed to a glass rod, Y, which was sealed to a glass tube containing a bar of iron, X. The entire stirrer was suspended from a phosphor-bronze spring supported at the top of V. The bottom of the cup rested in mercury, thereby sealing off the benzene vapor in the osmometer from the remainder of the stirrer tube. This cup was below the water level of the thermostat. The stirrer was operated by means of a solenoid mounted around V just below the center of the iron bar, X. The solenoid was connected to the 14-volt line and in series with an eccentric driven by a motor and reducing gears. This cut on and off the current through the solenoid, thereby pulling the stirrer down and up and hence agitating the solution. The inverted cup was raised and held above the mercury seal by means of the solenoid when the osmometer was being evacuated or when benzene was being distilled into it in order that pressure equilibrium could be established in the top of V.

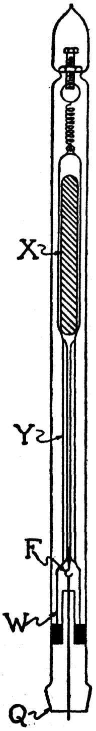

Fig. 2.—Stirrer mechanism.

R was the "inner" and S was the "outer" capillary of the osmometer. These two capillaries formed the manometer for measuring the osmotic pressure and they were about 65 cm. long. R was sealed to the cup supporting the disk. R and S met above the small bulb L whose mercury reservoir was M. A capillary tube T led from the solution side of the osmometer to the solution-introducing apparatus, U. These capillaries and the osmometer flask as high as the disk were visible from outside the thermostat through a narrow window. Doors in front of the window insulated it from without.

All the apparatus within the broken line in Fig. 1 was inside the thermostat and below the water level.

The Porous Disk.—A description of the porous disk, used to support the pure solvent and made from equal parts of Pyrex glass and a special clay, is given by Martin and Schultz.[5]

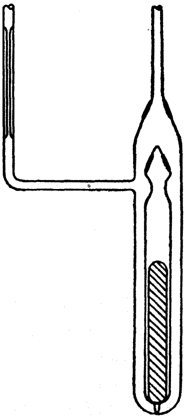

Fig. 3.—Valve for mercury traps.

Mercury Traps.—The mercury traps were similar to those designed by Martin and Schultz[5] except for the extra valve necessary for the elimination of a stopcock in contact with mercury. This valve (bulb **3**, Fig. 1, and shown in detail in Fig. **3**) was a ground-glass stopper sealed to a glass tube containing a bar of iron. This stopper, which floated in mercury, fitted into its ground-glass seat at the top of the bulb. It was pulled down by passing a current through a solenoid mounted around the bulb, **3**.

To close the trap, atmospheric pressure was admitted to bulb 4, Fig. 1, through stopcocks 5 and 8 and the stopper in **3** was pulled down by passing a current through the solenoid. Then the mercury was allowed to rise in *2* until the stopper was seated and mercury-sealed. To open the trap, the procedure was the same except that instead of atmospheric pressure, vacuum from an oil pump for the "secondary system" was admitted to bulb 4 through stopcocks 5 and 9

The mercury for the traps was purified by allowing it to drop through a long column of dilute nitric acid and then through distilled water, and finally distilling it under vacuum The mercury for the bulbs of the osmometer and of the solution-introducing apparatus was similarly purified, except that it was redistilled three times.

The Solute

The solute used in osmotic pressure measurements by this method obviously must be as nou-volatile as possible. Inorganic salts are the most desirable to use because of their low vapor pressure, but unfortunately very few of them are soluble to any extent in benzene. Furthermore, many of those which are soluble are associated in benzene solution.

An organic compound of high molecular weight and of high boiling point was selected as the solute: tetraphenylethylene. It melts at 221°, boils at 425° ("International Critical Tables") and has a molecular weight of 332.16. Hence it was felt that its vapor pressure at 25° and in dilute solutions would be sufficiently low for use in the present experiments. It is very soluble in benzene.

A freezing-point lowering determination of it in 0.1 molar benzene solution was made and it was found to behave normally. Its calculated molecular weight was 320.4 which, for the method employed, was considered within experimental error of the theoretical value.

The tetraphenylethylene had been carefully purified by Smith[10] for specific heat measurements. It gave a good freezing-point curve, so no further purification of the substance was deemed necessary.

Experimental

Purification **and** Deaeration of **the** Benzene.—The benzene used was Baker's *c.* P. benzene. It was purified according to Dr. Greer's method[11] and was stored over calcium chloride. Just before use the benzene was distilled off phosphorus pentoxide, the fraction boiling within 0.04" or less, of the boiling point being collected.

About 400 cc. of this benzene was poured into the bulb B, Fig. 1, and subsequently frozen. The top of the bulb was then sealed off and most of the air pumped out of the bulb. The benzene was further cooled with solid carbon dioxide and the space above it in the bulb was highly evacuated. After closing trap II, the benzene was allowed to melt. Water was circulated through the condenser above the bulb and a small electric light beneath the bulb supplied heat for refluxing the benzene. At frequent intervals the air above the benzene in the bulb was expanded into the outer evacuated system by closing trap I and opening trap II. The benzene could not be opened directly to the pumps, as there would have been a very rapid distillation of benzene into the solid carbon dioxide trap, A. This process was repeated for a number of days until less than 0.001 mm. of mercury air pressure developed overnight. This benzene was then distilled into another bulb connected to the main system and containing phosphorus pentoxide by placing ice around the phosphorus pentoxide bulb and warm water around the bulb B and opening the proper traps. The benzene was refluxed over the phosphorus pentoxide for about a week to dry it completely and remove the last traces of sulfur impurities. Then the benzene was distilled back into the first bulb and its deaeration was continued for several weeks until the air pressure which accumulated above it after stand-

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[10] Smith, "Dissertation," Johns Hopkins University, 1930.

[11] E. Juanita Greer, THIS JOURNAL, 52,4191 (1930).

ing two days was of the order of 10^{-5} mm. of mercury. Thereafter, the air was removed at less frequent intervals.

A new deaerator, designed by Dr. Taylor[12] of this Laboratory for the preparation of air-free liquids, was used in the deaeration of the benzene for the last experiment.

Cleansing and Deaeration of the Osmometer.—The osmometer, before mounting in the thermostat, was treated with a saturated solution of chromic oxide in concentrated nitric acid for four days, allowing the solution to run through the disk to the bulbs below. Then it was cleaned with dilute nitric acid for a day. It was then washed with distilled water and finally with conductivity water until the water which ran through the disk had practically the same conductivity as that put in the flask above the disk.

The osmometer was evacuated continuously for a couple of days to remove most of the air. Then benzene from one of the reservoir bulbs was distilled into it by closing trap I, opening the main system to one of the benzene reservoirs and running ice water down the sides of the osmometer flask in order to remove the last traces of grease and impurities in the flask. After admitting air to the osmometer, this wash benzene was drained out. The disk and disk cup also were carefully rinsed with pure benzene.

The osmometer was reevacuated for several days, at the end of which time an air pressure of only 2×10^{-4} mm. of mercury developed upon standing overnight. Air-free benzene from one of the reservoir bulbs was then distilled into the bulb below the disk by running ice water through condenser K, and then the benzene was raised upon thr mercury from the bulb M into the space under the disk. By pumping this benzene through the disk, out of the osmometer, most of the air left in the disk was removed and afterwards an almost negligible air pressure developed in the osmometer, which was now ready for measurements.

Procedure in Making Measurements.—Air-free benzene from a reservoir bulb was distilled under the disk by a method similar to that by which Martin and Schultz introduced water under the disk in their apparatus.[5] When sufficient benzene had been placed under the disk the mercury in R (and S) was pumped up by pumping air through stopcocks 13 and 12 until most of the benzene had been forced through the disk.

Air which had accumulated in the osmometer during this distillation was removed by evacuating the main system to a flat gage and then expanding the air in the osmometer into the evacuated system. After letting the benzene stand over the disk for half a day, the liquid was pulled down slowly through the disk by placing small tension5 (two centimeters of mercury) upon the benzene; that is, by lowering the mercury level in the outer capillary S a couple of centimeters below that in R. After all the benzene had been pulled through the disk, it was possible to place tensions up to 60 cm. of mercury upon the pure benzene without its breaking away from the disk.

Next, the solution was introduced into the osmometer, using the apparatus shown at U. Fig. 1. A solution of the desired concentration and volume was prepared under as dry conditions as possible. The benzene was protected from moisture by transferring it from one flask to another through small tubing and drying with phosphorus pentoxidc the air which was used to force over the liquid.

The solution-introducing apparatus was evacuated to dry the bulbs completely and the mercury. Air was readmitted to it through trap *h* which was surrounded with solid carbon dioxide. The solution was transferred from the flask in which it had been prepared into the bulb b, taking precautions to exclude as much moisture as possible. After mercury-sealing the stopper *m* at r, ice water was circulated through the condenser *g* and the solution was partially evacuated by opening and closing stopcock 19 frequently. This stopcock could not be left open continuously, or too much benzene would have distilled into the solid carbon dioxide trap, h.

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[12] R. K. Taylor, THIS JOURNAL, 52, 3576 (1930)

When most of the air had been removed from the solution, the mercury in T and f was lowered until the stopper in the valve e was released from its seat. The solution in b was then raised slowly by admitting air to the mercury bulb *a*, thereby forcing the solution into *f*, stopping before the mercury ran from *b* to *e*. Then air was admitted to *d* slowly, which forced the stopper in e into its seat and raised most of the solution into the osmometer. By means of a hand air pump, air pressure was pumped into d sufficient to force all the solution and about 100 cc. of mercury into the osmometer flask. The solution was floated on mercury to give better thermal equilibrium between the solvent under the disk and the thermostat. The mercury level was just below the disk. In this manner was introduced into the osmometer 200 cc of solution.

The deaeration of the solution was completed in the osmometer by repeatedly expanding the air into the outer evacuated system until no air pressure in the system was observed when it was tested with the McLeod gage. The stirrer for the solution was started and the air was again removed until an air pressure of the order of only 10^{-5} mm. of mercury developed after several hours of stirring

Meanwhile, the thermoregulator equipment was set in operation. When the temperature had been regulating for an hour to within ±0.0005° or less, measurements of the osmotic pressure of the solution were begun. Temperature variations of less than ±0.0002° were secured part of the time and gave much more reliable results.

Various tensions were placed upon the pure solvent and their corresponding rates of distillation were measured. Using tensions less than that corresponding to the osmotic pressure of the solution, distillation from the solvent to the solution took place; conversely, using tensions greater than that corresponding to the osmotic pressure of the solution, distillation from the solution to the solvent occurred. Distillations in both directions were measured in order to keep the concentration of the solution as nearly the same as possible; however, the maximum amount of benzene distilled in either direction was never over several tenths of a cubic centimeter.

Positions of the upper meniscus (that in the capillary R under the disk) and of the lower meniscus (that in the outer capillary S) were read to hundredths of millimeters with a cathetometer, and the times of reading the upper meniscus were noted. A reference line on the apparatus was also read each time because the apparatus shifted slightly and all the readings had to be corrected to the initial, or "zero," position of the osmometer.

After applying a tension, about an hour was allowed before readings were begun, in order that constant conditions would be established. Three readings of each meniscus and reference line were made at approximately hourly intervals. After determining the average of each set of readings, the height through which the upper meniscus had moved was calculated. This height was immediately plotted against its corresponding time. When three or four points lying approximately on a straight line were obtained, the slope of the best line drawn through them gave the rate of distillation for that tension and further readings on that tension were discontinued. A new tension was then applied and its rate was determined. The rates were plotted against their corresponding tensions and a line was drawn through these points. When a straight line was obtained from a number of rates, the measurements on that solution were complete. The point at which the line crossed the zero-rate axis gave the tension corresponding to the osmotic pressure of the solution — the observed osmotic pressure.

The tension exerted upon the pure solvent is made up of three parts: (a) the length of the mercury column from the lower to the upper meniscus; (b) the benzene column from the upper meniscus to the surface of the disk; and (c) the net height of benzene vapor from the surface of the disk to the surface of the solution, which, from equilibrium considerations and the laws of thermodynamics, must be equal to a benzene column of the same height. The mercury equivalents of parts (b) and (c) were calculated and added to (a) to determine the actual tension on the solvent.

The mean time for the tension and the mean position of the lower meniscus were determined for the points used in drawing the rate curve. All calculations were made at the temperature of the thermostat, namely, 26.85°.

The theoretical value of the osmotic pressure was calculated from the equation

$$PV_0 = xRT = (N/N_0)RT, \text{ or}$$
$$P = NRT/V_0N_0$$

where P = osmotic pressure in atmospheres, V_0 = molar volume of solvent, x = mole fraction of solute, N = number of moles of solute, N_0 = number of moles of solvent, R = gas constant and T = absolute temperature.

After starting a series of measurements, readings were taken on as many tensions as possible, usually three or four, so long as the thermostat was working properly. From four to six hours were needed for the measurement of each tension.

Analysis of Solution.—After completing the measurements of the tensions, three samples of the solution were removed for analysis in order to determine its concentration. The same apparatus that was used for introducing the solution was used for removing it. The solution was lowered into bulb *f*, Fig. 1, and then permitted to run slowly from f to b, by lowering the mercury level in *e* sufficiently to release the stopper in *e* from its seat. When enough solution had run into b, the remainder was forced back into the osmometer. After admitting air to b and removing the stopper *m*, the solution was sucked from b into three glass-stoppered flasks which held about 50 cc. each.

The weight molar concentration of the solution was determined by weighing (1) the flask and solution, (2) the flask and solute after evaporating off the solvent, and (3) the empty flask after dissolving out the solute and drying the flask.

Dilution of the Solution.—Knowing the approximate concentration of the solution in the osmometer, from the way in which it had been prepared, it was possible to calculate the approximate amount of solution which must be removed from the osmometer to leave the correct amount of solute for the next lower concentration. This calculated amount was the volume removed for analysis and was divided into the three samples. Also, this was the volume of pure benzene which had to be added to the solution for the next dilution.

To dilute the solution the outer system was evacuated to a flat gage, trap I was closed and trap II was opened. Ice water was placed around bulb G and the benzene for diluting the solution was distilled from a reservoir bulb into G. Trap II was closed when the proper amount of benzene was in G. Traps III and H were opened, water at a temperature of **31–35'** was placed around G and ice water was circulated through condenser J. This caused the benzene to distil from G to J and from there it ran into the solution. Reflux action between the benzene under the disk and the condenser J caused benzene to be distilled from under the disk into the solution. This was later replaced by more benzene.

When the dilution was completed, traps III and H were closed. The outer system was evacuated to a flat gage and any air in the osmometer was removed by repeated expansions into the outer evacuated system. The stirrer in the solution was set in motion and when the solution was as air-free as possible, measurements on this concentration were made.[13]

Experimental Results

A preliminary experiment was performed using pure benzene as the "solution" in order to test the possibilities of the apparatus and to learn how to manipulate it. Then the osmotic pressures of five solutions of tetraphenylethylene in benzene were measured, starting with the most concentrated solution and diluting down. The results of these experiments are given in Table I. The concentrations are weight molar and the osmotic pressures are millimeters of mercury at the temperature of the experiments, 26.85°.

The results of one experiment are given in detail in Table II. In the columns are listed, from left to right, the times at which the upper meniscus was read, the positions of the upper meniscus, of the lower meniscus and of the reference line, and the temperature variations of the thermostat as observed during the course of the experiment. Data for the other experiments were recorded in the same way.

TABLE I

Experiment number	Concentration, weight molar	Osmotic pressure, mm. Observed	Osmotic pressure, mm. Calculated
2	0.01919	313.2	312.7
3	.01502	242.9	244.8
4	.01007	162.1	164.1
5	.004057	66.7	66.1
6	.000466	10.5	7.6

As explained previously, from these data were calculated the distances through which the upper meniscus moved. By plotting these results the osmotic pressures, that is, the tensions for zero rates of distillation, were determined.

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[13] For a more detailed discussion of the operation of the apparatus see the author's dissertation, W. C. Eichelberger, "Dissertation,"The Johns Hopkins University, 1930.

Figure 4 is a graph of the height–time curves for Table II, illustrating the method of determining the rates of distillation. Figure 5 is a graph of the rate–tension curves for all the experiments, from which the osmotic pressures for Table I could be read. From this last figure one may observe the nearness of the points obtained to their respective lines and hence the relative accuracy of the results. The results of experiments 2 to 5 are within 1% of their values as calculated from the equation $PV_0 = xRT$. The result of the last experiment has about the same absolute

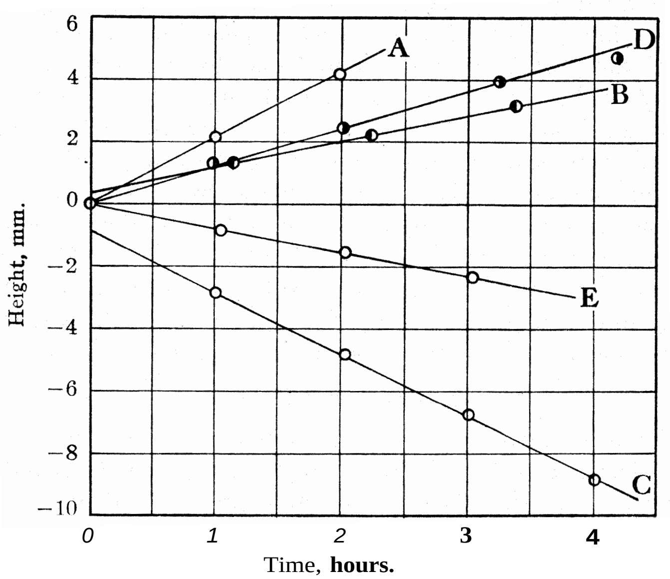

Fig. 4.

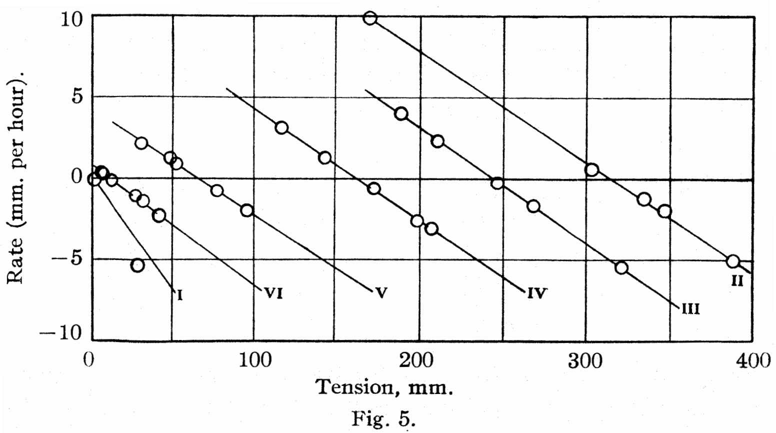

Fig. 5.

error as some of the others, but its percentage error is much greater because of the very dilute solution.

TABLE II

Concentration (weight molar)....	0.004057
Temperature (average)	26.851°
Osmotic pressure (mm of mercury, 26.85°), Observed........	66.7 mm
Calculated. .	66.11 mm

Tension A

Time, hours	Upper meniscus, mm	Lower meniscus, mm	Reference line, mm.	Temperature variations °C.
0	409.68	417.15	215.99	±0.0005
1.007	407.40	417.29	216.00	± .0002
1.985	405.21	417.27	216.01	± .0001

Average tension (mm. of mercury).............35.41 mm.
Rate of distillation..........................+2.12 mm./hr.

Tension B

0	353.95	382.73	215.97	±0.0002
1.151	352.68	382.75	216.11	± .0005
2.236	351.63	382.86	216.00	± .0002
3.386	350.56	382.90	215.95	± .001

Average tension (mm. of mercury).............53.23 mm.
Rate of distillation..........................+0.82 mm./hr.

Tension C

0	353.91	432.60	215.99	±0.0002
1.002	356.93	432.96	215.98	± .0002
2.034	359.02	433.23	215.97	± .0004
3.007	361.08	433.41	215.96	± .0002
4.005	363.40	433.59	215.99	± .0003

Average tension (mm. of mercury).............95.71 mm.
Rate of distillation..........................−1.99 mm./hr.

Tension D

0	361.52	384.95	215.93	±0.0004
0.984	360.21	385.33	216.00	± .0002
2.010	358.91	385.57	215.94	± .0005
3.244	357.43	385.74	216.11	± .001
4.182	356.45	385.96	215.93	± .0005

Average tension (mm. of mercury)..............48.48 mm.
Rate of distillation..........................+1.21 mm./hr.

Tension E

0	360.00	416.16	215.87	±0.0006
1.044	360.92	416.13	215.89	± .0002
2.032	361.72	416.18	215.97	± .0004
3.038	362.56	416.19	215.96	± .0002

Average tension (mm. of mercury).............77.48 mm.
Rate of distillation.........................−0.76 mm./hr.

By examining the graphs and the data sheets it was observed that in nearly every case where a point did not fall on or very close to the line drawn through the other points there were temperature variations greater than ±0.0005° in the thermostat. Very small temperature fluctuations would tend to compensate each other to some extent, but this was not usually the case with larger ones.

Considering the behavior of the apparatus and the results obtained, the author considers the apparatus suitable for measuring the osmotic pressures of dilute solutions over a certain range of concentration, the upper value of which is governed by the length of the capillary tubes R and S in the osmometer, Fig. 1. Better temperature regulation must be secured before very dilute solutions, those below **0.001** molar, can be measured accurately.

In conclusion the author wishes to express his great appreciation to Professors J. C. W. Frazer and W. A. Patrick, who suggested the problem and under whose kindly direction and counsel it was carried out.

Summary

1. An apparatus was developed with which it was shown possible to measure, with a fair degree of accuracy, the osmotic pressures of dilute solutions, benzene solutions of tetraphenylethylene being those measured. Greater precision should be possible if better temperature regulation could be secured.

2. **A** new type of thermoregulator employing a resistance thermometer and photoelectric cell was constructed for accurately controlling the temperatures of thermostats.

3. The elimination of stopcocks in vacuum systems containing vapors which will dissolve stopcock grease was successfully accomplished bv means of a modification of mercury traps.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 259]

THERMAL EXPANSION AND THE DEBYE-HÜCKEL HEAT OF DILUTION

BY GEORGE SCATCHARD

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The calculation of the heat of dilution from the Debye–Hückel theory has been based on the calculation[1,2,3,4] of the energy U from the work content A by the Gibbs–Helmholtz equation, that is, through a differentiation ***at constant volume.*** However, the experimental data used are the change in heat content H, the dielectric constant and its temperature coefficient, all measured ***at constant pressure.*** The difference between the two heat quantities is small and can be determined, that between the two dielectric constants is probably also very small, but that between the temperature coefficients at constant pressure and at constant volume is generally more important. The difficulty is removed most simply by carrying out the calculations, like the experiments, at constant pressure. This involves the addition of a term dependent on the thermal expansion of the solution.

The present treatment will be limited to the case of a single electrolyte which does not change the dielectric constant of the solution. The fundamental equation of the Debye–Hückel theory, in the extended form of Gronwall, La Mer and Sandved,[5] may be written

$$\psi_j = \frac{-KT}{\epsilon z_j} \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 z_j^2}{-KTDa}\right)^m X_m(x) \tag{1}$$

where ψ_j is the potential at the distance a from the center of the j'th ion, k is Boltzmann's constant, T the absolute temperature, ϵ the charge on the proton, z_j the valence of the j'th ion (negative for a negative ion), D is the dielectric constant of the solvent, a the mean collision diameter of the ions, which we will assume to be the same for both ions. Each $X_m(x)$ is a function of the ratio z_1/z_2 and of x, which latter is defined by the equation

$$x = \kappa a = \sqrt{\frac{-4\pi N\epsilon^2\nu\, z_1 z_2\, a^2 n}{1000\, KTDV}} \tag{2}$$

where N is Avogadro's number, ν the number of ions formed from one molecule of electrolyte, n the number of moles of electrolyte in V liters of solution.

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[1] Gross and Halpern, *Physik. Z.*, **26**, 403 (1926).

[2] E. Q. Adams, THIS JOURNAL, **48**, 621 (1926).

[3] N. Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

[4] Lange and Meixner, *Physik. Z.*, **30**, 670 (1929).

[5] Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928)

If we define a new variable as

$$Y_m(x) = \frac{1}{x^{2m}} \int_0^x y^{2m-1}\, X_m(y)\, \mathrm{d}y \tag{3}$$

the work of charging all the ions reversibly at the same rate is

$$W_e = -NKTn \sum_{j=1}^{2} \sum_{m=1}^{\infty} \nu_j \left(\frac{\epsilon^2 z_j^2}{-KTDa}\right)^m Y_m(x) \tag{4}$$

where ν_j is the number of ions of the j'th kind formed from one molecule of electrolyte.

The electrical contribution to the heat content may be obtained by the Gibbs–Helmholtz equation at constant pressure written in the form

$$H_e = \frac{\mathrm{d}(W_e/T)}{\mathrm{d}(1/T)} \tag{5}$$

where W_e varies with the temperature directly, and also because of the temperature variation of D, V and a. All four of these quantities occur in x and therefore in each $Y_m(x)$. Gronwall, La Mer and Sandved give the relation

$$\frac{\mathrm{d}Y_m(x)}{\mathrm{d}x} = \frac{X_m(x)}{x} - \frac{2mY_m(x)}{x} \tag{6}$$

The differentiation of x is obvious and

$$If, = -NKTn \sum_{j=1}^{2} \nu_j \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 z_j^2}{-KTDa}\right)^m \left[\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right)\frac{X_m(x)}{2} + \frac{\mathrm{d}\ln \mathrm{V}}{\mathrm{d}\ln \mathrm{T}}\left(\frac{X_m(x)}{2} - mY_m(x)\right) - \frac{\mathrm{d}\ln a}{\mathrm{d}\ln T}\left(X_m(x) - 3mY_m(x)\right)\right] \tag{7}$$

The total heat of dilution to zero concentration per mole Q_c^0 is

$$Q_c^0 = (H_e - H_e^0)/n \tag{8}$$

where II_e^0 is the value of II_e when x = 0.

Let us consider the Debye–Hückel approximation (m = 1). Since

$$x_1(x) = 1/(1 + x) \tag{9}$$

$$Q_c^0 = -NKT \sum_{j=1}^{2} \frac{\epsilon^2 \nu_j z_j^2}{2KTDa} \left\{ \frac{x}{1+x}\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right) + \frac{1}{x^2}\left[1 + x - \frac{1}{1+x} - 2\ln(1+x)\right]\frac{\mathrm{d}\ln V}{\mathrm{d}\ln T} + \frac{2}{x^2}\left[\frac{x^2}{1+x} + \frac{x^2}{2} - 3x + 3\ln(1+x)\right]\frac{\mathrm{d}\ln a}{\mathrm{d}\ln T} \right. \tag{10}$$

$$= -NKT \sum_{j=1}^{2} \frac{\epsilon^2 \nu_j z_j^2}{2KTD}\left[\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T} + \frac{1}{3}\frac{\mathrm{d}\ln V}{\mathrm{d}\ln T}\right)\kappa - \left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T} + \frac{1}{2}\frac{\mathrm{d}\ln V}{\mathrm{d}\ln T} - \frac{1}{2}\frac{\mathrm{d}\ln a}{\mathrm{d}\ln T}\right)\right]\kappa^2 a + \ldots \tag{11}$$

The earlier calculations all omit the term in d ln V/d In T.[6] Gross and Halpern[1] apparently used the rest of equation (10) although they

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[6] If the heat quantities on the left-hand side are energies rather than heat contents, and if the dielectric constant and its temperature coefficient are also measured at constant volume, the equations are correct with this omission.

did not publish their equation. Adams[2] gave the rest of the first term of equation (11) as the limiting law. Bjerrum[3] gave the first term of equation (10) and Lange and Meixner[4] gave the first term of equation (7). Bjerrum and Lange and Meixner drop the term in d ln a/d ln T because this coefficient cannot be determined independently and because it does not appear in the limiting law. Since $X_m(x)$ and $Y_m(x)$ for m greater than one disappear at $x = 0$ (they do not even appear in the limiting law) the complete value of Q_c^0 may be obtained by adding to Q_c^0 for $m = 1$ the contribution of the higher terms to H_e.

We are particularly interested in the term in d ln V/d ln T which has previously been omitted. We may note that it is in general, including the higher terms of equation (7), proportional to one minus the osmotic coefficient or to the j of Lewis and Randall. From the first term of equation (11) we see that it appears in the limiting law, and by comparing the two terms of this equation we see that for more concentrated solutions it increases less rapidly than the term in $(1 + \text{d ln } D/\text{d ln } T)$. A detailed study of the higher terms shows that its relative importance decreases with increasing values of m. The relative value of the two terms depends, of course, upon the two temperature coefficients. For water at 25° $\frac{1}{3}\frac{\text{d ln } V}{\text{d ln } T}$ is 0.0256, and Wyman's value[7] for $(1 + \text{d ln } D/\text{d ln } T)$ is -0.371, so that the error in the limiting law due to the neglect of the thermal expansion is +7.2%. This is about the difference between $(1 + \text{d ln } D/\text{d ln } T)$ of Wyman and of Drude,[8] and about the error of measurement of the heat of dilution in very dilute solutions.[9] It is probable that in the near future both of these experimental uncertainties will be reduced. For other substances the measurements of the temperature coefficient of the dielectric constant are less certain. The values for ethyl alcohol given in the "International Critical Tables"[10] indicate an error of 13% if the thermal expansion is neglected.

Summary

It is pointed out that it is incorrect to calculate the heat of dilution from the Debye–Hückel theory by differentiating at constant volume. The complete equation is derived for a solution containing a single electrolyte with the dielectric constant independent of the concentration. It is shown that neglect of the thermal expansion leads to a considerable error even in the limiting law.

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[7] J. Wyman, *Phys.* Review, 35,623 *(1930).*

[8] Drude, Ann. *phys.*, **59,** 48 (1896).

[9] For references see Lange and Robinson, *Z physik Chem* , **148A,** 97 (1930)

[10] "International Critical Tables." Vol VI, 1929, p. 85

[CONTRIBUTION NO. 657 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

THE ACTIVITY COEFFICIENTS AND HEATS OF TRANSFER OF CADMIUM SULFATE FROM ELECTROMOTIVE FORCE MEASUREMENTS AT 25 AND 0°. APPLICATION OF THE EXTENDED THEORY OF DEBYE AND HÜCKEL

BY VICTOR K. LA MER AND W. GEORGE PARKS[1]

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Introduction

The activity coefficients of many typical electrolytes have been determined in both dilute and concentrated solutions, but few results have been reported for cadmium sulfate. The only available data are found in the work of Getman[2] on the electromotive force of galvanic cells and in the table of activity coefficients compiled by Lewis and Randall.[3] The latter results were calculated from the freezing point data collected in the paper of Lewis and Linhart.[4] The results of Getman are not consistent, while those tabulated by Lewis and Randall do not extend below a concentration of 0.01 molal.

Since it is well known that the halides of cadmium are somewhat anomalous in their behavior as electrolytes, this research was undertaken to establish the activity of the sulfate over the entire concentration range by measuring the electromotive force of the cell

$$\text{Cd-Hg (2 phase)} \mid CdSO_4\ (M) \mid PbSO_4\ (s) \mid \text{Pb-Hg (2 phase)} \qquad (1)$$

and to obtain data on an electrolyte of the symmetrical (2–2) valence type, which are well suited for testing the mathematical extension of the Debye–Hückel theory given by Gronwall, La Mer and Sandved.[5]

The previous electromotive force studies on cadmium sulfate have always involved the mercurous sulfate half-cell, but since lead sulfate is about one-tenth as soluble as mercurous sulfate, it is obvious that precise measurements can be extended to much lower concentration with the lead sulfate–lead half-cell.

If the temperature coefficient of such a cell is also measured, it becomes possible to determine not only the change in heat content of the reaction through the Gibbs–Helmholtz equation, but also to evaluate the electrical heat of transfer arising from electrostatic interaction by taking advantage of the accurate extrapolation afforded by the extension of the Debye–

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[1] This paper is constructed from a dissertation submitted by W. George Parks in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1930.

[2] Getman, J. Phys. Chem., 32, 91 (1928).

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 362.

[4] Lewis and Linhart, THIS JOURNAL, 41, 1951 (1919).

[5] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928), see p. 388, eq. 107.

Hückel theory given by Gronwall, La Mer and Sandved. Although free energy measurements at two temperatures alone afford only a partial answer to the question of electrical heats of dilution, they are sufficient to determine the temperature coefficient of the parameter "a" representing the distance of closest approach of the ions. The value of ∂"a"$/\partial T$ is of considerable theoretical interest in considering heats of dilution.

Theoretical

Although there have been many experimental investigations which have demonstrated that the activity coefficients of strong electrolytes in aqueous solution agree with the predictions given by the equations of Debye and Hückel sufficiently well to establish inter-ionic attraction as the explanation of the anomalies of strong electrolytes, nevertheless, it is true that experimental data exist which exhibit serious discrepancies from these equations in regions of high dilution. These discrepancies are quite unexpected on the basis of the Debye–Hückel equations. They appear most conspicuously in the case of high valence types in water as well as for univalent types in media of lower dielectric constant. On the other hand, data on higher valence types furnish the most convincing tests of the theory since the deviations measured are more significant and not subject to the same degree of experimental uncertainty that accompanies the data for lower valence types.

In this Laboratory we have held that the incomplete mathematical solution for the Poisson–Boltzmann equation as given by Debye and Hückel should first be completed and the data tested from that viewpoint, before ascribing the discrepancies between the abridged theory and experiment to new physical hypotheses such as incomplete dissociation, deformability of the ions, or even the ion-association hypothesis of Bjerrum.[6] This procedure has the advantage that the theory is not weakened by the immediate introduction of further arbitrary parameters which accompany new physical assumptions. Evidence that a more complete mathematical treatment without further assumptions is sufficient to account for data which are in apparent disagreement with the theory should furnish one of the most satisfying experimental proofs possible.

Whenever it is found that the general solution of the Poisson–Boltzmann equation is incapable of describing the behavior quantitatively on the basis of a constant and physically reasonable value of "a," it then becomes appropriate to ascribe such discrepancies to incomplete dissociation as embodied in the term "weak salt."[7]

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[6] Bjerrum, *Det. Kgl. Danske Videnskab. Math.-fys. Medd.*, *VII*, No. 9 (1926). Bjerrum's ion-association introduces no new parameter but necessitates an arbitrary distinction between free and associated ions which becomes superfluous in the extension of Gronwall, La Mer and Sandved.

[7] Randall and Scott, THIS JOURNAL, 49, 647 (1927); Randall and Allen, *ibid.*, 52, 1814 (1930).

Since the extended theory of Debye and Huckel makes no pretense of dealing with factors other than electrostatic interaction it is important to ascertain to what concentration limit it is competent to account for the facts under the present incorrect but necessary approximation that the dielectric constant of the solution D is equal to the dielectric constant of the pure solvent D_0.

We shall be primarily concerned with the error introduced by Debye and Hiickel in retaining only the linear term of the expansion of the expression for the density of electricity ρ valid for a symmetrical electrolyte like cadmium sulfate where $z_1 = -z_2 = z = 2$

$$\rho = nz\epsilon\,(e^{-z\epsilon\psi/kT} - e^{z\epsilon\psi/kT}) \cong -2n\epsilon^2z^2\psi/kT \tag{2}$$

when this approximation for ρ is introduced into the Poisson equation

$$\nabla^2\psi = \frac{-4\pi\rho}{D} \cong \kappa^2\psi \tag{3}$$

where

$$\kappa = \sqrt{\frac{8\pi n\epsilon^2z^2}{DkT}} \tag{4}$$

The complete solution[5] of (2) and *(3)* for the activity coefficient of a salt of the symmetrical type takes the form

$$\log f = \frac{-\epsilon^2z^2}{kTDa}\cdot\frac{1}{2}\cdot\frac{x}{1+x} + \sum_{m=1}^{\infty}\left(\frac{\epsilon^2z^2}{kTDa}\right)^{2m+1}\left[\frac{1}{2}X_{2m+1}(x) - 2m\,Y_{2m+1}(x)\right] \tag{5}$$

where x = "a"κ and $X(x)$ and $Y(x)$ are functions of x defined and tabulated through the fifth approximation,[5] *i. e.*, $m = 2$. Employing Drude's value of D = 78.77 for 25°, $\kappa = 0.3283\,z\sqrt{M}$, we get the working equation suitable for numerical calculation

$$-\log_{10} f = 1.53636\left(\frac{z^2}{a}\right)\frac{x}{1+x} - 0.15382\left(\frac{z^2}{a}\right)^3\cdot 10^3\left[\frac{1}{2}X_3(x) - 2Y_3(x)\right] - 0.0770\left(\frac{z^2}{a}\right)^5\cdot 10^5\left[\frac{1}{2}X_5(x) - 4Y_5(x)\right] \tag{6}$$

A rough computation will show that whenever a/z^2 is assigned values **>1.5 Å.,** only the first term corresponding to the Debye–Hückel approximation need be considered in most work. However, when $a/z^2 <$ **1.5 Å.,** which means "a" < 6 Å. for a bi-bivalent salt, the contribution of the higher **terms** cannot be neglected. They will be important for **(2–2)** salts since **6** . is a large ion size. In low dielectric solvents the higher terms become important, in fact, may occasionally predominate over the first approximation even for **(1–1)** valence types, since the significant parameter is Da/z^2.

In the first approximation as given by Debye and Hiickel the limiting law is the asymptote when either "a" or the concentration factor $\kappa =$ **0.3283** $z\sqrt{M}$ is assigned values approaching zero, whereas in the general development of Gronwall, La Mer and Sandved, the limiting law is the asymptotic form *only* when κ approaches zero. In the general solution the correction terms assume infinite values ***whenever*** "a" ⟶ 0. The correctness[8] of this latter statement will be immediately evident when one recognizes that the field strength at the surface of a point charge is infinite. An assembly of point charges would condense together and it would require an infinite amount of work to separate such hypothetical ions. In other words, the logarithm of the activity coefficient would be infinite when "a" is set equal to zero. The indiscriminate use of the Debye–Hückel approximation may therefore easily yield absurd values for "*a*" when their equations are employed in the computation of experimental data on higher valence electrolytes. The general solution[5] overcomes this mathematical difficulty and should yield positive and physically reasonable values for "*a*" which are constant over a legitimate concentration range, provided the theory is correct in its fundamental postulates. It is our purpose to test this point.

The electromotive force of the cell (1) corresponding to the process

$$\mathrm{Cd\ (solid)} + \mathrm{PbSO_4\ (solid)} = \mathrm{Pb\ (solid)} + \mathrm{CdSO_4}\ (M) \qquad (7)$$

is given by the equation valid for 25°

$$E = E_0 - 0.05915 \log m - 0.05915 \log f \text{ (volts)} \qquad (8)$$

For convenience in plotting and calculating the activity coefficient $f_{\mathrm{CdSO_4}} = \sqrt{f_{\mathrm{Cd}^{++}} \cdot f_{\mathrm{SO_4''}}}$, we calculate the quantity E_0', where

$$E_0' = E + 0.05915 \log M, \text{ and} \qquad (9)$$

$$E_0' = E_0 - 0.05915 \log f \qquad (10)$$

If we use the Debye–Hückel limiting law valid for a bi-bivalent salt, namely

$$\log f = -4.04 \sqrt{M} \qquad (11)$$

we get

$$E_0' = E_0 - 0.239 \sqrt{M} \qquad (12)$$

It is evident that a plot of E_0' against $\sqrt{M}$ should approach a limiting tangent with slope 0.239, the intercept being E_0. Although this method of extrapolating for E_0 is widely used, it is open to the objection that it places the most weight upon the points in dilute solution, which are the most difficult to determine with accuracy. Furthermore, it assumes that the Debye–Hückel limiting law is obeyed exactly throughout the region of extrapolation.

A consideration of the magnitude of the third and fifth approximations ($m = 1$ and 2) in equation (5) shows that this assumption is not justified for any physically attainable concentration for a (2–2) salt. In fact, it cannot be emphasized too strongly that the *percentage error* in log *f* due to the neglect of the higher terms is most significant in the region of highly dilute solutions, *i. e.*, from about *0.0001* to 0.001 molal. The first approximation as given by Debye and Hückel predicts just the opposite.

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[8] La Mer, *Trans. Am. Electrochem. Soc.*, **61**, **543** (1927). A mathematical proof is given in Ref. 5, Chapt. 2, p. 360.

We therefore employ the method of assuming an "a" value and calculate the value of E_0 through equations (6) and (10). That value of "a" which gives a constant E_0 value over the range of concentration for which it is legitimate to employ equation (6) under the assumption $D = D_0$ is taken as the true value. This method assigns equal weight to all the experimental points, and is not open to personal interpretation as is a graphical extrapolation.

From the data it is possible to compute the free energy of transfer accompanying changes in concentration of the solution. The free energy change $AF = \Delta\bar{F}_{CdSO_4}$ involved in transferring a mole of salt from a molality M_1 to a molality M_2 is given by the formula

$$-\Delta F = \frac{2 \times \Delta E \times 96{,}500}{4.182} \text{ calories} \tag{13}$$

where AE is the electromotive force of the cell

$$\text{Pb, PbSO}_4 - \underset{M_1}{\text{CdSO}_4} - \text{Cd} - \underset{M_2}{\text{CdSO}_4} - \text{PbSO}_4\text{, Pb}$$

corresponding to the process $CdSO_4$ (MI) ⟶ $CdSO_4$ (M_2).

The thermal change accompanying a chemical reaction can be calculated readily from the temperature coefficient of the electromotive force of a cell in which the particular reaction takes place. Thus, on substituting in the Gibbs–Helmholtz equation

$$-\Delta H = n\mathrm{F}\left(E - T\frac{\partial E}{\partial T}\right) \tag{14}$$

the observed value of E, at the temperature T, and the value of $(\partial E/\partial T)$ derived from the observed variation of E with T, we calculate the value of AH at the temperature T and molality M, where the solid cadmium and lead are saturated with mercury.

Owing to experimental difficulties which will be discussed later, sufficient data have not as yet been obtained for an exact calculation of the heat of the reaction. However, as a first approximation we may assume that $(\Delta E/\Delta T)_M = (\partial E/\partial T)_M$ and complete the calculation indicated by Equation 14, taking E for 12.5° as the mean of $E_{25°}$ and $E_{0°}$.

Preparation of Materials

Lead Nitrate.—The best grade of C. P. salt was recrystallized three times from boiling distilled water and the crystals were dried in air.

Cadmium Sulfate.—Since cadmium sulfate has a negative temperature coefficient of solubility, forming solid hydrates at low temperatures, the best grade of salt was recrystallized three times from boiling distilled water by slowly evaporating the solution to about one-third of its original volume. The crystals were then powdered in an agate mortar and heated in a large quartz dish to about 250° for six hours, forming anhydrous cadmium sulfate. According to Mellor,[9] when cadmium sulfate is recrystallized from water above 74" the product obtained is $CdSO_4 \cdot H_2O$. This monohydrate Mylius and

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[9] Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. IV, p. 616.

Funk[10] found decomposed into the anhydrous salt at 112°. Coniglio[11] reports for this transition temperature 150 to 170°. Partridge[12] in preparing his highly purified cadmium sulfate heated it to 200° for six hours. The prepared salt was preserved until used in a weighing bottle over phosphorus pentoxide.

Lead Sulfate.—The lead sulfate was precipitated from a cadmium sulfate solution by adding a 5% solution of the purified lead nitrate to an excess of a 10% solution of the purified cadmium sulfate. The solution containing the precipitate was heated to boiling for fifteen minutes, at the end of which time the lead sulfate had assumed a definite crystalline form. It was washed with distilled water, drained on a Biichner funnel, and preserved under distilled water in a Non-Sol battle until needed in the electrodes.

Mercury.—Redistilled mercury was stirred under dilute nitric acid for twenty-four hours and then twice redistilled by the Hulett[13] method in a slow current of air.

Lead Amalgam.—Lead amalgam was prepared by electrolyzing the purified lead nitrate solution using purified mercury as the cathode. The anode consisted of a platinum wire placed in another beaker filled with 1 *N* nitric acid, and connected to the first beaker by means of a Y-tube. This was necessary because lead peroxide forms at the anode during electrolysis. A paddle stirrer was placed in the cathode beaker to slowly stir the mercury. A current of 0.2 ampere was run until the concentration of lead in the amalgam was about 6%. Fay and North[14] report that all amalgams between the limits of 2 and 55% of lead form a two-phase system at 25°, consisting of a granular phase of constant composition represented by Pb_2Hg, and a liquid phase which also has a definite composition when equilibrium is reached. Puschin[15] found that all amalgams between 1.8 and 66% lead have the same electromotive force. Likewise Henderson and Stegeman[16] report that in their work they found the same value for the electromotive force of any amalgam containing between 2.5 and 6% lead.

The prepared amalgam was washed, dried, heated until it became one phase and filtered through a capillary tube into the evacuated reservoir, which was then filled with purified nitrogen and stored ready for use.

Cadmium Amalgam.—Using a mercury cathode, as in the case of the lead amalgam, cadmium was electrolyzed from a solution of purified cadmium sulfate. The anode consisted of a bar of C. P. cadmium, scraped clean of oxide. A current of 0.2 ampere was employed until the concentration of cadmium in the amalgam was about 11%. Frilley[17] reports that all amalgams of less than 5% are liquid. The solubility of cadmium in mercury was found by Hulett and deLury[18] to be 5.574 g. per 100 g. of mercury at 25°. Bijl[19] shows that all amalgams between 5 and 14% of cadmium have the same electromotive force when measured against any constant electrode at room temperature. The solid phase in the amalgam is reported by Kerp and Böttger[20] to have the composition represented by Cd_2Hg_7. However, they admit that there is some evidence that the solid phase may be a mixed crystal.

This amalgam was washed, dried, heated and stored under nitrogen in the same way

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[10] Mylius and Funk, *Ber.*, 30, 825 (1897).

[11] Coniglio, *Rend. accad. Sci.*, (Napoli), [3] 34, 119 (1928).

[12] Partridge, *Am. J. Sci.*, [3] 40,381 (1890).

[13] Hulett, *Phys. Rev.*, 21,288 (1905); *ibid.*, 33,307 (1911).

[14] Fay and North, *Am. Chem. J.*, 25,216 (1901).

[15] Puschin, *Z. anorg. Chem.*, 36,210 (1903).

[16] Henderson and Stegeman, THIS JOURNAL, 40, 84 (1918).

[17] Frilley, *Rev. métal.*, 8, 541 (1911).

[18] Hulett and deLury, THIS JOURNAL, 30,1811 (1908).

[19] Bijl, *Z. physik. Chem.*, 41,641 (1902).

[20] Kerp and Böttger, *Z. anorg. Chem.*, 25, 54 (1900).

as the lead. In the preparation of both amalgams the concentration of electrolyte was kept high and the potential drop between the electrodes low so that the deposition of possible impurities was negligible. **A** concentration of metal in the amalgams was used such that the temperature could be varied from 0 to 50° and a two-phase system would result when equilibrium was attained.

Nitrogen.—Tank nitrogen was purified by passing it first through potassium pyrogallate, freshly prepared according to the method of Berthelot,[21] and then over-heated copper gauze in a quartz tube. The gas passed through a gas washing bottle filled with dilute sulfuric acid, followed by a tower filled with soda lime. Before entering the cell vessel the gas bubbled through a long upright tube filled with some of the solution in the cell to ensure the same aqueous tension

Experimental Method

Cell and Electrodes.—Although the attempts of some previous investigators to use the lead–lead sulfate electrode were unsuccessful, Henderson and Stegeman[16] obtained constant and reproducible results with the electrode in the presence of sodium sulfate. U. B. Bray[23] made a careful study of the electrode in the presence of zinc sulfate. He found that: (1) oxygen must be excluded. (2) A definite crystalline form of lead sulfate is essential. **(3)** It is best to establish equilibrium between the solid lead sulfate and the solution before the electrode is made up. (4) The use of two-phase amalgams is highly desirable, making the electrode easily reproducible without analysis. We confirm Bray's findings that the lead sulfate electrode is highly reproducible if these conditions are observed, but since his experimental details are scanty and we also had initial difficulties we give our procedure in some detail.

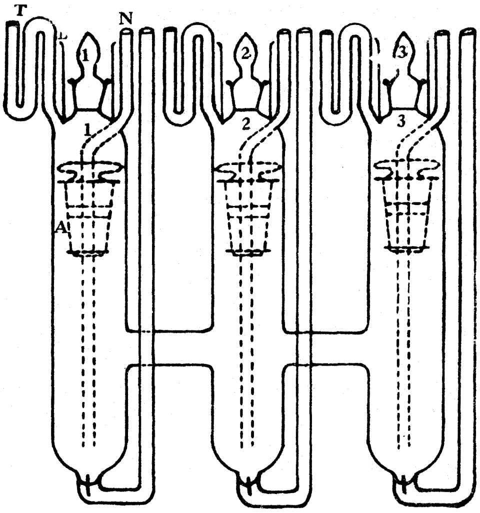

Fig. 1.

Figure 1 is a side view; Fig. *2* is a top view of the cell used. It is composed of six electrodes divided into two groups of three each by the stopcocks at A. On one side three similar lead electrodes, on the other side three similar cadmium electrodes were set up. These served as a convenient and satisfactory means of checking the constancy and reproducibility of each half-cell. Through the tubes marked N nitrogen could be

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[21] White, "Gas and Fuel Analysis," McGraw-Hill Book Co., Inc., New York, 1920, p. 33.

[22] Lewis and Brighton, THIS JOURNAL, **39,** 1906 (1917); Horsch, *ibid.,* 41, 1788 (1919).

[23] U. B. Bray, *ibid.,* 49, 2372 (1927).

passed through the solutions to remove oxygen and facilitate equilibrium by stirring. These tubes were connected to a glass manifold made of Pyrex tubing carrying capillary tubing outlets for equalizing the flow of gas. The connections to the cell vessel were made with small bits of rubber tubing carrying pinch clamps to further regulate the flow when necessary. All rubber tubing was painted with castor oil and shellac. Small glass traps, marked T, were sealed on each electrode so that when the flow of nitrogen was stopped a few drops of mercury in each trap would prevent the diffusion of air into the cell. The lines on Fig. i marked B designate short pieces of large glass tubing sealed on each electrode with "picein" cement so that a mercury seal could be made over each ground glass joint. Later this method was discarded, the tubes were removed, and a few drops of castor oil placed in the gutter of each ground joint, a method which proved entirely satisfactory.

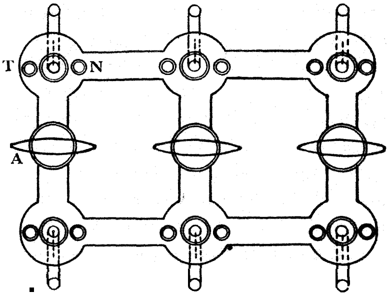

Fig. *2.*

The technique for filling the cell was as follows. The cadmium sulfate solution to be used was divided into two parts. To one part was added several grams of solid lead sulfate which had previously been washed with the cadmium sulfate solution, and the mixture rotated for fourteen hours in the thermostat. After carefully cleaning and drying the electrode vessel it was filled with nitrogen. One side of the cell was then filled with the cadmium sulfate solution saturated with lead sulfate and the other side with the pure cadmium sulfate solution. The cell was put in the thermostat and nitrogen bubbled through for one hour. At the end of this time the amalgams were added from the reservoirs in which they were stored. **A** sketch of one of these reservoirs is given in Fig. **3.** Boiling water was poured into the outside jacket marked A in order to heat the amalgam until it became one phase. Then after a few drops had been run out at the stopcock B to remove any amalgam that may have been in the tube in contact with the air, the electrode vessel **was** placed under the reservoir and the required amount of amalgam dropped through a very small funnel into the proper cell. Any oxide which is formed in the preparation of the amalgams is almost entirely removed on filling the reservoirs through the fine capillary tube C (Fig. **3).** The possibility of contamination from the traces of oxide remaining on the surface of the amalgams in the reservoirs is eliminated by filling each electrode with amalgam drawn from the bottom (stopcock B) and by passing the amalgam through the small funnel holding a filter paper with a pin hole opening. The cell was replaced in the thermostat, nitrogen continued for two hours more and the apparatus **then** sealed. Gas was passing through each electrode while the amalgams were being added. Large stopcocks (5 mm. bore) and short tubes at A (Fig. **2)** made it possible to measure the electromotive force with the stopcocks closed in all cases except for the solutions of about 0.002 molal and less. For these solutions, the hole in each stopcock held ***a*** plug of cotton previously soaked in the cadmium sulfate solution being used; also the level of the solution on the side containing no lead sulfate was made higher so that when the

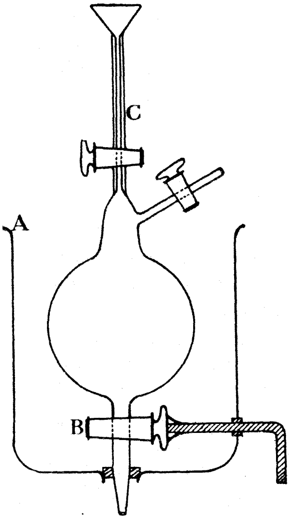

Fig. **3.**

stopcocks were temporarily opened for making a reading no lead sulfate could possibly siphon over to the cadmium side. A slight movement of the solution in the other direction is of no consequence, since it soon becomes saturated with lead sulfate.

The reproducibility of the cadmium electrodes was usually to within 0.01 millivolt. In the more dilute solutions a check of 0.06 millivolt was considered satisfactory for the lead electrodes. In the more concentrated solutions the agreement was much better. Frequently, as with the cadmium electrodes, no difference greater than ±0.01 millivolt was observed. Readings were taken for at least twenty-four hours after the cells had reached their final constant value, which was usnally about six hours after preparation. In the concentrated solutions, 1 molal and greater, this time of equilibrium was extended over forty-eight to seventy-two hours. The average reading of the nine combinations remained constant to 0.04–0.05 millivolt for from thirty-six to forty-eight hours after the equilibrium value was reached. In nearly all of the solutions below 0.008 molal check determinations were made. The values for the lowest three concentrations reported were not as reproducible as desired and will be discussed in more detail later.

When attempts were made to measure the electromotive force at 37.5 and 50° the agreement was never better than one to two millivolts, so no results are recorded for these temperatures. This failure at the higher temperatures is attributed to the transition of a-cadmium to β-cadmium. Getman[24] reports that α-cadmium is the stable form at ordinary temperatures and that this form changes to β-cadmium at 37 to 40° depending upon the thermal history of the metal employed, whereas Cohen and Helderman[25] give the transition point in the vicinity of 64°.

In making the measurements at the different temperatures, the cell vessel, after the electromotive force had been measured at 25°, was treated in the following manner. In order to prevent the change in pressure from drawing the mercury from the traps into the cell or forcing out of any of the cell contents, small corks were forced into the traps on top of the mercury and capped by a few drops of castor oil. The glass stopcock on the nitrogen inlet manifold was closed. The slight change in pressure in the system due to changing temperature was too small to produce a measurable change in volume of the liquid and solid reactants.

The equilibrium value at 0" was usually reached in from twelve to sixteen hours. No measurements were attempted below a concentration of 0.0007 molal at 0° because the internal resistance of the cell was then too great. A variation of from 0.05 to 0.1 millivolt in the most dilute solutions was considered satisfactory at this temperature.

Preparation and **Analysis** of **Cadmium** Solutions.—For all concentrations above **0.1** molal the solutions were made up by direct weighing of the salt and water. For the concentrations below 0.1 molal stock solutions of cadmium sulfate were diluted by weight. The distilled water averaged 1.2 X 10^{-6} reciprocal ohms for the specific conductivity; occasionally water with *a* specific conductivity of 0.7 × 10^{-6} r. o. was obtained.

The stock solutions were analyzed electrolytically by depositing the cadmium on a platinum gauze electrode from *a* cyanide bath. A weighed sample of the solution to be analyzed was made decidedly alkaline with potassium hydroxide and then just enough potassium cyanide added to dissolve the precipitate. A current of 0.5 ampere was passed through the solution for twenty-four hours using a platinum wire anode and a platinum gauze cathode of 30 sq. cm. in area. The solution was slowly stirred all the time. At the end of this time not the faintest trace of color could be obtained by passing hydrogen sulfide into the solution. The cathode was then washed with alcohol and ether,

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[24] Getman, THIS JOURNAL, 39, 1806 (1917).

[25] E. Cohen, "Physico-Chemical Metamorphosis and Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, 1928, pp. 40–50.

dried and weighed. It was possible to obtain triplicate determinations which agreed to within 0.1%. On several occasions the results checked to 0.05%. Using this method of analysis the average cadmium content of the purified anhydrous cadmium sulfate agreed within one part in 20,000 of the theoretical value.

Other methods of analysis were tried, including the precipitation of cadmium as cadmium sulfide and the precipitation of sulfate as barium sulfate. These methods were not as reproducible as the electrolytic method nor did they check well with one another.

The Apparatus.—For measurements at 25° a large water thermostat was maintained to ±0.01°. The Beckmann thermometer was checked against the laboratory standard, and also against a thermometer calibrated by the Bureau of Standards. For the measurements at 0° a small bath of ice and water mush was used, having air lift pumps to provide adequate circulation. This bath was maintained to ±0.05°. The potentiometer was a Leeds and Northrup type K, with a high resistance galvanometer No. 2500 type R, having a sensitivity of 424 megohms, a period of 2.8 seconds, and an external critical damping resistance of 2000 ohms. The potentiometer was calibrated, and the Weston standard cell was certified by the Bureau of Standards. The standard cell was kept in an insulated, water-tight, copper container in the thermostat at 25° The entire measuring apparatus was protected from stray electrical effects by the equipotential shielding method recommended by White.[26]

Experimental Data

The experimental values of the electromotive force at 25° are given in Table I, along with the value of the calculated function E_0'. The observed electromotive force given in Column *3* is in each case the average of the six electrodes previously described. A correction for the solubility of lead sulfate is necessary at concentrations of 0.0056 molal and less. This was made by calculating the increase in sulfate-ion concentration in the solution arising from the solubility of the lead sulfate, and calculating the potential resulting therefrom. Böttger[27] reports the solubility of lead sulfate at 25° to be 1.34×10^{-4}, while Kohlrausch[28] finds 1.45×10^{-4} mole per liter. The value used in these calculations is the average, namely, 1.4×10^{-4} mole per liter. The Debye–Hückel theory gives 0.90 for f_{PbSO_4} at this concentration, assuming a value of *3* Å. for "a." Making use of f_{PbSO_4} we find the activity solubility product of lead sulfate to be 1.59×10^{-8}. In order to calculate the increase in sulfate-ion concentration we made use of the equation

$$M_{Pb^{++}} . f_{\pm} . M_{SO_4''} f_{\pm} = a_{Pb^{++}} . a_{SO_4''}$$

or

$$M_{Pb^{++}} = \frac{K(a)}{M_{SO_4''} \cdot (f_{\pm})^2}$$

By successive approximations the concentration of sulfate ion from the lead sulfate is found, since it is equal to the concentration of lead ion in the cadmium sulfate solution. The ideal individual ion potentials for the cadmium and sulfate ions are calculated in Columns 5 and 6. These two

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[26] White, THIS JOURNAL, **36**, 2011 (1914).

[27] Bottger, *Z. physik. Chem.*, **46**, **604** (1903).

[28] Kohlrausch, *ibid.*, **64**, 129 (1908).

factors when added to the observed electromotive force give E'_0 (equation 9). Since these calculations were completed, another determination of the solubility of lead sulfate has been reported[29] which agrees very well with the results of Kohlrausch. If these calculations were to be repeated, even more weight would now be placed on the data of Kohlrausch. The effect on the final result is too small to make recalculation worth while.

Table II gives the experimental values of the electromotive force at 0° along with the calculated function E'_0. The solubility of lead sulfate at 0° is 1.08×10^{-4} mole per liter. This value was obtained by plotting the data of Böttger[27] and Kohlrausch[28] as shown in Fig. 4 and extrapolating to the desired temperature, taking the average of the results thus obtained.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL Pb–Hg (2 PHASE), $PbSO_4$ (s), $CdSO_4$, Cd–Hg (2 PHASE) AT 25°

No.	Molality of $CdSO_4$	E, obs.	M''_{SO_4} (total)	0.02957 log $M_{Cd^{++}}$	0.02957 log M''_{SO_4}	E'_0
1	0.0004580	0.20241	0.0005043	−0.09875	−0.09752	+0.00614
2	.0005107	.20029	,0005536	− 09736	− .09632	+ ,00661
3	.0005320	.19948	.0005737	− .09683	− .09586	+ .00679
4	.0006070	.19790	.0006451	− ,09514	− .09436	+ .00840
5	.0007267	.19427	.0007604	− .09283	− .09224	+ .00920
6	.0008675	.19055	.0008972	− .09055	− .09012	+ .00988
7	.0009609	.18846	.0009886	− .08924	− .08887	+ .01035
8	.0009819	.18802	.001009	− .08896	− .08861	+ .01045
9	.001077	.18610	.001103	− ,08777	− .08747	+ .01086
10	.001119	.18539	.001144	− ,08728	− .08700	+ .01111
11	.001332	.18178	.001354	− .08504	− .08483	+ .01191
12	.001993	.17380	.002010	− .07987	− .07976	+ .01417
13	.002994	.16596	.003007	− .07464	− .07458	+ .01674
14	.003807	.16146	.003819	− .07155	− ,07151	+ .01840
15	.004371	.15899	.004382	− .06978	− .06975	+ .01946
16	.005618	.15456	.005627	− .06656	− .06654	+ 02146
17	.007544	.14931	.007544	− .06277	− .06277	+ 02377
18	.007901	.14851	.007901	− .06218	− .06218	+ .02415
19	.008351	,14752	.008351	− .06146	− .06146	+ .02460
20	.009307	.14558	.009307	− .06007	− .06007	+ .02544
21	.009409	.14541	.009409	− ,05993	− .05993	+ .02555
22	.01096	.14275	.01096	− .05797	− .05797	+ .02681
23	.02237	.13104	.02237	− .04881	− .04881	+ .03342
24	,05291	.11901	.05291	− .03775	− .03775	+ .04351
25	.1268	.10859	.1268	− .02653	− .02653	+ .05553
26	.3496	.09628	.3496	− .01350	− .01350	+ .06928
27	1.027	.08259	1.027	+ .00034	+ .00034	+ .08327
28	1.886	.07432	1.886	+ .00815	+ .00815	+ .09062
29	2.632	.06944	2.632	+ .01243	+ .01243	+ .09430
30	3.698[a]	.04639	3.698	+ .01679	+ .01679	+ 09752

[a] Saturated.

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[29] Huybrechts and de Langeron, *Bull. soc. chim. Belg.*, 39, 43 (1930).

TABLE II

ELECTROMOTIVE FORCE OF THE CELL Pb–Hg (2 PHASE), $PbSO_4$ (s), $CdSO_4$ (M), Cd–Hg (2 PHASE) AT 0°

Yo	Molality of $CdSO_4$	E, obs	M''_{SO_4} (total)	0 02709 log $M_{Cd^{++}}$	0 02709 log M''_{O_4}	E'_0
1	0 0007267	0 19313	0 0007472	−0.08503	−0.08470	+0 02340
2	0008675	,18969	0008855	− ,08294	− 08270	+ 02405
3	001077	18556	001092	− 08040	− .08023	+ 02498
4	001119	,18474	001134	− 07995	− 07979	+ 02500
5	001332	18132	.001345	− 07790	− 07778	+ 02564
6	.001993	17381	002003	− 07316	− 07310	+ 02755
7	.002994	16646	003002	− 06837	− 06834	+ 02975
8	003807	16216	003814	− 06554	− 06552	+ 03110
9	004371	15982	004371	− .06392	− 06392	+ 03198
10	005618	15566	005618	− 06096	− 06996	+ 03374
11	007544	15098	007544	− 05750	− 05750	+ 03598
12	007901	15028	007901	− 05695	− 05695	+ 03638
13	009307	14754	009307	− 05502	− .05502	+ 03750
14	01096	14485	.01096	− 05310	− .05310	+ 03865
15	05291	.12280	05291	− 03458	− .03458	+ 05364
16	1268	11248	1268	− 02430	− .02430	+ .06388
17	3496	10022	3496	− 01236	− 01236	+ 07550
18	1.886	.07327	1.886	+ ,00764	+ .00764	+ .08820
19	3 698	.05773	3 698	+ 01539	+ .01539	+ .08851

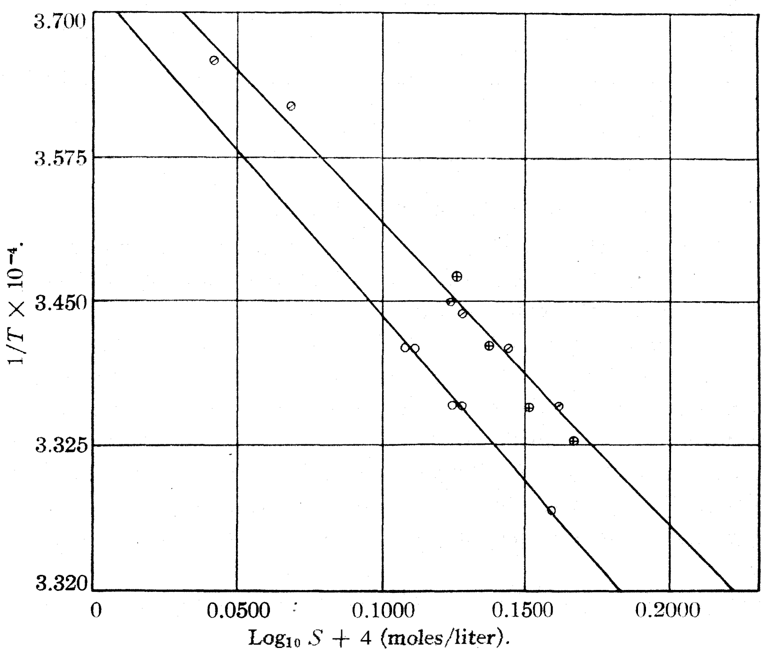

Fig. 4.—Solubility of lead sulfate in water. ⊖, Kohlrausch; ○, Böttger; ⊕, Huybrechts and de Langeron.

The data of Huybrechts and de Langeron are also given on this plot but were not used in the calculations. The Debye-Huckel theory gives 0.913 for f_{PbSO_4} at 0°, and the activity solubility product is 0.972 X 10^{-8}.

The values of E_0' for dilute solutions at both temperatures (Tables I and II) are shown graphically in Fig. 5. The Debye–Huckel limiting law is shown by the broken line. The insert at the lower right-hand portion is for concentrated solutions and shows that the curves for 0 and 25° cross above 1 molal.

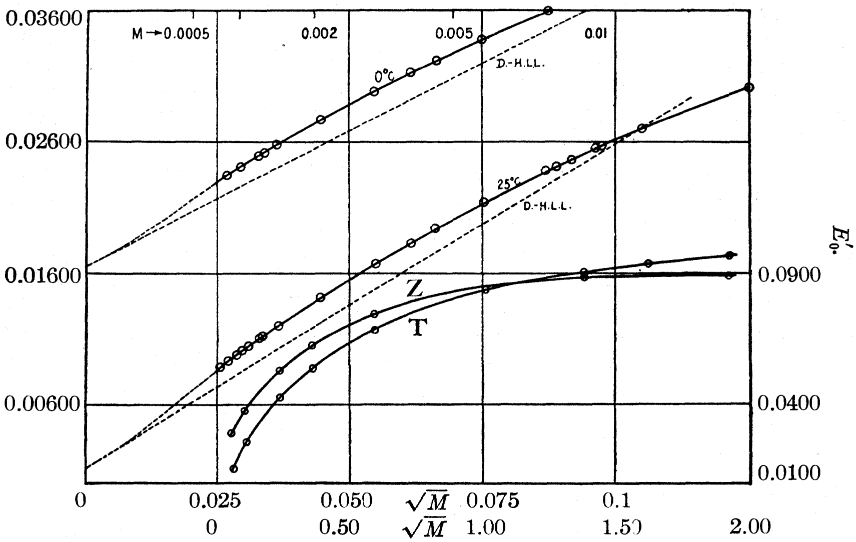

Fig. 5.—The cadmium–lead cell. T, 25°; Z, 0°.

Discussion of Results

Table III gives the values of E_0 obtained when we insert the arbitrary values for "a" = **3,** 3.6 and 4 Å. for cadmium sulfate in expression 6 in order to determine the value of log f.

When the molality of cadmium sulfate is less than 0.0006 molal, the dissolved lead sulfate constitutes more than 6% of the total sulfate-ion concentration. At such very low concentrations of cadmium sulfate the cell can no longer be considered strictly as one without transfer and liquid junction potential, and the cell process would not correspond exactly to the one given in Equation **7.** Since the experimental data were also somewhat erratic we have not included the first three measurements in our computations.

The values of E_0 computed in Table III are plotted in Fig. 6 as a function of $\sqrt{M}$. It is clearly evident that the correct value for E_0 is 0.00142 volt at 25° and that an ion size corresponding to "a" = 3.6 Å. yields values of E_0 having an average deviation of only 0.06 mv. for the nineteen determina-

Table III

Values of E_0

	"a" = 3 0 Å		"a" = 3.6 Å.		"a" = 4.0 Å.	
No	E_0	Deviation from mean	E_0	Deviation from mean	E_0	Deviation from mean
4	+0 00041	+0 00193	+0.00132	−0.00010	$0.00169	−0.00084
5	+ .00037	+ .00189	+ .00143	+ .00001	+ .00185	− .00068
A	+ ,00015	+ .00167	+ .00137	− .00005	+ .00186	− .00067
7	+ .00007	+ .00149	+ .00138	− .00004	+ .00191	− .00062
8	+ .00004	+ .00146	+ .00138	− .00004	+ .00192	− .00061
9	− .00008	+ .00144	+ .00136	− .00006	+ .00194	− .00059
10	− ,00005	+ .00147	+ .00143	+ .00001	+ .00202	− ,00051
11	− .00042	+ .00110	+ .00135	− .00007	+ .00202	− .00051
12	− ,00086	+ .00066	+ .00136	− .00006	+ .00224	− .00029
13	− .00153	− .00001	+ .00134	− .00008	+ .00246	− .00007
14	− .00196	− .00044	+ .00133	− .00009	+ .00261	+ .00008
15	− .00214	− .00062	+ .00139	− .00003	+ .00276	+ .00023
16	− .00248	− .00096	+ .00150	+ .00008	+ .00304	+ .00051
17	− ,00299	− .00147	+ .00150	+ .00008	+ ,00322	+ .00069
18	− ,00306	− .00154	+ .00151	+ .00009	+ .00326	+ .00073
19	− 00315	− .00163	+ .00151	+ .00009	+ .00329	+ .00076
20	− 00335	− .00183	+ .00147	+ .00005	+ ,00331	+ .00078
21	− .00335	− .00183	+ .00149	+ .00007	+ .00334	+ .00081
22	− ,00356	− .00204	+ .00149	+ .00007	+ .00342	+ .00089
23	− .00365	......	+ .00198	......	+ .00421	......

Mean = −0 00152 **Mean** = +0.00142 ± 0.00006 **Mean** = +0.00253

tions extending from 0.0006070 to 0.01096 molal. The maximum deviation is 0.1 mv. for the measurement corresponding to M = 0.0006070.

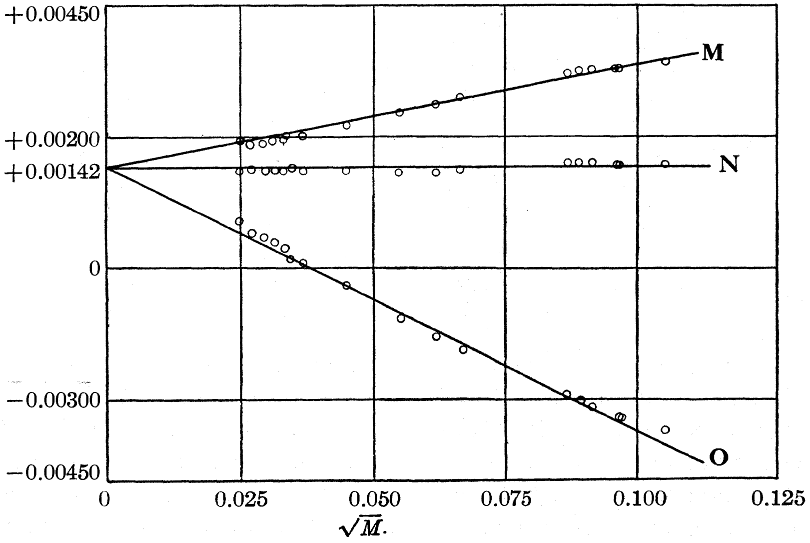

Fig. 6.—M, 4.0 Å.; N, 3.6 Å.; O, 3.0 Å.

In other words, E_0 is constant within the limits of experimental error under the assumption "a" = 3.6 Å., whereas the values of E_0 drift when other values of "a" are employed in Equation 6. Had we extrapolated the E_0', $\sqrt{M}$ curve in Fig. 6 to zero concentration using a Debye limiting law slope passing through the points of lowest concentration, as previous investigators have done, we would obtain the erroneous value $E_0 = 0.00180$ volt, differing from our E_0 by 0.00038 volt, which is about six times the experimental error. The apparent slope of the E_0' against $\sqrt{M}$ curve at 25° between $M = 0$ to $M = 0.0006$ is 0.275 instead of 0.239 as predicted by the Debye limiting law (equation 11), and emphasizes that this law is not obeyed even at such a low concentration range.

In Table IV are given the calculated values of "a" both from the Gebye approximation $[-\log f = 1.53636 z^2\kappa/(1 + \kappa\text{“}a\text{”})]$ and the Gronwall, La Mer and Sandved extension[6] through a fifth approximation.

TABLE IV

COMPARISON OF THE "a" VALUES FOR CADMIUM SULFATE AT 25° COMPUTED FROM THE DEBYE AND FROM THE FIFTH APPROXIMATION ($E_0 = 0.00142$)

No.	Molality	"a" (Debye), Å.	"a" (fifth approx.), Å
4	0.0006070	−9.74	+3.72
5	.0007267	−9.78	+3.64
6	.0008675	−8.74	+3.68
7	.0009609	−8.43	+3.68
8	.0009819	−8.35	+3.68
9	.001077	−7.90	+3.68
10	.001119	−8.02	+3.60
11	.001332	−7.08	+3.64
12	.001993	−5.58	+3.62
13	.002994	−4.11	+3.61
14	.003807	−3.28	+3.61
15	.004371	−2.89	+3.60
16	.005618	−2.18	+3.56
17	.007544	−1.27	+3.52
18	.007901	−1.14	+3.56
19	.008351	−0.98	+3.56
20	.009307	− .65	+3.52
21	.009409	− .64	+3.52
22	.01096	− .23	+3.52
23	.02237	+1.18	+3.04

It is readily seen that the Debye approximation gives values for "a" (Column 3) which drift steadily from −9.78 to −0.23 Å. at 0.01 molal. These values are physically absurd. On the other hand, use of the higher terms gives constant, physically plausible, positive values of "a" as shown in Column 4. The slight drift in these values of "a" may be due to neglecting the seventh approximation. These data (Table TV), although they emphasize the inadequacy of the Debye approximation in dilute solution in a very striking manner, nevertheless confirm in an equally striking manner the validity of the basic assumptions of the theory when given simply the more complete mathematical treatment.

From a large scale plot of E_0' against $\sqrt{M}$, values of E_0' at round concentrations were read, and the corresponding activity coefficients were calculated by Equation 10, using the value of E_0 obtained by extrapolation. These values are given in Table V along with the activity coefficients calculated from the theory.

TABLE V

THE ACTIVITY COEFFICIENTS OF CADMIUM SULFATE AT 25°

No.	Molality	Calculated activity coefficient (equation (5), "a" = 3.6 Å.)	Observed activity coefficient (from e. m. f., equation (10)) $E_0 = 0.00142$	Difference
1	0.0005	0.775	0.774	−0,001
2	.001	.700	.699	− .001
3	.003	.549	.551	+ .002
4	.005	.476	.476	± .000
5	.01	.384	.383	− .001
6	.03	.265	.254	− .011
7	.05	.220	.199	− .021
8	.1	.166	.137	− .029
9	.5		.0605	
10	1.0		.0418	
11	1.5		.0385	
12	2.0		.0304	
13	2.5		.0282	
14	3.0		.0261	
15	3.5		.0260	

Up to 0.01 molal (ionic strength of 0.04) the agreement is within 0.4%, which is well within the experimental error. This is striking when one considers that even at 0.01 molal the activity coefficient has fallen to 0.383.

The results obtained by repeating this method of extrapolation for E_0 at 0° are summarized in Table VI and are shown graphically in Fig. 7. Evaluating the constants in Equation 5 for use at 0° we obtain the following

$$-\log f = \frac{z^2}{a}\,1.49701\,\frac{x}{1+x} - \left(\frac{z^2}{a}\right)^3 0.142297\cdot 10^3 \left[\frac{1}{2}X_3(x) - 2Y_3(x)\right] - \left(\frac{z^2}{a}\right)^5 0.06763\cdot 10^5\left[\frac{1}{2}X_5(x) - 4Y_5(x)\right] \tag{15}$$

The best value for "a" at this temperature is certainly between 3.6 and 3.7. The change in "a" from 25 to 0° is then less than 0.1 Å., which means that $(\partial\text{“}a\text{”}/\partial T)$ is very small, that is, of the order of 0.004 Å. per degree as a maximum. As far as we are aware this is the first time that $(\partial\text{“}a\text{”}/\partial T)$ has been determined directly in a region of concentration where it can be interpreted theoretically. The fact that $(\partial\text{“}a\text{”}/\partial T)$ for cadmium

TABLE VI

CALCULATED VALUES

	"a" = 3.6 Å.		"a" – 3.7 Å.	
No.	E_0	Deviation from mean	E_0	Deviation from mean
1	+0.01666	+0.00012	+0.01676	–0.00004
2	+ .01667	+ .00013	+ .01679	– .00001
3	+ .01670	+ .00018	+ .01683	+ .00003
4	+ .01661	+ .00009	+ .01675	– .00005
5	+ .01650	– .00002	+ .01665	– .00015
6	+ .01645	– .00007	+ .01666	– .00014
7	+ .01639	– .00012	+ .01666	– .00014
8	+ .01628	– .00022	+ .01668	– .00012
9	+ .01628	– .00022	+ .01661	– .00019
10	+ .01638	– .00014	+ ,01674	– .00006
11	+ .01657	+ .00005	+ .01698	+ .00018
12	+ .01664	+ ,00012	+ ,01706	+ .00026
13	+ .01658	+ .00006	+ .01703	+ .00023
14	+ .01652	* .00000	+ .01700	+ .00020
	Mean = 0.01652		Mean = 0.01680	

sulfate is virtually zero lends support to the hypothesis that the value "a" is primarily a measure of the distance of closest approach of the ions without including their surrounding shells of polarized water molecules. Otherwise, larger values of "a" would be demanded which should decrease with rising temperature owing to decreasing hydration.[30a]

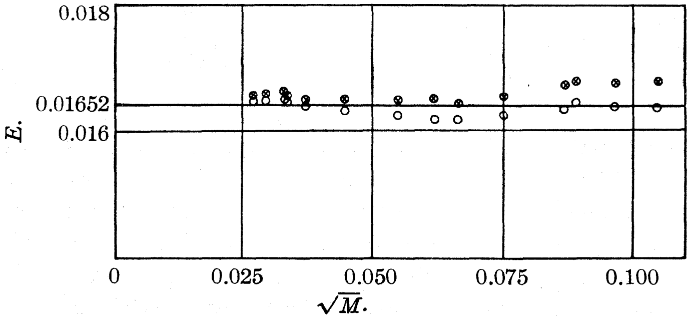

Fig. 7.—○, a = 3.6 Å.; ⊗, a = 3.7 Å.

A comparison of the experimental and theoretical activity coefficients at round concentrations is given in Table VII. The agreement is satisfactory to concentrations including 0.01 molal.

Gronwall, La Mer and Sandved[5] found for Bray's data on zinc sulfate that Equation 5 does not fit the experimental data when M exceeds 0.01096 or κ exceeds 0.0687. Tables III and VI show that the same is true for cadmium sulfate. There are several reasons for this failure of Equation 5 to hold above this concentration. First, this concentration corresponds

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[30] (*a*) Bjerrum, *Trans. Faraday Soc.*, 23,445 (1927); (b) *Ber.*, 62,1091 (1929).

TABLE VII

THE ACTIVITY COEFFICIENTS OF CADMIUM SULFATE AT 0°

No.	Molality	Calculated activity coefficient (eq. (15), "a" = 3.8 Å.)	Observed activity coefficient (from e. m. f., eq (10)) $E_0 = 0.01652$	Difference
1	0 0005	0.786	0.779	−0.0007
2	.001	.714	.710	− .004
3	.005	.494	.494	± .000
4	.01	.402	.399	− .003
6	.05	.232	.217	− .015
6	.1	.176	.149	− 027
7	.5		.0734	
8	1.0		.0574	
9	2.0		.0484	
10	3.0		.0475	

to a value of $x = "a" \times \kappa = 3.6 \times 0.0687 = 0.25$. Although a 0.01 M or 0.04μ solution is ordinarily considered a quite dilute solution from a chemist's standpoint, nevertheless it is concentrated from the standpoint of the Debye–Hückel theory. Thus, when x reaches a value of 0.25 the fundamental approximations of the theory certainly can no longer hold exactly, for this value of x means that $1/\kappa$, namely, the distance from a given ion at which the electric potential due to the ion atmosphere has fallen to $1/e$ of its value at the distance r = "a," is equal to four times the value of "a." Secondly, a comparison of Equation 5 with the unabridged Equation (34a) of Gronwall, La Mer and Sandved[5] shows that each approximation contains the factor $\left(1-10^{-3}c\frac{\partial V}{\partial n}\right)\left(1-\frac{c\mathrm{d}D}{D\mathrm{d}c}\right)$. The quantity $\left(1-10^{-3}c\frac{\partial V}{\partial n}\right)$ is known to be negligible in dilute solutions, but the quantity $\left(1-\frac{c\mathrm{d}D}{D\mathrm{d}c}\right)$ representing the change in dielectric constant with concentration is very likely not equal to unity at concentrations above 0.01 molal. Unfortunately, no one has succeeded as yet in measuring accurately the dielectric constant of conducting solutions at appreciable concentrations.[31] Until this question has been defined and settled experimentally one must make the approximation that $\left(1-\frac{c\mathrm{d}D}{D\mathrm{d}c}\right)$ is equal to unity, with the result that we cannot expect Equation 5 to hold precisely above 0.01 molal.

To avoid misunderstanding it is important to emphasize that the assumption $\left(1-\frac{c}{D}\frac{\mathrm{d}D}{\mathrm{d}c}\right) = 1$ is equivalent to the customary one that $D = D_0$ where the subscript zero refers to the pure solvent. The major effect of this assumption will usually reside in the first approximation and not in the higher terms, *i. e.*, in the difference between the first and last terms of Equation 34a of Reference 5. The unabridged Equation 34a thus embodies

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[31] Debye, "Polar Molecules," Chemical Catalog Co., Inc., *New* York, 1929, p. 124.

the well-known dielectric correction suggested by Hiickel [*Physik. Z.*, 26, 93–147 (1925)] but does it in a more general manner since no restrictions, such as the linear variation of D with c assumed by Hiickel, are made in obtaining the final equation. To employ 34a it will be necessary to know D and dD/dc only at the concentration in question.

Other factors such as the employment of local smoothing in calculating the charge density, the forces resulting from the deformability of the ions and the interpretation of the dielectric constant in the neighborhood of an ion undoubtedly influence the value of "*a*" computed by equations $(6)_{25°}$ and $(15)_{0°}$. However, unless some peculiar and unlikely effects are just compensating one another in the case of cadmium sulfate as well as for zinc sulfate,[32] it hardly seems necessary to take the extreme view given by Fowler[33] that "*a*" is only an "*omnium gatherum*" correction and does not have the significance of an ionic diameter. The evidence now at hand indicates that this viewpoint and the one by Bjerrum,[30b] namely, that "*a*" is "stark temperatur empfindlich" appear to have been based too much

TABLE VIII

PARTIAL MOLAL FREE ENERGY OF TRANSFER OF CADMIUM SULFATE AT 25°

Concn., M_1	Concn., M_2	AE	$\Delta\bar{F}$ (obs.), cal.	$\Delta\bar{F}$ (excess), cal.
3.0	2.0	0.00606	+280	+ 40
2.0	1.0	.00966	+446	+ 35
1.0	0.1	.02865	+1322	− 43
0.5	.05	.02807	+1295	− 80
.1	.01	.03271	+1510	+145
.05	.005	.03672	+1695	+330
.03	.003	.03915	+1807	+442
.01	.001	.04334	+2000	+635
.005	.0005	.04557	+2103	+738

TABLE IX

PARTIAL MOLAL FREE ENERGY OF TRANSFER OF CADMIUM SULFATE AT 0°

Concn., M_1	Concn., M_2	AE	$\Delta\bar{F}$ (obs.), cal.	$\Delta\bar{F}$ (excess), cal
3.0	2.0	0.00887	+ 409	+189
2.0	1.0	.01233	+ 569	+193
1.0	0.1	.03147	+1450	+200
0.5	.05	.02851	+1317	+ 67
.1	.01	.03103	+1432	+182
.05	.005	.03481	+1606	+356
.01	.001	.04045	+1867	+617
.005	.0005	.04284	+1977	+727

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[32] Cowperthwaite and La Mer (to be published) in their studies on the corresponding zinc sulfate cell find the following values for "a": 3.6 Å. (0°), 3.64 Å. (12.5°), 3.64 Å. (25°), 3.60 Å. (37.5°), 3.73 Å. (50°).

[33] Fowler, "Statistical Mechanics," Cambridge University Press. London. 1929. p. 322.

upon results obtained by using the Debye approximation without giving sufficient weight to the contribution of the higher approximations. It will be highly important to ascertain what the same simple state of affairs obtains for the "*a*" value of other 2-2 electrolytes.

In Table VIII are given the calculated values of the free energy of transfer of one mole of cadmium sulfate from concentration M_1 to concentration M_2 at 25°. The excess free energy of transfer is given in Column 5. Table IX gives the corresponding values at 0°.

The Gibbs–Helmholtz Equation (14) enables one to calculate the heats of transfer arising from electrical interaction. Substituting for E in (14) its value

$$E = E_0 - \frac{RT}{nF}\ln M - \frac{RT}{nF}\ln f \tag{16}$$

we get

$$\Delta H = nF\left[E_0 - T\frac{\partial E_0}{\partial T} + \frac{RT^2}{nF}\frac{\partial \ln f}{\partial T}\right] \tag{17}$$

Now

$$E_0' = E_0 - \frac{RT}{nF}\ln f \tag{18}$$

so Equation 17 can be written in a form more directly applicable to the experimental data, namely

$$-\Delta H = nF\left[E_0' - T\frac{\partial E_0'}{\partial T}\right] \tag{19}$$

Since measurements were made at only two temperatures we are obliged to assume that $(\Delta E/\Delta T)_M = (\partial E/\partial T)_M$, an approximation which will be most nearly correct for 12.5°. We have therefore calculated the mean heat of transfer for the total process (7) defined as

$$\begin{aligned} -\Delta H_{285\cdot 6} &= nF\left[\frac{E'_{0(25°)} + E'_{0(0°)}}{2} - T\,\frac{E'_{0(25°)} - E'_{0(0°)}}{25}\right] \\ &= nF\left[E'_{0(12\cdot 5°)} - T_{285\cdot 6}\frac{\Delta E_0'}{\Delta T}\right] \end{aligned} \tag{20}$$

These values are given in Table X, Column 6.

When M = 0, Equation 20 gives $-\Delta H^{\circ}_{285.6} = 8375$ cal., that is, the value of $-\Delta H$ for the total process (7), which is free from any contribution due to electrical interaction.

In Column 7 (Table X) we give the values of the excess or electrical partial molal heat of transfer $-\overline{H}_{(e)}$, defined as

$$-\Delta H - (-\Delta H^{\circ}) = \overline{H}_{CdSO_4} - \overline{H}^{\circ}_{CdSO_4} = -\overline{H}_{(e)} \tag{21}$$

$(-\overline{H}_{(e)})$ is the quantity of heat which is liberated by the forces of electrical interaction when one mole of cadmium sulfate is reversibly transferred from a very large volume of solution of molality M to a similar volume of solution where M equals zero.

TABLE X
CALCULATED VALUES

No.	Molality of $CdSO_4$	$E'_0(25°)$	$E'_0(0°)$	$E'_0(25) - E'_0(0°)$	$-\Delta H_{(285.6)}$, cal.	$-\Delta\overline{H}_{(e)}$, cal.
1	**0.0000**	**0.00142**	**0.01652**	**−0.01510**	+8375	....
2	.0005	.00795	.02235	− .01440	+8291	+ 84
3	.001	.01062	.02458	− .01396	+8167	+ 208
4	.002	.01415	.02754	− .01339	+8026	+ 349
5	.005	.02050	.03313	− .01263	+7893	+ 482
6	.01	.02607	.03813	− .01206	+7834	+ 541
7	.02	.03224	.04300	− .01076	+7403	+ 972
8	.05	.04290	.05250	− .00960	+7262	+1113
9	.1	.05250	.06123	− .00873	+7224	+1151
10	.5	.07398	.07816	− .00418	+5712	+2663
11	1.0	.08300	.08400	− .00100	+4381	+3994
12	2.0	.09115	.08796	+ .00319	+2446	+5929
13	3.0	.09550	.08851	+ .00699	+ 555	+7820

The values of $-\Delta\overline{H}_{(e)}$ are plotted as a function of $\sqrt{M}$ in Fig. 8.

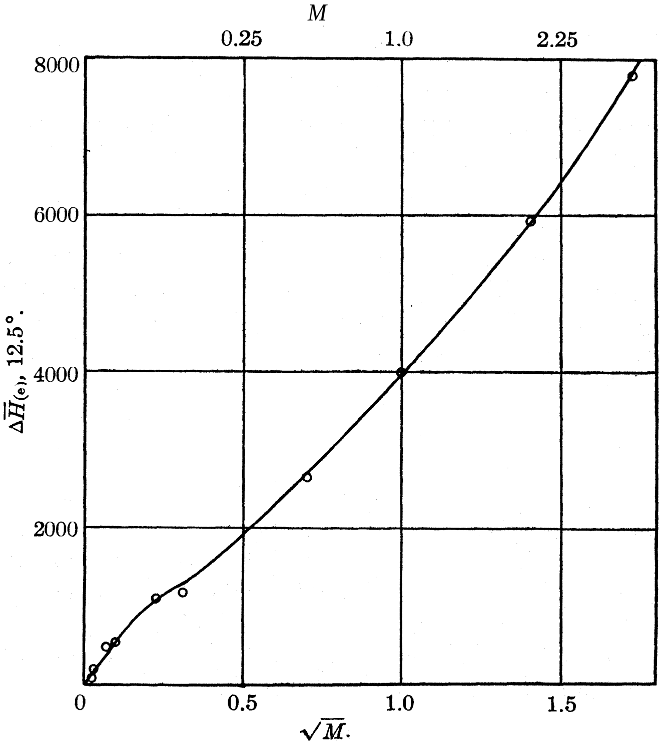

Fig. 8.

Summary

Precise electromotive force measurements are reported at 25 and 0° for the cell Cd–Hg (2 phase), $CdSO_4$ (M), $PbSO_4$ (s), Pb–Hg (2 phase) over the

concentration range 0.0004580 to 3.698 molal. The potential of the cell (E_0) when the ion activities of cadmium sulfate are hypothetically one molal has been found to be 0.00142 volt at 25° and 0.01652 volt at 0°.

The experimental results furnish excellent confirmation of the extension of the Debye–Huckel theory as given by Gronwall, La Mer and Sandved for the region 0.0006 to 0.01 molal, since their extension yields constant and positive, physically plausible values of "*a*" (3.6 Å.) where "*a*" is the distance of closest approach of the ions. The Debye–Huckel approximation gives steadily drifting and physically absurd, negative values of "*a*." This extension furnishes an excellent control on the extrapolation to infinite dilution, since constant values for E_0 are obtained up to 0.01 molal.

The activity coefficients and the partial molal free energies of transfer of cadmium sulfate have been computed at 25 and 0° for the concentration range 0.0005 molal to saturation.

If cadmium sulfate is incompletely dissociated in the classical sense, this influence on the activity coefficient is too small to be detected below 0.01 molal.

It has been shown by direct measurement that $(\partial``a"/\partial T)$ is very small, if not actually zero. This may be taken as support for the view that hydration of the ions is not involved in the value "*a*."

The mean heat of the cell reaction, Cd (solid, satd. with Hg) + $PbSO_4$ (solid) = $CdSO_4$ (M) + Pb (solid, satd. with Hg), for 12.5" and the corresponding excess electrical heats of transfer of cadmium sulfate have been computed using the Gibbs–Helmholtz equation.

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THE THERMAL DECOMPOSITION OF DIMETHYL-TRIAZENE. A HOMOGENEOUS UNIMOLECULAR REACTION

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During the past four years a considerable amount of experimental data has given support to certain theories of unimolecular reaction velocity which postulate that activation occurs by kinetic theory collisions. The rate of production of activated molecules by collisions is a second order process but if only a very small fraction of those molecules which become activated decompose spontaneously the rate of decomposition is first order. At sufficiently low pressures collisions can no longer maintain the Maxwell–Boltzmann quota of activated molecules; consequently the rate falls off until finally at still lower pressures the rate approaches the rate of activation and is second order.

Now that the rate of decomposition of nitrogen pentoxide has at last also been shown to decrease at very low pressures,[1,2] every example of a homogeneous unimolecular reaction shows such a decrease or else theory does not require it in the pressure range studied.

We have now studied the decomposition of dimethyl-triazene and find that this reaction also is first order at high pressures but falls off in rate at pressures below about one centimeter. Rate measurements have been made at temperatures from 200 to 230° and at pressures from 0.02 to 8.0 cm. of mercury.

Preparation of Dimethyl-triazene.—Dimethyl-triazene was prepared by the method of Dimroth.[3]

The copper salt of dimethyl-triazene was first prepared. Methyl azide was formed by dropping dimethyl sulfate upon a stirred and refluxed aqueous solution of sodium azide. The gas was passed through a warm tube containing calcium chloride and into an ice cooled solution of methylmagnesium iodide ($CH_3—N=N\equiv N + CH_3MgI = CH_3—N=N—NCH_3MgI$). The resulting ether solution was hydrolyzed at zero degrees with an aqueous solution of ammonium chloride and ammonium hydroxide, and the dimethyl-triazene so formed was converted to its copper salt by shaking with ammoniacal cuprous chloride solution. The copper salt was separated from the water layer by repeated extraction with ether; the ether solution was dried with anhydrous sodium sulfate and the ether distilled from the salt. The solid green copper salt was recrystallized from warm anhydrous ether and dried over concentrated sulfuric acid.

The free dimethyl-triazene was prepared from its copper salt by warming it with solid diazoaminobenzene prepared according to Fischer.[4] The liberation and purification of the dimethyl-triazene was carried out on a vacuum line.

The vacuum system was of Pyrex glass and consisted of a 30-cc. flask connected in series with a 3 × 1-cm. tube filled with C. P., ground, fused calcium chloride; a receiver of 3-cc. capacity; a 12 X 1-cm. tube filled with calcium chloride; and a small combination distilling flask of 3-cc. capacity and water-cooled reflux column. The exit tube of the reflux column led to another 3-cc. receiver which was separated from the high-vacuum line by a stopcock. Equivalent quantities, *2* g. of the copper salt and 3 g. of diazoaminobenzene, were mixed and introduced into the flask and the latter was sealed off at the neck. The system was evacuated and the flask heated slowly to a temperature of 90° by means of a glycerin bath. The dimethyl-triazene vapor was allowed to pass through the first tube of calcium chloride and was condensed in the first receiver by a mixture of solid carbon dioxide and ether at −78°. When the vapor had all been condensed the receiver was sealed off from the flask and its contents were allowed to distil through the second larger calcium chloride tube into the distilling flask, where they were recondensed with the ether–carbon dioxide mixture. The liquid was allowed to distil back to the receiver in the same manner, this process was repeated several times, and with the liquid finally frozen out in the distilling flask the latter was sealed off from the calcium chloride tube. The amount of liquid dimethyl-triazene was about 1.5 cc. Air was then let into the system at a pressure of 75 mm. and the liquid was slowly distilled into the second receiving flask, which was cooled as before to −78°. During the distilla-

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[1] Ramsperger and Tolman, *Proc. Nat. Acad. Sci.*, **16**, *6* (1930)

[2] Schumacher and Sprenger, *ibid.*, 16, 129 (1930)

[3] Dimroth, *Ber.*, 39, 3905 (1906).

[4] Fischer, *ibid.*, **17**, 641 (1884).

tion a glycerin bath served to control the temperature of the distilling flask, and water was run into the condenser around the reflux column to insure careful fractionation. About three drops of a liquid which did not solidify at −78° came over below 40°. These were pumped out and rejected. With the exception of the last several drops, which were also rejected, the remainder of the liquid boiled between 43.0 and 43.1° under 75 mm. pressure. The distilling flask was finally sealed off from the receiver. The solid in the receiving flask melted fairly sharply at about −12.0° to give a perfectly clear, colorless liquid. In order to free the dimethyl-triazene from any dissolved air. the liquid was distilled into the top of the container by means of a bath of solid carbon dioxide and the flask was evacuated. This process was repeated several times. The sample was used for the rate determinations without further treatment.

Nature of Reaction

When dimethyl-triazene is completely decomposed at constant volume, the final pressure is 2.175 times the initial pressure. This fact, together with a titration for basic constituents and some freezing-out data, make possible a rough estimate of the reaction products.

The gas resulting from the complete decomposition of dimethyl-triazene was collected in a 120-cc. bulb at 9.60 cm. pressure. A tube sealed to the bottom of the bulb was surrounded with baths at various temperatures and the pressure was read on an attached mercury manometer. The following readings (corrected for the lower temperature of the gas in the cold bath) were obtained.

t, °C.	P, cm.	% Uncondensed
20	9.60	100
−20	9.05	94
−79	6.80	71
−111	6.25	65
−183	5.25	55

Titration with 0.01 N hydrochloric acid and phenolphthalein showed that 29.6% of the gas was basic, assuming one equivalent of acid per mole of base.

When dimethyl-triazene spontaneously decomposes it may be expected to break up into various radicals which may combine with one another or react with one another so as to give the reaction products. We shall try to represent the reaction products which seemed likely to form from such a process by stoichiometric equations and then test these equations with the above data.

$$\text{(a)}\quad 0.82\ CH_3—N{=}N—NHCH_3 = 0.82\ N_2 + 0.41(CH_3)_2NH + 0.205\ C_2H_6 + 0.205\ CH_3—NH—NH—CH_3$$

$$\text{(b)}\quad 0.18\ CH_3—N{=}N—NHCH_3 = 0.18\ CH_4 + 0.27\ N_2 + 0.09\ C_2H_6$$

$$\text{(c)}\quad 0.18\ CH_3—N{=}N—NHCH_3 = 0.18\ C_2H_6 + 0.27\ N_2 + 0.09\ H_2$$

The number of moles in each equation (0.82 and 0.18) has been so chosen that a combination of equation (a) with (b) or of (a) with (c) will give the correct ratio of final to initial pressure. Equation (a) gives some dimethylhydrazine (supposedly by a combination of two CH_3NH radicals) and thus accounts for the gas which freezes out at −20°. With phenolphthalein it would neutralize an equivalent of acid and together with the $(CH_3)_2NH$ accounts for 27% of the gas which is nearly equal to the 29.6% observed. The combination of (a) with (b) gives 58% non-condensable with liquid air ($N_2 + CH_4$), while (a) with (c) gives 54% ($N_2 + H_2$), both of which are close to the value found (55%). Evidently no choice can be made between (b) and (c). It is not claimed that the agreement found with these stoichiometric equations is a very accurate description of the nature of the reaction.

Apparatus and Procedure

The rate of decomposition was followed by the increase in pressure at constant volume. The 250-cc. Pyrex reaction flask was placed in an oil-bath the temperature of which was automatically controlled to 0.05'. The thermometer used was calibrated against a Bureau of Standards thermometer.

In the high-pressure runs Nos. 39 to 50 the supply bulb was connected to a metal stopcock of the Bodenstein type,[5] which was connected directly to the cell. One arm of a mercury U-trap was sealed to this connecting tube and the other arm led to the high-vacuum line. The stopcock and mercury trap were surrounded by a cardboard structure containing a glass window. Warm air was circulated through this structure so as to maintain a temperature of about 50°. This was necessary to prevent condensation of dimethyl-triazene in the system outside the thermostat. The volume outside the thermostat was at most 1% of the total volume. In making a run the cell was evacuated to about 1×10^{-5} mm., mercury was let up into the trap, the desired amount of gas let into the reaction vessel through the metal stopcock and the stop watch started. The pressure in the U-trap was read immediately and at intervals during the course of the run.

The low-pressure measurements were made with a clicker system.[6] The supply was connected to an ordinary vacuum stopcock. This led to one arm of a mercury trap, the other arm of which was connected directly to the cell. A lead to vacuum was sealed in about 3 cm. above the bottom of the U-tube on the reaction vessel side. This lead had a stopcock separating it from the vacuum line. The clicker of about 0.5-cc. capacity and having a click constant of 0.150 cm. pressure was sealed by a small tube to the reaction vessel. A larger tube fitting around the clicker, and sealed to it by *a* ring seal at its base, was connected to a McLeod gage of 130-cc. capacity and to a number of capillary tubes. By evacuating through these capillary tubes it was possible slowly to change the pressure on the clicker as the critical clicking pressure was approached. Air could be let in through another capillary to reset the clicker. The limit of accuracy of this pressure measurement system was the reproducibility of the clicker,

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[5] Bodenstein and Dux, *Z. physik. Chem.*, 85, 305 (1913).

[6] Smith and Taylor, THIS JOURNAL, 46, 1393 (1924).

which appeared to be better than 0.001 cm. The outside volume was less than 1% of the total volume of the reaction vessel. After letting the desired amount of gas into the reaction cell the mercury was raised in the U-trap and the air pressure surrounding the clicker was adjusted to get the click. Due to the fact that a short time was required to obtain the first click it was necessary to extrapolate the pressure readings back to zero time. The extrapolation was usually only about 2 to 3%, even at the higher temperatures. A similar extrapolation was sometimes necessary for the high pressure experiments.

Experimental Data

The partial pressure of dimethyl-triazene (P_T) was calculated for each reading by the expression $P_T = (2.175P_0 - P)/1.175$, where P_0 is the initial pressure at zero time and P is the total pressure at that reading. The factor of 2.175 is required because the final pressure is 2.175 times the initial pressure. First order rate constants were calculated by the interval method, that is, by using the equation

$$k_1 = \log_{10} P_{T_t}/P_{T_{t'}} \times 2.303/(t' - t)$$

where P_{T_t} is the partial pressure of dimethyl-triazene at time t, and $P_{T_{t'}}$ is its partial pressure at the following reading taken at time t'. First order

TABLE I

DATA FOR RUNS

Run number 17; $P_{final}/P_0 = 2.175$; $T = 210.0'$; $P_0 = 0.2340$ cm.

p, cm.	P_T	t, sec.	$k_1 \times 10^4$ (sec.$^{-1}$)
0.2340	0.2340	0	
.2410	.2280	120	
.2648	.2078	645	1.76
.2935	.1835	1510	1.38
.3128	.1670	2190	1.39
.3298	.1525	2865	1.35
.3623	.1250	4380	1.41
.3815	.1088	5415	1.37
.4010	.0915	6675	1.37
.4348	.0560	9750	1.59
.5090	.0000	∞	

Run number 35; $P_{final}/P_0 = 2.175$; $T = 200.0°$; $P_0 = 2.987$ cm.

p, cm.	P_T	t, sec.	$k_1 \times 10^5$ (sec.$^{-1}$)
2.987	2.987	0	
3.087	2.902	290	
3.550	2.508	1710	10.25
4.006	2.119	3360	10.21
4.438	1.752	5320	9.71
4.791	1.451	7290	9.56
5.106	1.187	9340	9.80
5.400	0.937	12060	8.68
5.700	0.682	15300	9.78

TABLE I (*Concluded)*

Run number 31; P_{final}/P_0 = 2.175; T = 230.0"; P_0 = 0.0400 cm.

p, cm.	P_T	t, sec.	k_1 × 104 (sec.$^{-1}$)
0.0400	0.0400	0	
.0413	.0389	75	
.0475	.0336	635	2.62
.0528	.0291	1070	3.28
.0571	.0254	1600	2.58
.0619	.0214	2185	2.94
.0663	.0176	2855	2 88
.0711	.0135	3600	3 57
.0750	.0107	4595	2.79

rate constants were calculated for from five to twelve intervals so chosen as to give nearly equal pressure increases and until decomposition was 70 to 80% complete. The complete data of three typical runs are given in Table I.

In Table II is a summary of all of the runs with the exception of the first thirteen and runs 45 to 48, inclusive.

TABLE II

SUMMARY OF ALL RUNS

Number	Temp., °C.	Initial press., cm.	Number of constants	Average deviation	k_1 (sec.$^{-1}$)
35	200.0	2.987	7	0.31 X 10^{-5}	9.71 X 10^{-5}
36	200.0	1.595	6	.56	9.98
37	200.0	0.2995	8	.21	6.62
34	200.0	.1464	6	.24	5.19
38	200.0	.0794	8	.23	4.27
33	200.0	0317	5	1.08	4.15
18	210.05	1.520	11	0.14 X 10^{-4}	2 07 X 10^{-4}
16	210.0	0 956	9	.12	1.97
19	210.05	0.5825	12	.10	1.70
17	210.0	.2340	8	.11	1.45
21	219.9	1.520	7	.21	4.03
20	219.9	0.2620	10	.17	2.60
14	225.4	.763	7	.21	4.54
15	225.4	.111	5	.26	3.06
26	230.0	2.946	9	.42	8.35
25	230.0	1.505	6	.27	8.62
24	230.0	0 683	7	.26	7.40
29	230.0	.2945	7	.50	6.25
23	230.0	.2500	7	.26	5.23
27	230.0	1652	6	57	6.05
28	230.0	0980	7	.34	4.59
22	230.0	0560	4	.16	3.44
31	230.0	.0400	7	.24	2 95
32	230.0	0296	5	.24	2.88
30	230.0	.0192	5	.23	2.93

TABLE II *(Concluded)*

New Compound

Numher	Temp , °C.	Initial press , cm.	Number of constants	Average deviation	k_1 (sec.$^{-1}$)
44	200.0	4.84	8	0 99 $\times 10^{-5}$	9 12 $\times 10^{-5}$
43	200.0	2.10	7	1.01	9 28
42	230.0	8.00	4	0.62 $\times 10^{-4}$	7.02 $\times 10^{-4}$
41	230.0	2.25	5	1 01	6.71
40	230.0	2.18	4	1.54	7.03
39	230 0	1.75	4	0.59	7.11
Added Surface 11.5 Times Original					
49	200.0	2.46	5	1.05 $\times 10^{-5}$	8.93 $\times 10^{-5}$
50	230.0	2 24	7	0.87 $\times 10^{-4}$	7.09 $\times 10^{-4}$

The first thirteen preliminary runs were carried out with an impure sample and a rough method of following the pressure. They differed but little from the later runs. Runs 45 to 48 will be discussed later.

While no trend in the constants during a given run was common to all of the runs, there seems often to have been a slightly higher rate at the start of the run as shown by run 17.

In runs 45 to 50 the surface was increased by adding Pyrex tubing, thus increasing the surface to volume ratio by 11.5 fold. The first run made after introducing the extra surface (Run 45) was 12% higher in rate but this effect disappeared gradually during the next three runs and then the rate constants were identical with runs made without extra surface. Earlier preliminary runs had likewise shown that opening the cell to the air or washing it out gave a slightly higher rate for the next two or three runs, so that apparently some conditioning of the surface or removal of impurities was necessary to eliminate catalysis completely. We conclude that the reaction rates reported were not influenced by the extent of wall surface and that the reaction is therefore homogeneous.

Runs 39 to 50 were made with a different sample of dimethyl-triazene and were made with the arrangement of apparatus described for the high-pressure measurements, while all the others reported were made with the low-pressure arrangement. Although the initial pressure to final pressure ratio was uniformly 2.175 for the first sample, it was not constant for these later runs but varied from 2.06 to 2.19. The experimental accuracy was not quite as good and they are all uniformly lower in rate than the earlier runs at similar pressures. It seems likely that this sample was impure. The metal stopcock became discolored and may have affected the sample. These runs show, however, that the first order rate constant has become independent of pressure above about 1 cm.

Interpretation of the Data

This reaction has the same characteristics as many other unimolecular reactions, namely, a true first order rate only at high pressures and a falling of the first order rate constant at lower pressures. In Fig. 1 is plotted the log of the rate constant against the reciprocal of the absolute temperature. Only the rate constants at the higher pressures where the first order rate is independent of pressure have been used in this plot. Prom the slope of the best straight line through the points we find for the heat of activation Q = 33,800 cal. per mole. The equation for the high pressure rate constant is given by the expression $k_\infty = 4.05 \times 10^{11}e^{-33,800/RT}$

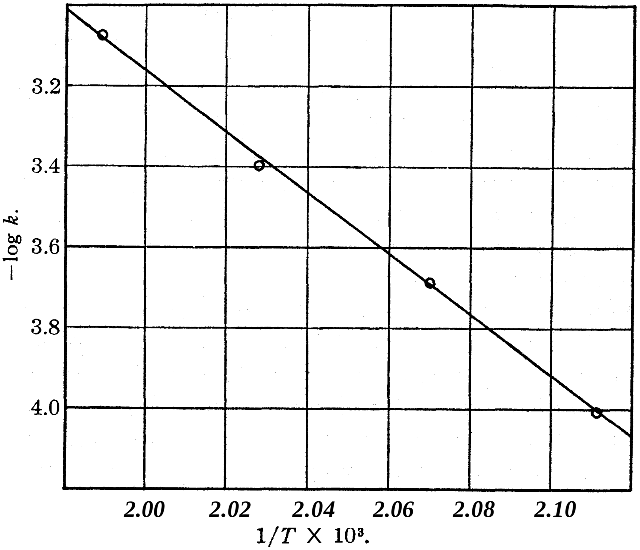

Fig. 1.

Figure 2 shows the usual plot of log k/k_∞ against log P. The curves are theoretical and the points are the experimental values for the runs at 200 and 230° with the first sample. The lower curve is for Theory I and the upper two curves are for Theory II.[7] The uppermost curve is for 200° and the other one close to it is for 230°. The number of squared terms chosen to fit the data best was 14 and the diameter of the molecule 10.0 X 10^{-8} cm. for Theory I and 6.0 X 10^{-8} cm. for Theory II. For Theory I the critical energy ϵ_0 is 39,800 cal. per mole and for Theory II $\epsilon_0 = 33,300$ cal. per mole. It is evident that it is not possible to decide definitely between the two theories on the basis of the data shown.

Discussion

During the past six years the experimental data on unimolecular reactions have been increased from one single reaction, namely, the decomposition of nitrogen pentoxide, to at least thirteen reactions that are

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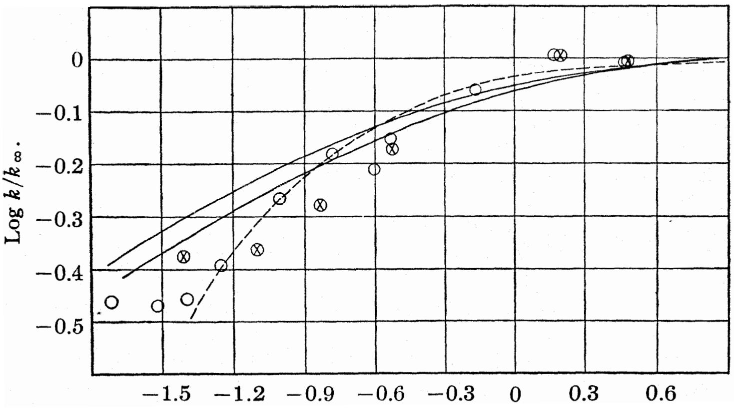
[7] Rice and Ramsperger, THIS JOURNAL, 49, 1617 (1927).

now definitely recognized as being of this type. These reactions are listed in Table III. The pressure and temperature range over which they have been investigated are given and the constants in the rate expression $k_\infty = Ae^{-Q/RT}$ are listed. The values given for n designate the number of squared terms required to fit the data with either Theory **11**[7] or Theory III.[8] Ordinary kinetic theory diameters are used throughout.



Log P,,.

Fig. 2.

All but three of these thirteen reactions show a falling off in rate at low pressures. Of these three, ethylene oxide and pinene have not been investigated at sufficiently low pressures and azoisopropane is sufficiently complex a molecule that it is not required that its rate of decomposition fall off until very low pressures **are** reached. Thus from a qualitative point of view the experimental data are in complete accord with the present theoretical method of treatment. Furthermore, with the possible exception of the decomposition of nitrogen pentoxide, there is no quantitative disagreement with Theories II or III or their modified quantum treatments. As Kassel[9] has indicated, it is possible even to account for the rate of decomposition of nitrogen pentoxide if one uses Kassel's quantum treatment[10] and permits the use of a vibrational specific heat of at least 20 cal./mole and a molecular diameter of 17 X 10^{-8} cm. There are no specific heat data for nitrogen pentoxide but it seems likely that 20 cal./mole of vibrational specific heat will be found too high. In this connection it must be remembered that the requirement of an exact numerical agreement can be carried too far, since any actual molecule is not exactly of the type postulated either by the classical or quantum theory.

[8] **Kassel, J.** *Phys. Chem.,* **32, 225 (1928).**

[9] **Kassel, THIS JOURNAL, 52, 3972 (1930).**

[10] **Kassel,** *J. Phys. Chem.,* **32,** *1065* **(1928).**

TABLE III

DATA FOR UNIMOLECULAR REACTIONS

Substance reacting	P, cm.	T, °C.	4	Q, cal./mole	n
C_2H_5CHO[11]	2.0 to 40.0	450 to 600	$>1.38 \times 10^{12}$	54000	11
$C_2H_5—O—C_2H_5$[12]	2.5 to 50.0	426 to 588	$>3.09 \times 10^{11}$	53000	6–8
$CH_3—O—CH_3$[13]	3.0 to 90.0	422 to 552	1.52×10^{13}	58500	11–12
$CH_3—O—C_2H_5$[14]	2.6 to 54.0	386 to 460	$>9.23 \times 10^{11}$	47000	9
$CH_3—O—C_3H_7$[14]	2.2 to 33.6	400 to 450	$>2.21 \times 10^{12}$	49000	12
$CH_3—N{=}N—CH_3$[15,16]	0.026 to 70.79	278 to 327	1.07×10^{16}	51200	25
$CH_3—N{=}N—C_3H_7$[17]	0.0058 to 13.12	250 to 332	2.80×10^{15}	47480	33
$C_3H_7—N{=}N—C_3H_7$[18]	0.025 to 4.60	250 to 290	5.6×10^{13}	40900	>40
$CH_3—N{=}N—NHCH_3$[19]	0.019 to 8.0	200 to 230	4.05×10^{11}	33800	14
d-Pinene[20,21]	17.0 to 116.0	184 to 237	5.40×10^{14}	43700	>20
Ethylene oxide[22]	2.4 to 90.5	378 to 445	9.9×10^{12}	52000	>14
N_2O_5[23,24,25]	0.00056 to 70.0	0 to 65	4.5×10^{13}	24700	30^9
N_2O[26,27]	8.1 to 800	560 to 667	4.0×10^{9}	53000	2

The mass of evidence so far presented indicates strongly that activation is by collision and that reaction occurs when the critical energy becomes localized in a particular part of the molecule.

Summary

The thermal decomposition of dimethyl-triazene has been studied at temperatures from 200 to 230° and at pressures of 0.019 to 8.0 cm.

The reaction has been found to be homogeneous and first order at high pressures, but the rate begins to decrease at pressures below about 1 cm. and has dropped to about one-third of the high pressure value at the lowest pressures studied. The high pressure rate constant is given by the expression $k_\infty = 4.05 \times 10^{11}e^{-33,800/RT}$.

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[11] Hinshelwood and Thompson, Proc. Roy. *Soc.* (London), **A113,** 221 (1926).

[12] Hinshelwood, ibid., A114, 84 (1927).

[13] Hinshelwood and Askey, ibid., **A115,** 215 (1927).

[14] Glass and Hinshelwood, *J. Chem. Soc.*, 1805 (1929).

[15,16] Ramsperger, THIS JOURNAL, 49, 912, 1495 (1927).

[17] Ramsperger, ibid., 51, 2134 (1929).

[18] Ramsperger, ibid., 50, 714 (1928).

[19] Ramsperger and Leermakers, *ibid.*, 53, 2061 (1931).

[20] D. F. Smith, ibid., 49, 43 (1927).

[21] Kassel, *ibid.*, 52, 1935 (1930).

[22] Heckert and Mack, ibid., 51, 2706 (1929).

[23] Daniels and Johnson, ibid., 43, 53 (1921).

[24] Ramsperger and Tolman, Proc. *Nat.* Acad. *Sci.*, 16, 6 (1930).

[25] Schumacher and Sprenger, ibid., 16, 129 (1930).

[26] Volmer and Kummerow, *Z. physik. Chem.*, **9B,** 141 (1930)

[27] Nagasako and Volmer, *ibid.*, **10B,** 414 (1930).

The data can be fitted equally well by either Theories I or II of Rice and Ramsperger by using fourteen squared terms.

A table summarizing the present data on unimolecular reactions is given and discussed.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE TEMPERATURE COEFFICIENT OF THE THERMAL DECOMPOSITION OF AMMONIA ON PLATINUM

BY J. K. DIXON[1]

RECEIVED FEBRUARY 27, 1931 PUBLISHED JUNE 8, 1931

The heat of activation of the thermal decomposition of ammonia on the surface of a number of metals is about 40,000 to 50,000 calories per mole up to 800°. In particular, Kunsman has found this to be true for tungsten, molybdenum, nickel, iron and supported iron catalysts.[2] The same value was found for a copper catalyst.[3] At pressures below 25 mm. Schwab and Schmidt found 44,000 calories per mole for platinum; but above 25 mm. the value observed was 144,000.[4] No intermediate values for the heat of activation were observed. Since facilities were at hand it seemed well worth while to confirm or correct this abnormally high temperature coefficient.

Experimental

Experiments were carried out by a dynamic method which has been described.[3] The only changes made were in the catalyst and the tube which held the catalyst. A platinum wire gauze was made into a small roll, 6 cm. long, and placed in a fused quartz tube of 10-mm. bore. The platinum wire was 0.010 cm. in diameter and its total apparent surface 310 sq. cm. This catalyst approximates that used by Schwab and Schmidt. The quartz tubing was connected to the rest of the apparatus by means of graded quartz–Pyrex seals. The rate of decomposition of ammonia on this catalyst was determined in the way previously described, with and without added hydrogen or nitrogen, at the temperatures 776, 826 and 858".

Results

A summary of a number of typical experiments is given in Table I. The first column gives the number of the experiment; the second the barometric pressure in centimeters of mercury; the third, fourth and fifth

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[1] National Research Council Fellow.

[2] Kunsman, THIS JOURNAL, 50, 2100 (1928); 51, 688 (1929); see also Elod and Banholzer, *Z. Elektrochem.*, 32, 555 (1926).

[3] Dixon, THIS JOURNAL, 53, 1763 (1931)

[4] Schwab and Schmidt, *Z. physik. Chem*, B3, 337 (1929)

columns give the inlet flow rates of ammonia, nitrogen and hydrogen, respectively, each in cc. per minute reduced to 25° and 760 mm.; the sixth column gives the percentage decomposition in passing through the catalyst tube; the seventh, the temperature in degrees centigrade; and the eighth column gives the velocity constant. The constants were calculated according to the assumption that the rate of decomposition was proportional to the ammonia partial pressure and independent of the pressure of hydrogen and nitrogen. That is

$$k = (v'_N + v'_H + 2v') \ln \frac{v^1}{v_f} + v_f - v'$$

where v'_N, v'_H and v' are the inlet flow rates of nitrogen, hydrogen and ammonia, respectively, and v_f is the outlet flow rate of ammonia.[3] The small changes in barometric pressure were neglected.

TABLE I

THE RATE OF DECOMPOSITION OF AMMONIA ON PLATINUM WIRE

Expt.	Barometric pressure, cm.	Inlet NH_3, cc./min.	Inlet N_2, cc./min.	Inlet H_2, cc./min.	% NH_3 decomposed	t, °C.	k
33, 35	76.1	40.4	0.0	0.0	21.50	858	10.6
34	76.0	40.4	.0	25.0	13.80	858	10.2
36	76.2	40.4	.0	14.0	16.90	858	10.9
37	76.1	15.5	.0	14.0	14.15	826	4.7
38	76.1	15.5	.0	0.0	22.65	826	4.4
46	75.6	21.9	.0	.0	29.45	858	8.8
47	75.6	21.9	7.3	.0	28.35	859	10.8
48	75.7	43.4	0.0	.0	16.43	858	8.4
52	75.8	43.4	.0	.0	16.83	858	8.7
53	75.8	43.4	.0	60.5	8.86	858	8.9

Apparently the addition of hydrogen has no effect other than that of reducing the ammonia pressure. With nitrogen present, the rate of decomposition is higher than expected. Since nitrogen reduces both the partial pressure of the ammonia and that of the hydrogen formed by decomposition, we can explain the increased velocity in the presence of nitrogen by assuming that hydrogen actually inhibits the decomposition process. At low pressures of hydrogen the rate of decomposition is inversely proportional to these pressures, but at high pressures the inhibiting effect reaches a constant value and the reaction proceeds as if it were unimolecular with respect to the ammonia. A calculation shows that when the average hydrogen pressure falls below about 10 cm., the constants, according to Equation 1, begin to increase. In between the low and high pressure regions the hydrogen should inhibit in a way which is intermediate between the two extreme cases.[5] Over the length of the catalyst each of the three cases may exist, but the constants, such as are given in Table I,

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[5] Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford Press, p. 196.

are sufficiently comparable and accurate to determine the temperature coefficient of the reaction.

The experiments were complicated because of a small amount of decomposition of the ammonia on the quartz tube which held the catalyst. The area of the quartz surface was 78 sq. cm. At the end of the experiments with platinum, the wire gauze was removed, the tube cleaned with aqua regia, the empty tube sealed to the apparatus again and the amount of decomposition determined. The results are given in Table II.

TABLE II

THE DECOMPOSITION OF AMMONIA ON QUARTZ

Expt.	Barometric pressure, cm.	Inlet NH$_3$, cc./min.	% NH$_3$ decomposed	t, °C.
1, 4	76.9	43.4	2.58	858
2	76.9	43.4	4.72	902
3	76.9	43.4	1.99	826

If hydrogen inhibits the decomposition on quartz, the values of the percentage decomposition due to quartz in Table II would have been even smaller if the platinum had been present. The figures in Table I have not been corrected for the decomposition on quartz.

Since the catalyst showed a decrease in activity during the course of its entire use, the temperature coefficient has been determined from comparable experiments at different temperatures. Table III shows clearly which experiments have been compared, excepting that the runs with added nitrogen have been omitted. The first column gives the experiments from which the constants in columns two, four and six were calculated. The temperatures of the experiments are given at the top of the table and the ratios of the constants for two successive temperatures are given in columns three and five. The inlet flow rate of ammonia is given in the last column.

TABLE III

TEMPERATURE COEFFICIENT OF THE DECOMPOSITION OF AMMONIA ON PLATINUM WIRE

Expt.	t = 772°C. k	Ratio	t = 826°C. k	Ratio	t = 858°C. k	Inlet NH$_3$, cc./min.
23–30	2.4	2.34	5.6	1.75	9.9	30.4
31–36	2.5	2.72	6.8	1.57	10.6	40.4
37-44			4.6	1.71	7.8	15.5
45–47			*5.2*	1.70	*8.8*	21.9
48–53	hi		5.0	1.72	8.6	43.4
Mean		2.53		1.7		

The heat of activation calculated from the temperature coefficient between 772 and 826° is **39,000** calories per mole and between 826 and 858° is **41,000** calories per mole. The average hydrogen pressure increases with the temperature and consequently the calculated temperature coefficients may be slightly low. The heat of activation which was found by Schwab and Schmidt at low pressures was 44,000 calories; hence the agreement is good.

The fact that the temperature coefficient is nearly the same for all metals seems to indicate that the mechanism of the ammonia decomposition is the same on each metal. Since experiments on different metals have not been carried out under comparable conditions, it is fruitless to attempt to find a relation between the velocity of decomposition and the heat of reaction.

Summary

The decomposition of ammonia on platinum gauze has been studied by a flowing method between 772 and 858°. The rate of decomposition is proportional to the ammonia pressure and inversely proportional to the hydrogen pressure. As the pressure of the hydrogen increases, its inhibiting effect reaches a constant value and the reaction proceeds unimolecularly with respect to the ammonia. The heat of activation of the reaction is 40,000 calories per mole. This value is in agreement with those found for a number of other metals.

PRINCETON, NEW JERSEY

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

REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION. IV. THE OXIDATION OF IODINE TO IODATE ION BY HYDROGEN PEROXIDE[1]

BY HERMAN A. LIEBHAFSKY

RECEIVED MARCH 5, 1931 PUBLISHED JUNE 8, 1931

A preliminary study of the reaction

$$I_2 + 5H_2O_2 = 2H^+ + 2IO_3^- + 4H_2O \qquad (1)$$

has led Bray and Caulkins (II) to conclude from the rate law

$$-\frac{dI_2}{dt} = k\,(I_2) \qquad (2)$$

which it obeys in a rather large region of concentrations, that its principal rate-determining steps are the reactions

$$I_2 + H_2O \xrightarrow{k_1} HIO + I^- + H^+ \qquad (3a)$$

and

$$HIO + H^+ + I^- \xrightarrow{k_2} I_2 + H_2O \qquad (3b)$$

which taken together constitute the hydrolysis equilibrium of iodine. They found reasonable agreement between their value of k(k = 0.6 at 25°) and the value of the specific rate for the iodine hydrolysis (k_1 = 0.25 at

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[1] The earlier papers of this series are (a) Bray and Liebhafsky, THIS JOURNAL, 53, 38 (1931); (b) Bray and Caulkins, ibid., 53, 44 (1931); (c) Liebhafsky, *ibid.*, 53, 896 (1931).

25°), which Abel[2] has deduced from another reaction system. In this paper are presented the results of a more extended investigation of Reaction 1. It was hoped that k_1 could be determined as a maximum limiting value of k, and that a study of the variation of k under extreme concentration conditions might cast some light upon the mechanism of the various rapid reactions following the rate-determining steps 3a and **3b.**

When hydrogen peroxide and iodine solutions are mixed[3] with the peroxide in moderate excess, no great change in the concentration of iodine occurs even after several weeks, but the hydrogen peroxide gradually disappears. For the oxidation of iodine to iodate, therefore, such a reaction system passes through an infinite induction period. If the mixture is made acid, this induction period may be greatly shortened; if iodate ion is added also, and in sufficient quantity, the initial delay may be eliminated entirely and iodate is formed. The time then required, at room temperature, for half the iodine to be oxidized is approximately one minute.

Accurate measurements of the rate of this reaction are best undertaken at zero degrees for two reasons: first, the rate at that temperature is low enough to permit of careful manipulation, and, second, the concentration of iodine at the steady state is smaller at zero degrees than at room temperature, so that relatively a larger range of iodine concentrations can be covered before catalytic decomposition of hydrogen peroxide complicates the pure oxidation of iodine. The experimental method employed in following the rate of disappearance of iodine in a given reaction mixture consists simply in withdrawing samples of it at known intervals, "freezing" the reaction by shaking the sample with carbon tetrachloride to extract the iodine, and titrating the iodine thus obtained with thiosulfate solution.

Reagents and Analytical Methods.—C. P. chemicals not further purified were used in all work. Perchloric and iodic acids were used as sources of hydrogen ion. For certain of the experiments requiring a high concentration of both iodine and iodate ion, a solution of iodine and potassium iodate, saturated with respect to both, was employed.

Sodium thiosulfate solutions were standardized through permanganate against sodium oxalate according to the method of Bray and Miller.[4] Sodium carbonate prepared by fusing the pure bicarbonate was the reference substance for all standard acids. The hydrogen peroxide was determined with permanganate; the iodate solutions were standardized iodimetrically.[5] An iodimetric method was used in the determinations of total oxidizing power.

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[2] Abel, *Z. physik.* Chem., 136, 161 (1928). Other references are given in 1a.

[3] For a more comprehensive summary of the reactions which may take place in this system see I, Table I.

[4] Bray and Miller, THIS JOURNAL, 46, 2204 (1924).

[5] A method identical in all essential respects with the method of **this** paper was used by Bray and Livingston [*ibid.*, 50, 1654 (1928)] to determine hydrogen peroxide.

The determination of the iodine in the reaction mixture was carried out according to a method elsewhere described.[6]

Experimental Method

The reaction vessel was a 500-cc. glass-stoppered flask placed in the large Dewar flask which served as thermostat. With finely divided ice in the Dewar, the temperature in the flask was 0.1 ± 0.1°. In all experiments, except in those done to ascertain the effect of the order of mixing the reagents, the peroxide, at 0°, was added to the rest of the reaction mixture, also at 0°, in order to start the reaction. Immediately after the rapid addition of the peroxide, the flask was vigorously shaken; the time of shaking was taken as the initial time for the reaction. Samples were withdrawn in the following manner: fifteen seconds before the minute which was to be the time of the sample, a 20-cc. pipet was placed in the reaction mixture and filled. This volume of reaction mixture was then blown into a separatory funnel having a short, beveled exit tube so that the tip of the pipet was below the surface of the 25 cc. of cold carbon tetrachloride in the funnel. The reaction was "frozen" on the minute by shaking the separatory funnel vigorously enough to insure virtually instantaneous extraction of the iodine. The carbon tetrachloride layer was then run into a 125-cc. glass-stoppered flask containing 50 cc. of distilled water. After the small amount of carbon tetrachloride from a second extraction of the reaction mixture had been added to the flask, it was vigorously shaken in order that the carbon tetrachloride layer might be washed free of iodate and peroxide. After allowing the carbon tetrachloride to settle, the water was carefully poured off, and the washing process twice repeated. Care must be observed in the washing—first, that the flasks are scrupulously clean to prevent adhesion of the carbon tetrachloride; second, that the shaking is not violent enough to emulsify the carbon tetrachloride; and third, that no carbon tetrachloride remains on the surface of the water layer. No correction need be applied for the iodine dissolved in the water since its concentration, assuming equilibrium, will always be proportional to the (I_2) in the carbon tetrachloride layer: the first order rate constant will thus not be affected so long as the volume of carbon tetrachloride, size of sample, amount of water used for washing and similar factors remain the same.

The samples obtained in this manner were titrated with 0.004 N sodium thiosulfate by the method previously mentioned.[6] As the reaction neared completion, the concentration of iodine became so small that samples larger than 20 cc. had to be taken to secure sufficient accuracy in the titration of the iodine; since, at low (I_2)[7] speed in manipulation is less imperative, this could conveniently be done.

Detailed Experimental Results.—The detailed results of several of the rate experiments performed by the above method are shown in Figs. 1 and 2, and Table I. In Fig. 1 (I_2) as ordinate is plotted on semi-logarithmic paper against the time *t*, in minutes, to give a conventional rate plot for a first order reaction. Zero time for each succeeding experiment is placed further to the right to prevent superposition of the curves. Results as concordant as those shown in the plot were obtained only after long practice had improved the experimental technique. The slope of the steepest line through the experimental points (multiplied by 2.3) was taken for the

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[6] Liebhafsky, THIS JOURNAL, 53, 165 (1931).

[7] ( ) denotes "concentration of"; thus, (I_2) is "concentration of iodine." The units, when such are necessary, are moles per liter.

TABLE I

DATA FOR EXPERIMENTS IN FIGURES 1 AND 2

No.	Fig.	(H^+)	(IO_3^-)	(H_2O_2)	k
81	1	0.0268	0.214	0.0038	0.046
82	1	.0134	.214	.0038	.044
83	1 and 2	.0107	.214	.0038	.041
60	1 and 2	.0535	.00022	.103	.0072
78[a]	1	.0535	.214	.00076	.04
32	2	.148	.0142	.112	.019
71	2	.0535	.214	.103	.037
73	2	.0535	.214	.010	.037
74	2	.0535	.214	.0038	.039

[a] Titrations during the next twenty-four hour period gave no indication of a further change in (I_2); k is given by the first four points.

value of k as defined in the rate law (Equation 2) previously established for Reaction 1.

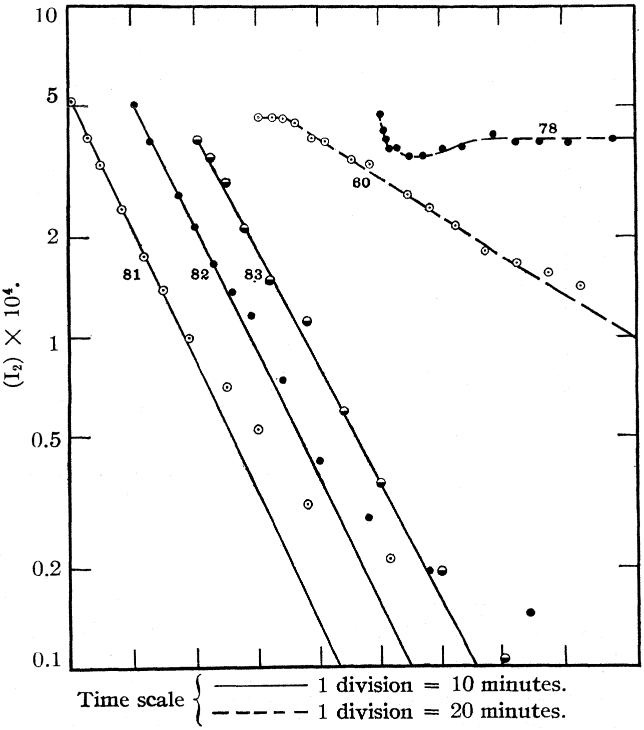

Fig. 1.—Typical experiments. (The plot is on semi-logarithmic paper; for composition of reaction mixtures, see Table I.)

The curves in Fig. 2 represent the dependence of *k* on (I_2) (*cf.* II, Fig. 1) for a number of experiments carried out under various concentration conditions. The values of k for any one experiment were computed from tangents to a smooth curve drawn through the experimental points plotted as in Fig. 1. Because of the erratic nature of many results at low (I_2) (i.e., approximately $5(10^{-5})$ M), this procedure was not generally adopted; even a qualitative interpretation of these results was usually impossible. The behavior of k as the reaction proceeds is typified by Nos. 74 and 83 rather than by the other experiments: *i. e.*, k usually remained constant until 50–75% of the iodine had been consumed, and then decreased. This decrease began at higher values of (I_2) the higher (H_2O_2) (as is shown by Nos. 71, 73 and 74), and the higher (H^+) (as is shown by Nos. 74, 83, 71 and 32). For (IO_3^-) variation no such conclusion could be drawn. We shall revert to this behavior of k in a later section.

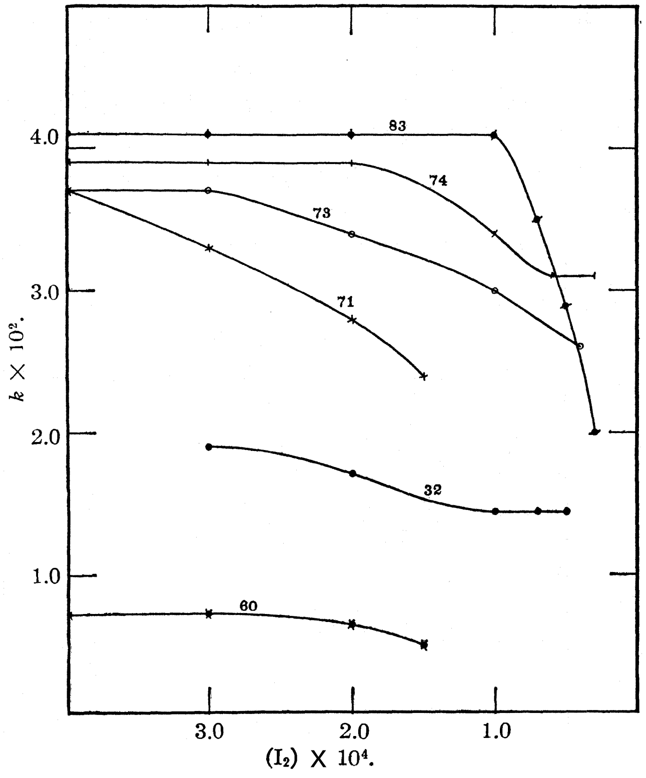

Fig. 2.—Variation of k with (I_2) (see Table I).

It follows at once from the conclusion drawn in 11—namely, that the ***principal*** rate-determining steps for Reaction 1 are Reactions 3a and b—that Equation 2 may be written

$$-\frac{d(I_2)}{dt} = k(I_2) = k_1(I_2) - k_2(H^+)(I^-)(HIO) \tag{4}$$

Were our reaction system a simple one, we should accept as conclusive the close agreement of experiments like Nos. 81, 82 and **83** with a first order rate law, and we should identify the highest (constant) values of k with k_1, the specific rate for the iodine hydrolysis. We should say that k decreases at very low concentrations of iodine because of iodine formation from the Reaction 3b, and that such iodine formation is negligible in the region where k is truly constant. Unfortunately, the complexity of the reaction system precludes the complete acceptance of this simple explanation, and we shall, in a later section, be forced to examine the possibility that Reaction 3b is of importance throughout the entire range of iodine concentrations.

Effect of External Factors on the Reaction.—Experiments designed to reveal any effect on the reaction of either light or glass wool gave conclusive negative results.

Experiments on the effect of different orders of mixing the reagents resulted as follows. If the peroxide was added to an acid iodine solution containing iodate ion (the method of mixing previously described), reproducible results were obtained in all cases where the oxidation of iodine began immediately and was unaccompanied by too much catalytic decomposition of hydrogen peroxide. If an *acid* iodine–peroxide mixture was allowed to stand, and iodic acid added to start the reaction, reproducible results were likewise obtained. If an iodine–peroxide solution is allowed to stand, and iodic acid added as before, there is an increase of iodine (which is caused by oxidation of the iodide ion formed on standing) on mixing; the rate constant in such an experiment was often low. If 30% hydrogen peroxide is added to an iodine solution containing iodic acid, and the reaction mixture is neither stirred nor shaken, the entire rate curve may be altered. (This effect will be mentioned again later.)

Variation of the Rate Constant with Changes in (10,–).—The effect on the rate constant of a variation in the iodate concentration is given in Fig. **3** by Curve I for very low, and by Curve II for moderate, concentrations of peroxide. Whether k has a finite value at zero concentration of iodate ion cannot be settled by our experimental methods for the induction periods at low (IO_3^-) are long enough to permit of some iodate formation.

Curve I shows that the value of the rate constant increases from 0.015 to 0.06 as the iodate concentration is increased from a very small value to that for a saturated solution of potassium iodate; Curve II indicates that k approaches a limiting value, k = 0.03 when the same change is made. If Curve II, which was first established, were the only experimental evidence for the dependence of k on (IO_3^-), we should conclude—in agreement with II and with Abel's results—that k = 0.03 was the value of the specific rate for the iodine hydrolysis at 0°. Curve I, however, does not agree with this simple conclusion. An inspection of the concentration conditions obtaining for the curves will show that, although the acid concentrations differ somewhat, the chief difference lies in the concentration of hydrogen peroxide, which is approximately forty times greater for the experiments on Curve II than for those on Curve I. How this difference in peroxide concentrations may explain the difference in the curves will be mentioned in a later section.

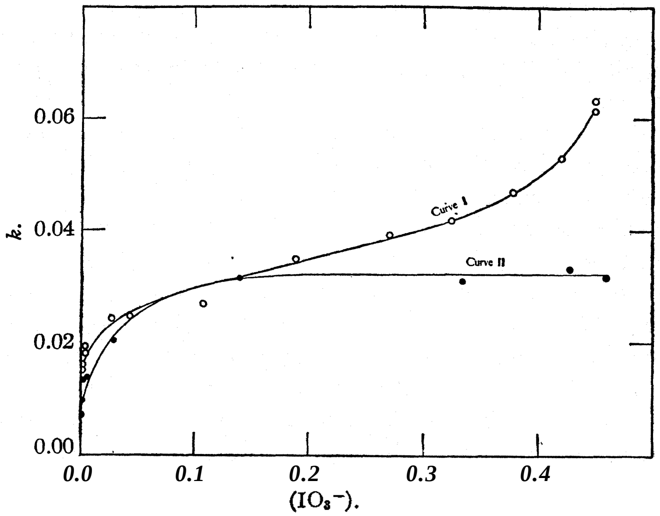

Fig. 3.—*Variation of k* with change in (IO_3^-). Curve *I*, $(H^+) = 0.0268$; $(H_2O_2) = 0.0039\text{-}0.0018$; Curve II, $(H^+) = 0.054\text{-}0.071$; $(H_2O_2) = 0.10$.

The Removal **of Iodide** Ion.—We shall now consider evidence for the assumption that the primary function of IO_3^- is to assist in the removal of the iodide ion formed by the hydrolysis of iodine. Abel[8] and his co-workers, in revising Dushman's[9] work, have shown that the rate law for the oxidation of iodide ion by iodate ion in acid solution is the following

$$-\frac{d(IO_3^-)}{dt} = (IO_3^-)(I^-)(H^+)^2[\kappa f^2 + k'F(I^-) + k''F(I_3^-)] \tag{5}$$

where, at 25°

$$\kappa = 2.4(10^4);\quad k' = 7.6(10^{10});\quad k'' = 5.5(10^{10})$$

(The "f" terms involve activity coefficients.) For the **very** approximate calculation which we shall make, I_3^- will be considered simply as I^- and the factors involving activity coefficients will be neglected. The 25° values of the constants will be changed to corresponding values for 0° by employing the temperature coefficient 1.3 found by Dushman in a region of $(I-)$ where the fifth order reaction is of primary importance.

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[8] (a) Abel and Stadler, *Z. physik. Chem.*, 122, *49 (1926)*; (b) Abel and Hilferding, *Z. physik. Chem.*, 136, *186 (1928)*.

[9] Dushman, *J. Phys. Chem.*, *8,453 (1904)*.

Equation (5) may now be written

$$-\frac{d(IO_3^-)}{dt} = (IO_3^-)(I^-)(H^+)^2[3(10^{10})(I^-) + 1(10^4)] \text{ at } 0^\circ \qquad (6)$$

In order to apply this equation to our reaction system, we must write it to give the number of moles of iodide reacting directly with iodate per minute in a liter of reaction mixture. Since two molecules of iodide are involved in the fifth order reaction, the value $3(10^{10})$ must be doubled. We now have.

$$\text{moles of } I^- \text{ reacting with } IO_3^-/\text{min.} = (IO_3^-)(I^-)(H^+)^2[6(10^{10})(I-) + 10^4] \qquad (6a)$$

The oxidation of iodine through its hydrolysis products to iodate ion requires the oxidation of one mole of I^- and of one mole of HIO for every mole of iodine consumed in Reaction 1. If we now assume that all the I^- which is transformed into iodate reacts first with iodate ion, we may calculate an approximate upper limit for the (I–) in our reaction system; for we may then write

$$-\frac{d(I_2)}{dt} = k(I_2) = \text{moles } I^- \text{ reacting with } IO_3^-/\text{min.} = (IO_3^-)(I^-)(H^+)^2[6(10^{10})(I^-) + 10^4] \qquad (7)$$

Using this equation and the values of k given by Curve I, Fig. **3,** for different values of (IO_3^-), the last column of Table II was computed.

TABLE II

MAXIMUM (I–) IN THE REACTION SYSTEM AT VARIOUS (IO_3^-)

(IO_3)	(H^+)	(H_2O_2)	(I_2)	k	(I^-)
$2(10^{-1})$	0.0268	0.0034	$5(10^{-4})$	0.060	$1.8(10^{-6})$
$1(10^{-2})$	.0268	.0034	$5(10^{-4})$	.020	$4.8(10^{-6})$
$1(10^{-3})$	.0268	.0034	$5(10^{-4})$	.015	$1.4(10^{-5})$
$1(10^{-5})$	.0268	.0034	$5(10^{-4})$	.016	$1.3(10^{-4})$

The (I–) values calculated for the two highest iodate concentrations in Table II are of a reasonable order of magnitude; we shall therefore assume that the chief function of iodate ion is to assist in the removal of iodide ion. If iodide is oxidized to a valence above zero by other substances also, the actual (I–) obtaining in the reaction mixture will be less than that calculated from Equation 7.

When (IO_3^-) decreases below 10^{-2}, however, the (I–) values of Table II become much too large. The value $(I-) = 1.3(10^{-4})$ calculated for $(IO_3^-) = 10^{-5}$ represents an appreciable part of the initial (I_2); this concentration of iodide could never be established in such a reaction mixture, for the iodide initially present from hydrolysis is less than 0.01% of the iodine with which it was in equilibrium, and the amount of iodine disappearing during an induction period is always relatively small. The maintenance of the concentration of iodide ion at a reasonable value in these reaction mixtures therefore requires the action of another oxidizing agent in addition to iodate ion. Hydrogen peroxide is far too slow;[10] but HIO_2 remains as a

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[10] References 12a, 12b, 12c, from Ref. 1a.

logical possibility. We shall assume that, at low (IO_3^-), iodous acid reacts first with the major part of the iodide which is converted finally into iodate. The importance of this reaction at higher (IO_3^-) is uncertain; the greater its importance, the farther will the (I–) of the reaction system be below that calculated from Equation 7.

An examination of the work of Abel and Hilferding[Sb] shows that iodate ion cannot to an appreciable extent oxidize HIO. If this reaction were of importance, they could not have found their simple fourth order rate law for the oxidation of iodide by iodate, since the concentration of HIO in their experiments ((H^+) and (I–) were sensibly constant) must have undergone a concentration variation parallel to that of iodine.

The relation of the curves of Fig. **3** to the value of the specific rate for the iodine hydrolysis will be discussed later.

Catalysis in Relation to the Rate Measurements.—Whenever, in a reaction system involving the action of hydrogen peroxide as an oxidizing agent, that substance acts as a reducing agent also, the catalytic decomposition of hydrogen peroxide will constitute a side reaction taking place in the system. So long as there is no appreciable decomposition of iodine compounds to liberate oxygen, the decrease in the oxidizing power of our reaction mixture will furnish a quantitative measure of the amount of peroxide reduced, which will be half that catalytically decomposed. This method of determining the amount of such catalysis will cease to be accurate when the total oxidizing power is very much greater than the decrease due to such catalysis.

In Table III some of the catalysis results are given. The seventh column shows the amount of catalysis, expressed as an increment of the peroxide concentration, observed for each reaction mixture during the time interval given in the sixth column. In the last column are given the ratios (R's) of this concentration change to the amount of peroxide, equal to $5(I_2)$, which is equivalent in Reaction 1 to the iodine initially present in a liter of reaction mixture.

TABLE III

CATALYSIS RESULTS

No.	(H^+)	(IO_3^-)	$(H_2O_2)10^3$	k	Time, hrs.	$\Delta(H_2O_2)(10^3)$	R
97	0.0268	0.0017	3 9	0.018	20	0.27	0.14
103	.0268	.00108	3.4	(018)	8	.43	.22
104	.0268	.00053	3.4	.015	8	.33	.17
107	.0677	.0142	110	.023	15	4.4	2 2
108	.0677	.0142	560	.0067	7	77	39

In each case $2(10^{-3})$ moles of hydrogen peroxide would be required to oxidize the iodine initially present to iodate; the initial (I_2) was approximately $4(10^{-4})$.

The titrations of oxidizing power carried on during the course of the two experiments involving the largest absolute amounts of catalysis show that the rate of this catalysis diminishes markedly as the concentration of iodine decreases. **A** comparison of Experiment 108 with No. 107 (Table III) shows that a large absolute amount of catalysis brings with it a sharp reduction in k; the iodine formation causing this decrease in k we attribute to the increased rate of Reaction 3b brought about by the higher (I^-) which obtains in the system when the absolute amount of catalysis is large. These low constants at high (H_2O_2) were generally observed and will again be mentioned in a later section. Titration of samples from an initially neutral iodine solution, 0.005 *M* in peroxide, over a period of days showed the catalysis to be proportional to (H_2O_2). The (I_2) of the solution underwent little change during the experiment.

From these facts we conclude that the major part of the catalysis encountered in our reaction system is due to those steady states which Abel[11] has so thoroughly investigated. The fact that this catalytic rate may be made very low shows, according to conclusions presented in Part I, that hydrogen peroxide cannot, in our reaction system, oxidize HIO. Neither can it oxidize the I^- in this system[12] at a rate comparable with the dI_2/dt measured. Since changes in (H_2O_2) do not proportionately alter k (see the section on variation of k with (H_2O_2)), we conclude that hydrogen peroxide cannot oxidize iodine directly with sufficient speed to explain the removal of iodine. Yet for every mole of iodine disappearing by hydrolysis, one mole of I^- and one mole of HIO must be removed. We have, therefore, to devise a mechanism by which the oxidation of iodine to iodate can be accomplished in our reaction system without *appreciable* direct oxidation of either I_2, I^- or *HIO* by hydrogen peroxide, the only oxidizing agent appearing as reactant in the stoichiometric equation for the change.

We have found such a mechanism only by assuming that the fourth order $IO_3^- - I^-$ reaction proceeds as follows

Relatively rapid equilibrium $IO_3^- + I^- + 2H^+ \rightleftharpoons H_2I_2O_3$ (8a)

Rate-determining step $H_2I_2O_3 \longrightarrow HIO + HIO_2$ (8c)

This formulation of the fourth order reaction indicates that $H_2I_2O_3$ decomposes the more readily into iodate and iodide ions. In our reaction system hypoiodous acid is removed as rapidly as it is formed; we shall assume that this removal is accomplished by the reaction

$$HIO_2 + HIO = H_2I_2O_3 \qquad (8b)$$

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[11] For bibliography see 1a. Two differences between Abel's system and ours must here be observed. In the former, much of the HIO must be formed by the oxidizing action of H_2O_2 on I^-; the rate of this step governs the rate of the catalysis. In our system, HIO can be formed from I^- by the action of IO_3^-, HIO_2 and $H_2I_2O_3$; the rate of the catalysis is here governed by the rate at which H_2O_2 reduces HIO at the extremely small concentration obtaining for the latter in this system. Here, also, H_2O_2 may possibly reduce IO_3^-, HIO_2 and $H_2I_2O_3$; these reactions may account in part for the catalysis observed.

[12] See 1a, References 12a, 12b, 12c.

which is the reverse of Reaction 8c. Bray,[13] in correlating a number of halogen reactions, has rendered plausible the assumption of Reaction 8b. In order to accomplish iodate formation, the oxidizing action of hydrogen peroxide need now be assumed only in the reactions

$$H_2I_2O_3 + H_2O_2 = 2HIO_2 + H_2O \qquad (9)$$

and

$$H_2O_2 + HIO_2 = H^+ + IO_3^- + H_2O \qquad (10)$$

If the oxidation of iodine is to proceed, these reactions must be rapid enough to keep $H_2I_2O_3$ at or below the equilibrium concentration for Reaction 8a; this restriction imposes a lower limit on the values we may assume for the specific rates of Reactions 9 and 10 in order that the oxidation of iodine by hydrogen peroxide may take place in the manner above prescribed. Its applicability to this reaction system is strong additional evidence for the mechanism assigned by Bray to the IO_3^-–I^- reaction.

Using measurements made in Experiments 107 and 108, Table III, on the rates of decrease in oxidizing power, we may, on the assumption that all of the hydrogen peroxide is oxidized according to the equation

$$HIO + H_2O_2 = H^+ + I^- + O_2 + H_2O \qquad (11)$$

calculate a value[14] for (HIO) in the reaction system; the value 10^{-8}–10^{-9} M thus obtained sets an upper limit for the concentration of hypoiodous acid.

The Induction Period.—Most of the experiments proceeded without an appreciable induction period; in general, if there was an induction period, it was longer the lower the (IO_3^-), the lower the (H^+) (as is shown in Tables IV and V), and the higher the (H_2O_2). The shape of the induction period curves (Experiment 60, Fig. 1, is an example) shows that it is terminated by an autocatalytic reaction. At low (H^+) (Expts. 17, 19 and 21, Table IV), and high (H_2O_2), it is particularly unreproducible.

A comparison of experiments at low (IO_3^-) shows that the concentration of iodate ion in the system is not, other initial concentrations being con-

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[13] Bray, THIS JOURNAL, 52, 3580 (1930). For purposes of this paper $H_2I_2O_3$ and I_2O_2 may be considered identical.

[14] In Experiment 108, $-dH_2O_2/dt$ in moles/min./liter calculated for Reaction 11 from the decrease in oxidizing power is $4.4(10^{-4})$; in Experiment 107, it is $1.3(10^{-5})$. Taking the value $3(10^4)$ for the specific rate of Reaction 11 at 0° [Abel, Ref. 2, gives $3.3(10^5)$ for this specific rate at 25°; at our acid concentrations (0.01 M and over) the oxidation of H_2O_2 by IO^- may be neglected], we obtain for 108, $(HIO) = 2.6(10^{-8})$, and for 107, $(HIO) = 4(10^{-9})$ on substitution of the (H_2O_2) values from Table III. Using the value

$$K = \frac{(HIO)(I^-)(H^+)}{(I_2)} = 9(10^{-15}) \text{ at } 0°$$

[Grinnell Jones, THIS JOURNAL, 37, 256 (1915)] we find that, at $(H^+) = 2(10^{-2})$ and $(I_2) = 5(10^{-4})$, the limiting value of the product $(HIO)(I^-)$ is $2.3(10^{-16})$. If (I^-) is 10^{-6} in order of magnitude, as the previous section would indicate, (HIO) cannot be above 10^{-10}. This calculation would indicate either that (I^-) of the previous section is too high, or that some of the catalysis does not involve HIO, or both.

stant, the only factor in determining whether or not the reaction is to suffer an induction period, for the amount of iodine disappearing before smooth oxidation begins is, in an experiment such as 106 or 104, Table IV, far less than the amount initially present in an experiment such as 97, Table IV, which also has an induction period. A comparison of the first group of experiments with the second shows how markedly the induction period is lengthened at low (H^+); the experiments in Table V, which were done at room temperature without initial iodate, show this also.

TABLE IV

LENGTH OR INDUCTION PERIOD IN VARIOUS RATE EXPERIMENTS

No.	(H^+)	(IO_3^-)	(H_2O_2)	k	**Induction period**
57	0.0546	0.00109	0.103	0 0133	8 min.
59	.0540	.00055	.103	.0096	24 min.
60	.0537	.00022	.103	0081	22 min
61	.0535	.000035	.103	.0081	31 min.
93, 94, 95, 96	.0268	.135–0.0135	.002–0.004	.039–0.024	Below 2 min.[a]
97	.0268	.0017	.0038	.018	27 min.
104	.0268	.00053	.0034	.015	Approx. 6 hrs.
106	.0268	None initially	.0034	.016	Approx. 9 hrs.
17	.0142	.0142	.112	.017	44 min.
19	.0142	.0142	.112	[b]	8 hrs.
21	.0142	.0142	.112		2 hrs.
35	.0677	.0142	.056	.021	None
30	.0677	.0142	.065	.015	10 min.[c]
28	.0677	.0142	.065	.015	12 min [c]

[a] The (IO_3^-), (H_2O_2) and k values for these experiments are concordant and lie within the limits given. [b] No rate constants obtained in these two experiments. [c] 30% hydrogen peroxide allowed to remain in contact with reaction mixture for several minutes without shaking; irregular induction often encountered at high (H_2O_2).

TABLE V[a]

INDUCTION PERIOD EXPERIMENTS WITHOUT INITIAL IODATE ION

(H^+)	(H_2O_2)	**Induction period**
0.9	0.005	8 hrs.
.2	.005	9 hrs.
.02	.005	14-21 hrs.[b]
.004	.005	8-11 days[b]
.0004	.005	m[c]
Neutral	.005	∞[c]

[a] These experiments were carried out at room temperature. [b] Induction period within these limits. [c] These experiments will be mentioned in the section on mechanism.

Since an induction period is usually required to establish the necessary concentrations of those intermediate products essential to a reaction, it is logical here also to ascribe the initial delay to this cause. We shall assume that an induction period is necessary to build up the concentration of HIO_2 requisite to the oxidation of iodine. This assumption is entirely in accord with our previous conclusion that at low (IO_3^-) HIO_2 oxidizes a large part of the iodide ion converted finally into iodate, for every experiment with $(IO_3^-) = 0.001$ *M* or less suffered an induction period.

The building up in the reaction system of appreciable concentrations of HIO_2 entails the lowering of (I^-); for if (I^-) is relatively high, the iodide ion will by reduction remove the first named substance. For this reason any factor tending toward either an increased initial (I^-) (*e.* g., low H^+), or an incomplete removal of I^- (again low (H^+), and low (IO_3^-)), or an increased formation of I^- (such as increased catalysis in which Reaction 11 is concerned) tends to lengthen the induction period.

In a system so complex that a large number of reactions is possible, the value of the rate constant may depend markedly on what reactions are favored in mixing the reactants. Experiments 35, 30 and 28, Table IV, represent one of two groups in which anomalous results were obtained because the 30% hydrogen peroxide used as a stock solution was left for an appreciable time in contact with the reaction mixture before shaking. Experiments 30 and 28 differ from 35 only in that respect. (The small difference in (H_2O_2) is unimportant since experiments with (H_2O_2) above 0.065 also gave constants of 0.02.) The induction period and the decrease in k which the first two experiments suffered we believe to be due to the large initial catalysis (with its consequent I^- formation) brought about by leaving the 30% peroxide in contact with the reaction mixture for several minutes.

Lower values of rate constants usually accompanied induction periods; if, in duplicate experiments, only one went through an initial delay, that one had the lowest k (e. g., No. 35 as contrasted with Nos. 28 and 30). This behavior was general enough to warrant the belief that the subsequent (I^-) concentration in an experiment with induction period was higher than it would have been had the smooth reaction begun immediately on mixing the reagents.

Because of the extreme unreproducibility of induction periods at high (H_2O_2), no data are given for induction periods of experiments with (H_2O_2) above 0.112 M. We shall say only that, if 30% hydrogen peroxide is added to make a reaction mixture concentrated in that substance, it must be so added as to secure thorough initial mixing; for there may otherwise be a long delay before the oxidation of iodine begins.

The autocatalytic reaction terminating the induction period is, we believe, concerned with the removal of I^-. While an autocatalytic removal of I^- can be accomplished in devious ways, its beginning could well depend on the reaction

$$HIO_2 + I^- + H^+ = 2HIO \qquad (12)$$

which has already been postulated to explain the removal of I^- at low (IO_3^-); assigning this function to Reaction 12 harmonizes with the idea that an induction period is necessary primarily to build up the concentration of HIO_2.

HIO_2 formation through Reaction 9 will explain the fact that the oxidation of iodine proceeds at all when (IO_3^-) is initially very low; if HIO_2 formation only through the IO_3^-–I^- reaction is assumed, no such simple explanation is possible. Building up an appreciable (HIO_2) by the latter mechanism might take months[15] instead of the ten hours or so actually observed. These considerations furnish further evidence for the existence of $H_2I_2O_3$.

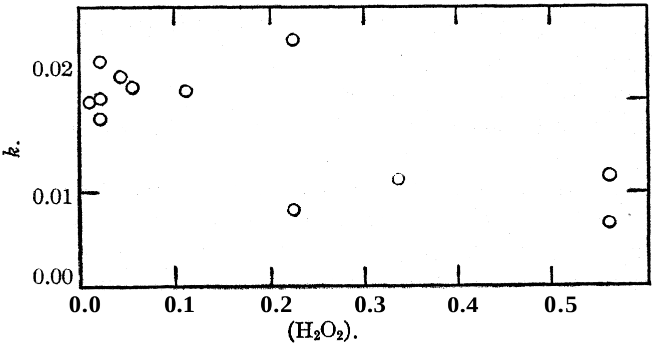

Fig. 4.—Variation of k with change in (H_2O_2). $(H^+) = 0.0677$; $(IO_3^-) = 0.0142$.

Variation of the Rate Constant with (H_2O_2) and (H^+).—The behavior of k as (H_2O_2) is changed is shown in Fig. 4, as (H^+) is changed, in Fig. 5. The curves show definitely that, for a rather large concentration range ((H_2O_2) from 0.01 to 0.56 *M*; (H^+) from **0.015** to 0.9 **M**) neither hydrogen peroxide nor hydrogen ion exerts on the rate of Reaction **1** an effect proportional to the change in concentration. The figures show, however, that increasing (H_2O_2) or (H^+) does result in a lower value of k. In experiments at the higher concentrations of acid, k often fell off to a reasonably constant lower value as the reaction proceeded; for such experiments both the higher and the lower values are plotted in Fig. 5—the lower value is indicated by a dot.

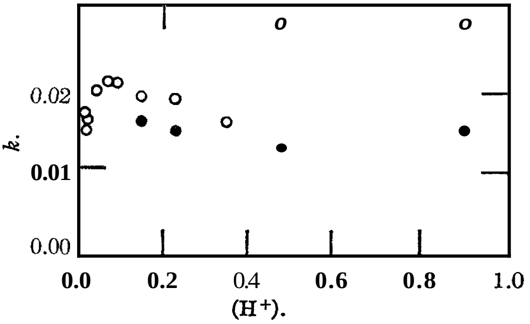

Fig. 5.—Variation of k with change in (H^+). ○, Earlier part of run, or complete run; ●, middle part of run.

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[15] At $(IO_3^-) = 10^{-8}$, $(I^-) = 10^{-6}$, $(H^+) = 2(10^{-2})$, dI^-/dt calculated from Equation 6 is $3(10^{-13})$ moles/liter/min.

The tendency for k to decrease in a run, causing the experimental points to diverge from straight lines (*cf.* Figs. 1 and 2, especially Expts. 32, 73 and 71 in the latter figure) is probably related to the lower values of k obtained at high (H^+) and high (H_2O_2). Both effects can be explained in terms of iodine formation through Reaction 3b; k will remain constant as long as this iodine formation remains proportional to (I_2), and k will become smaller when such iodine formation becomes relatively greater. These effects are found at high (H^+) because hydrogen ion is involved in Reaction 3b, and at high (H_2O_2) because catalytic decomposition of the peroxide brings about iodine formation in a manner already explained (see the section dealing with catalysis).

Results obtained in experiments where the initial (H_2O_2) was insufficient for the complete oxidation of I_2 are of interest. Experiment 78, Fig. 1, has a reaction curve typical for such experiments. The fact that the initial portions of the curves for these experiments are straight lines show that k is independent of (H_2O_2) even to very low concentrations of that substance. The peculiar character of the reaction curve after the initial straight line portion is doubtless due to a readjustment of the intermediate iodine compounds in the system.

Mechanism of the Oxidation.—The foregoing sections have served to indicate certain reactions which may be assumed to explain the oxidation of iodine to iodate ion by hydrogen peroxide. The mechanism which has been devised to explain the empirical fact that iodine is oxidized to iodate ion in our reaction system must explain, qualitatively at least, the diverse experimental results obtained and be in harmony with past work on the chemistry of iodine. This mechanism will now be summarized.

Rate-determining step $I_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H^+ + I^- + HIO$ **(3a and b)**
Iodide removal $IO_3^- + I^- + 2H^+ = H_2I_2O_3$ (8a)
Oxidation to HIO_2 by H_2O_2 $2(H_2I_2O_3 + H_2O_2 = 2HIO_2 + H_2O)$ (9)
Oxidation of HIO $HIO_2 + HIO = H_2I_2O_3$ (8b)
Iodate formation $3(HIO_2 + H_2O_2 = IO_3^- + H^+ + H_2O)$ (10)
Main reaction (sum of above) $I_2 + 5H_2O_2 = 2IO_3^- + 2H^+ + 5H_2O$

I^- removal is accomplished also by

$$HIO_2 + I^- + H^+ = 2HIO \qquad (12)$$
$$H_2I_2O_3 \text{ (or } I_2O_2 + H_2O) + I^- = I_3O_2^- + H_2O \text{ (See Ref. 13)}$$

I^- formation is accomplished also by

$$HIO + H_2O_2 = H^+ + I^- + H_2O + O_2 \qquad (11)$$

I_2 formation is accomplished only by

$$H^+ + I^- + HIO = I_2 + H_2O \qquad (3b)$$

We may explain finally in terms of this mechanism why iodine is reduced to iodide by hydrogen peroxide, in dilute acid solution (below $4(10^{-3})$ *N*) although that same oxidizing agent will convert it to iodate at concentrations of hydrogen ion greater than this. The two last experiments in Table IV show an infinite induction period with respect to iodate formation because at this low (H^+) the iodide formed by the Reaction 11 cannot be effectively removed, and continues to accumulate until the "main" reaction occurring in the system is the catalytic decomposition of hydrogen peroxide by the I_2–I^- couple. When all the peroxide has been thus decomposed, the system consists of I_2, $\underline{H}^+$, $\underline{I}^-$ and HIO, with the substances underlined present at higher concentrations than obtain in an aqueous iodine solution.

As (H^+) is increased, the formation of $H_2I_2O_3$ in the second stage of the reaction mechanism is favored. When the $(H_2I_2O_3)$ has been thus sufficiently augmented to permit of the establishment of the (HIO_2) essential to iodate formation, the iodine will, by the action of hydrogen peroxide, be converted to iodate instead of to iodide ion.

The Specific Rate of Iodine Hydrolysis.—Although the preceding sections have yielded a plausible mechanism for the oxidation of iodine by hydrogen peroxide, they have not established definitely the specific rate of the hydrolysis of iodine, the rate-determining step in that mechanism. With regard to the value of that constant, two possibilities, now to be sketched, present themselves.

The first of these, and the simpler, would assign to this specific rate the limiting value 0.03 given by Curve II, Fig. 3; the higher values on Curve I must then be attributed to an unknown reaction which consumes iodine and, directly or indirectly, involves iodate ion. Adopting this conclusion, we bring the investigations of Abel and investigations previously carried out in this Laboratory into complete agreement with the present work. We leave unsettled, however, not only the nature of this reaction, but a more troublesome matter as well, namely, why this reaction did not affect the experiments on Curve II; for these experiments differ essentially from the others only in a higher (H_2O_2) 0.1 M compared with 0.0034 M on Curve I.

The other possibility would say that the limiting rate which should be reached at sufficiently high (IO_3^-) had not yet been attained, that iodine formation from Reaction 3b is important at the beginning of an experiment as well as at the end,[16] and that the specific rate of the iodine hydrolysis is, at 0°, much greater than 0.06. The lower results on Curve II would be attributed to iodide formation resulting from the relatively larger amount of catalysis there obtaining. As arguments against this interpretation

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[16] The high values calculated for (I^-) and (HIO) in this reaction system (see footnote 14) support the conclusion that iodine formation from Reaction 3b is never negligible; but it must be remembered that the (I^-) and the (HIO) calculated were both upper limits.

we may mention its disagreement with conclusions of other investigators, the excellent agreement of many experiments in this paper with a first order rate law, and the definite character (which may be fortuitous) of the limiting value approached by Curve II. One argument for this interpretation is the simplicity of the resulting mechanism, for then iodine need be assumed to disappear only in the step

$$I_2 + H_2O \longrightarrow HIO + I^- + H^+ \qquad (3a)$$

and to be formed only in Reaction 3b. Experimental work, principally in other reaction systems, which should eliminate one of these possibilities has been undertaken in this Laboratory. Present indications point to a specific rate for Reaction 3a much greater than 0.6 at 25°, or 0.06 at 0°.

In the course of this investigation, and in the preparation of this paper as well, I have had the benefit of many conferences with Professor William C. Bray, and for these conferences I now wish to thank him.

Conclusion

From an extensive investigation of the oxidation of iodine by hydrogen peroxide, evidence has been adduced for each step in a mechanism involving $H_2I_2O_3$ as one of several intermediate products. While the complexities encountered have precluded the mathematical treatment essential to a definite establishment of this mechanism, the fact that it affords a qualitative explanation of these complexities justifies both its adoption and the further use of $H_2I_2O_3$ as an intermediate step. Since the rate constant for the reaction should approach the specific rate for the iodine hydrolysis as a limit if the latter is the only rate-determining step, its failure to do so at low concentrations of peroxide could not be reconciled with previously measured values of this specific rate.

BERKELEY, CALIFORNIA

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

THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. V. INTERNAL INDICATORS SUITABLE FOR USE IN DIRECT TITRATIONS

BY G. FREDERICK SMITH AND H. H. BLISS[1]

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Introduction

The present paper is the continuation of a series of studies dealing with the extended application of the use of bromates in volumetric analysis.[2] Undesirable features previously associated with the use of bromate in volumetric analysis have been the following: first, that the reduction of bromic acid may take either of two courses, reduction to bromide as in the oxidation of trivalent arsenic or antimony or to free bromine as in the oxidation of ferrous iron or chromic salts, oxalic and nitrous acids; second, that many of the possible applications of bromate in volumetric analysis involve the use of an excess of bromate followed by back titration requiring the undesirable use of an additional standard solution; third, suitable indicators have not been found for bromate oxidation reactions except in the case of the determination of arsenic and antimony, in which case methyl orange and indigo-sulfonic acid are employed which require undesirably high concentrations of hydrochloric acid at temperatures near the boiling point.

The first of these undesirable features has been eliminated by the use of the mercuric ion,[2] which brings about the reduction of bromate to bromide rather than to free bromine as in the cases already cited. The present paper has for its object the elimination of the second and third difficulties by the selection of a number of organic dyes suitable for use as indicators in bromate reactions. Back titrations following the use of an excess of bromate can be shown in various cases to be unnecessary through the use of these new indicators. Cold titrations at lower acid concentrations are possible. By selection of the indicator having the most desirable color transformation the interference of foreign colored ions is eliminated. It is to be observed that the application of the electrometric determination of the end-point would in many cases solve the problems. Visual end-point phenomena are more difficult to devise but are more practical in application.

In subsequent papers of this series, specific applications of the new indicators to individual determinations will be disclosed.

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[1] A portion of the thesis presented by H. H. Bliss in partial fulfilment of the requirements for the Ph.D. degree in the Graduate School of the University of Illinois.

[2] Smith and co-workers, THIS JOURNAL, 45, 1115, 1417, 1666 (1923); 46, 1577 (1924).

Method Used in Selection of Dyes

In the familiar bromate titration of trivalent arsenic or antimony in hot concentrated hydrochloric acid solution using methyl orange as indicator, the end-point reaction consists in the liberation of bromine from the action of the first drop excess of bromate on the hot hydrochloric acid of the solution. Under these conditions the helianthin indicator is destroyed by halogenation and the end-point of the reaction is defined. It is, therefore, logical in the study of possible new dyes for similar bromate reactions to select from that group least "fast" in color when chlorinated. Such use was made of the "Colour Index."[3]

This method of attack was found to be satisfactory after it was learned that a "chlorine fastness" number of 5 indicated too great ease of halogenation and that the red and yellow colors seemed better adapted than colors of the remainder of the spectrum. Quite as certain selections were subsequently made from those dyes unclassified in chlorine fastness by the British Colour Index (wool and silk dyes), using other and more intuitive methods of selection. The list of dyes about to be described is only a small portion of those examined and is not supposed to be an exhaustive one. The selections made, however, are thought to cover a wide range of possible working conditions and to include desirable color changes. With a single exception the color change is from colored to colorless. This naturally follows from the nature of the reaction bringing about the end-point change. The dyes examined and found satisfactory are classified and identified in Table I.

In the data of Table I the first column is given for convenience in referring to the various dyes in the British Colour Index and in the second column the compact formula is given for convenience in referring to the compounds in Beilstein. In column three a common name is given which seems to be quite generally accepted. In most cases it seems best to refer to the indicators by their British Colour Index number. Column four indicates that the chemical classifications most abundantly represented are the mono-azo dyes and those of the triphenylmethane series. Column four indicates the variety of colors to be selected from the various classes of dyes and it is observed that the greatest variety in color is shown by the triphenylmethane class. Chief qualifying characteristics for the various indicators are given in column six. As indicated in column five all the indicators are sufficiently soluble in water and the color produced is not materially affected by the addition of hydrochloric acid. In some cases the depth of color is favorably affected by the addition of hydrochloric acid and in the other cases the color is unfavorably affected. In general those indicators are most desirable which produce the deepest color, since this is less masked by colored ions.

[3] "Colour Index," The Society of Dyers and Colourists, 1924.

TABLE I

NEW INTERNAL OXIDATION INDICATORS FOR USE IN VOLUMETRIC BROMATE REACTIONS

British Colour Index number	Compact formula	Common name	Chemical Classification	Color in water and HCl solution	Remarks
21	$C_{13}H_{15}N_4Cl$	Chrysoidine R	Mono-azo	Yellow-red	Color bleached with reducing agents. Restored at end-point, then destroyed
27	$C_{16}H_{10}N_2O_7S_2Na_2$	Rainbow Orange G	Mono-azo	Orange-yellow	Suitable at moderate P_H and temp.
56	$C_{18}H_{13}N_3O_9S_2Na_2$	Chromotrope 6 B	Mono-azo	Violet red	Bright red to colorless, moderate P_H, low temperature
88	$C_{20}H_{12}N_2O_7S_2Na_2$	Bordeaux	Mono-azo	Red	Suitable at moderate P_H and low temperature
128	$C_{24}H_{14}N_3O_7ClS_3Na_2$	Diamine pink	Mono-azo	Red	Unsuited to low P_H and temp.
184	$C_{20}H_{11}N_2O_{10}S_3Na_3$	Amaranth	Mono-azo	Red	Suitable at moderate P_H and low temperature
185	$C_{20}H_{11}N_2O_{10}S_3Na_3$	Brilliant Ponceau 5R	Mono-azo	Scarlet red	Advantageously resists fading
246	$C_{22}H_{14}N_6O_9S_2Na_2$	Naphthol Blue-black	Di-azo	Blue	Quite satisfactory under ordinary conditions
375	$C_{32}H_{21}N_5O_7S_2Na_2$	Congo Corinth	Di-azo	Red-blue	Satisfactory for moderate P_H and boiling temperature
471	$C_{34}H_{25}N_5O_8S_2Na_2$	Bensoasurin 3 R	Di-azo	Violet	Faint color but satisfactory end-pt.
657	$C_{23}H_{25}N_2Cl$	Malachite green	Triphenylmethane	Green-reddish yellow	Satisfactory at moderate P_H and boiling temperature
667	$C_{37}H_{34}N_2O_6S_2ClNa$	Fast Acid Green B	Triphenylmethane	Blue-green	Satisfactory only at lower P_H
678	$C_{22}H_{24}N_3Cl$	Fuchsine	Triphenylmethane	Red-yellow	Very satisfactory. For lower temperature only
683	$C_{31}H_{34}N_3Cl$	Methyl violet	Triphenylmethane	Violet-brown	Very satisfactory at low P_H and boiling temperature
698	$C_{41}H_{44}N_3O_6S_2Na$	Acid violet	Triphenylmethane	Violet-green	Satisfactory at low P_H and higher temperature
793	$C_{19}H_{16}N_4O_3$	Phosphine	Acridine	Orange (fluorescent)	Satisfactory at low temp. and high P_H

A selection of indicators shown in Table I consists in a preference for the three numbers 185, **246** and **678.** Indicator number **678** serves admirably for the oxidation of trivalent to pentavalent arsenic and antimony. For this determination it is much more satisfactory than the commonly employed methyl orange since titrations may be made at room temperature and at lower acidities as was done electrometrically by Zintl and Wattenberg.[4]

Further data of a comparative nature relating the speed of the reaction of the oxidation of the indicators under varying conditions of hydrogen-ion concentrations are given in Table II.

TABLE II
CONDITIONS PRODUCING END-POINT INDICATOR OXIDATIONS AT VARIOUS ACID CONCENTRATIONS

0.2 cc. of 0.2% solution in water per 100 cc. of solution of chosen P_H = indicator concentration. Oxidizing agent, 0.05 cc. of $N/10$ solution of $KBrO_3$ or $HgOHBrO_3$. Temperatures in degrees centigrade ±5°. One star, slow reaction; two stars, moderately fast reaction; three stars, fast reaction

Indicator number	Equivalent normality of acid					
	0.1-0.15	0.25-0.3	0.5-0.6	0.9-1.0	1.5	3.0
21	..	80°*	..	60°**	45°**	45°**
27	..	90°**	...	55°**	65°***	...
56	..	**90°***	...	65°**	25°*	...
88	..	80°**	...	55°***	25°**	...
128	..	85°**	85°**	85°**	...	...
184	..	75°*	...	50°***	25°**	5°**
185	..	80°**	...	60°***	25°**	...
246	..	75°**	...	45°**	25°**	...
375	..	**100°****	40°**	....	...	...
471	100°*	80°**	55°**	....	...	...
657	..	90°***	85°**	55°**	...	25°**
667	..	75°**	...	60°**	45°**	...
678	..	....	...	25°**	...	25°**
683	..	75°***	...	25°**	...	...
698	..	80°**	...	60°**	60°**	...
793	**95°***	80°**	55°**	50°**	...	...

Interesting comparisons result upon examination of the data of Table II. All the indicators are rapidly destroyed in one normal acid by a concentration of 5 X 10^{-5} of bromate ion at a temperature ranging from 25–85'. Helianthin requires the same concentration of bromate ion at an acid concentration of three normal and a temperature not less than 60°.

It is not necessary to build up the required concentration of hydrogen ion using only hydrochloric acid. For example, it may be provided using sulfuric acid and enough hydrochloric acid added to increase the acid normality 0.1–0.2 unit just before the titration is begun or at a point slightly before the titration is complete, other conditions being equal. The same principle is applied in the following section of this paper and the results are similar to those reported in Table III.

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[4] **Zintl and Wattenberg, Ber., 56, 472 (1922).**

Indicator Oxidation Conditions Using Sulfuric and Hydrobromic Acid Solutions.—It would be a distinct advantage in many cases to be able to adjust conditions for the indicator oxidation in the absence of hydrochloric acid. The use of hydrobromic acid would be undesirable if it were substituted for hydrochloric acid without limiting the necessary concentration to a small amount for two reasons. One, because of the increased cost, and the other as a result of the low solubility of mercuric bromide. The reduction of bromate to bromide as influenced by the presence of mercuric mercury is more satisfactory in the absence of hydrochloric acid, as proved in previous papers of this series,[2] since mercuric bromide is less dissociated in solution than mercuric chloride.

A study was therefore made of the oxidation of the various indicators as influenced by moderate concentrations of sulfuric acid and small additions of hydrobromic acid. The results are recorded in Table III.

TABLE III

CONDITIONS PRODUCING END-POINT INDICATOR OXIDATIONS AT VARIOUS CONCENTRATIONS OF SULFURIC AND HYDROBROMIC ACIDS

0.2 cc. of 0.2% solution of indicator per 100 cc. of solution at normality of acid given. Oxidizing agent, 0.05 cc. of $N/10$ solution of $HgOHBrO_3$. Temperature in degrees centigrade ±5°. One star, slow reaction; two stars, moderately fast reaction; three stars, fast reaction

Indicator number	H_2SO_4 normality	Hydrobromic acid concentration normal 0 01	0.02	0.4	0 6	Color change
683	1.0	68°***	43°**	25°*	45°***	Yellow to lavender
	1.5	66°***	63°***	50°***	30°**	
	2.0	58°***	48°***	40°***	25°**	
246	1.0	....	85°***	65°***	....	Greenish-blue to colorless
	1.5	78°***				
	2.0	67°***	59°**	....	....	
185	1.0	75°***	70°***	45°**	....	Red to colorless
	1.5	50°***	....	.	30°**	
	2 0	....	....	40°***	25°**	

All the indicators described were employed under the various conditions given using the oxidation of trivalent arsenic (and in some cases trivalent antimony) and quantitative results obtained within a maximum error of 0.2 mg. in the titration of 100 milligrams of the element determined. More complete quantitative data using the indicators studied will appear in subsequent papers of this series.

Summary

1. Description has been given of the selection of a group of sixteen organic dyes suitable for use as internal indicators for volumetric bromate reactions.

2. The dyes described have been tabulated by chemical classes and the mono-azo dyes and those of the triphenylmethane series shown to be most abundantly represented.

3. A study has been made of the limitations of temperature and acidity for which the various indicators are suitable.

4. Colors ranging from red through yellow, green, blue and violet are included. Interfering colored ions may therefore be counteracted by the selection of the proper indicator color from the group described.

5. All the indicators described are suitable for use in the quantitative estimation of trivalent arsenic with an accuracy ordinarily required from the usual volumetric determinations.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. XII. DIPOLE MOMENT DATA FOR (A) NAPHTHALENE AND CERTAIN OF ITS DERIVATIVES. (B) ALPHA AND BETA BENZENE HEXACHLORIDES

BY JOHN WARREN WILLIAMS AND JOHN M. FOGELBERG

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In the last years it has been amply demonstrated that the symmetrical hydrocarbons have zero dipole moments. Such a molecule will become electrically dissymmetrical and possess a finite dipole moment if one of its hydrogen atoms is replaced by another atom or group of atoms; furthermore the moment will vary with the nature of the substituent. When two of its hydrogen atoms are replaced by these substituents, it will not generally be possible to compute the electric moment of the resulting molecules from the assumption that it is the vector sum of individual moments characteristic of the substituent groups because (a) it is necessary to take into account the stereochemistry of the atoms forming the substituent group and (b) it is necessary to take into account mutual attractions or repulsions between the groups unless they be sufficiently removed from one another in the molecule. These factors, first suggested by one of us[1] as possibilities in order to explain the fact that hydroquinone diethyl ether possesses a finite dipole moment, have now been quite completely described.[2,3] These studies, and now many others, have assisted materially in assigning configurations to benzene, methane and ethane, cyclohexane and certain of their derivatives.

In a few individual cases difficulties with the measurement and interpretation of the electric moment data have been encountered. Thus, iodine, symmetrical trinitrobenzene, and naphthalene have appeared to

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[1] Williams, *Physik. Z.*, 29, 271 (1928).

[2] Höjendahl, "Dissertation," Copenhagen, 1928; *Physik. Z.*, 30, 391 (1929).

[3] Williams, THIS JOURNAL, 50, 2350 (1928); *Z. physik. Chem.*, *[A]* 138, 75 (1928); Williams and Fogelberg, THIS JOURNAL, 52, 1356 (1930).

possess finite dipole moments although one would expect them to be non-polar from structural considerations. In a review of earlier work from this Laboratory,[4] these molecules were classified as being molecules for which the existence of a finite moment seemed questionable. There has been a considerable amount of work done since in order to clear up this apparent difficulty. In the case of trinitrobenzene Parts[6] has made a careful study of the polarization at several temperatures and has verified the value previously reported for its electric moment, ($\mu = 0.8 \times 10^{-18}$ e. s. u.) assuming that the atom polarization is zero. In order for the moment to be zero the atom polarization would have to be 14 cc., a value which is probably much too high. It appears therefore that the molecule actually is polar. Interpreted, this would mean that the vectors characteristic of the three NO_2 groups do not act in the plane of the benzene ring.

The difficulty in the case of iodine was assumed to be the result of chemical changes due to the solvent. This has definitely been established by Müller and Sack,[6] who found that when either hexane or cyclohexane was used as solvent the moment was zero. They were also able to find finite values of like magnitude as those reported by us when the iodine was dissolved in benzene.

The data of this article show conclusively that naphthalene has no moment. The value reported by Williams and Ogg,[7] $\mu = 0.7 \times 10^{-18}$ e. s. u., is too high because at the time the measurements were made it was impossible to measure with sufficient accuracy the dielectric constant changes produced in extremely dilute solutions. For this reason in the earlier papers the molar polarization of the solute molecule was determined by taking a tangent to the $P_{1,2}$ curve (molar polarization of the solution) at the point where the mole fraction of the reference liquid is unity, and prolonging it until it cut the axis where the mole fraction of the solute is unity. This is also the explanation for the fact that in so many cases the molar polarization of the solute appeared to be exactly constant. More recently the measurement of the dielectric constant in these extremely dilute solutions has been improved to such an extent that it has been possible to obtain the molar polarizations of the solute molecules for each concentration by means of the equation

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2$$

where the symbols have their usual significance. The P_2 values, obtained in this manner, are extrapolated back to zero concentration in order to measure the molar polarization of a free polar molecule not in interaction

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

Tarts, *Z. physik. Chem.*, *B4, 227* (1929).

[6] Muller and Sack, *Physik. Z.*, 31, 815 (1930).

[7] Williams and Ogg, THIS JOURNAL, 50, 94 (1928)

with any other polar molecules of the same kind. The use of a non-polar solvent precludes the possibility of the polar molecule being in interaction with other polar molecules of unlike kind.

The data of Section **A** give definite information with regard to, first, the importance of the so-called atom polarization, and, second, the structure of naphthalene and certain of its simple derivatives. The data of Section B are of interest in connection with the stereochemistry of derivatives of cyclohexane.

Experimental

The electric moments of naphthalene, 2,6-dichloronaphthalene, ***a***-benzene hexachloride and @-benzknehexachloride have been determined by the method of the binary mixture, using benzene as solvent. All dielectric constant and density determinations were made in a thermostat carefully regulated to **25** ± 0.05°. All chemicals were subjected to rigorous purifications—in short it may be claimed that every known precaution for precision measurements was taken. **A** frequency of 10^6 cycles was used for the dielectric constant measurements. The dielectric constant differences, obtained using the heterodyne beat method consisting of standard oscillator, variable oscillator and detector-amplifier circuits previously described,[8] are believed to be accurate to ±0.0002.

The dielectric constant and density data are presented in Table I. The symbols of the previous articles have been retained throughout, f_1 is the mole fraction of the solvent, in this case benzene; d_4^{25} is the density of the solution; ϵ is its dielectric constant; $P_{1,2}\left(=\frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{f_1M_1 + f_2M_2}{\mathbf{d}}\right)$ is the molar polarization of the solution; and P_2 is the molar polarization of the solute molecule.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA

Naphthalene

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.0000	0.8735	2.276	26.66	43.3
0.9972	.8741	2.277	26.71	43.2
.9931	.8751	2 279	26 77	43.0
.9862	.8766	2.282	26.89	43.8
.9723	.8796	2.288	27.12	43.3

2,6-Dichloronaphthalene

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.0000	0.8735	2.276	26.66	54.3
0.9982	.8748	2.277	26.71	55.0
.9955	.8769	2.280	26.79	56.2
.9928	.8788	2.283	26.89	58.3
.9866	.8833	2.289	27.09	58.8

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[8] **Williams,** *Fortschritte Chem., Physik physik. Chem.,* 20, 257 (1930).

TABLE I (Concluded)

or-Benzene Hexachloride

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.0000	0 8735	2.276	26 66	156
0.9988	.8755	2 285	26 82	159
.9969	.8782	2.298	27.06	156
.9939	.8830	2.319	27 45	155
.9909	.8877	2.340	27.83	155

β-Benzene Hexachloride

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.0000	0.8735	2.276	26.66	66.9
0.9988	.8755	2.277	26.71	66.7
.9975	.8774	2.278	26.76	67.3
.9969	.8783	2.279	26.79	66.7

In Table II are presented the electric moments of the solute molecules, calculated from the P_2 values in infinitely dilute solution. The latter were obtained by direct extrapolation of the P_2 values calculated for the dilute solutions. The quantity P_2'' is that part of the total polarization of the solute molecule contributed by the deformation of the molecule and is given by the quantity $\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d}$, where n_D is the refractive index for the "D" line at 25°, and P_2' is that part of the total polarization of the solute molecule contributed by its actual orientation in the field and is given by the quantity $\frac{4s}{3} N \frac{\mu^2}{3kT}$ where μ is the electric moment of the molecule in question.

TABLE II

ELECTRIC MOMENTS OF SOLUTE MOLECULES

Molecule	P_2	P_2''	Po'	$\mu \times 10^{18}$
$C_{10}H_8$	43.3	43.3	0	0
2,6-$C_{10}H_6Cl_2$	54.3	54.2	0.1	0
α-$C_6H_6Cl_6$	156	57.5	98.5	2.15
β-$C_6H_6Cl_6$	66.9	57.5	9.4	0.70

Discussion, Section A

The molar polarization is made up of two parts, a polarization due to deformation or distortion, and a polarization due to orientation. In order to determine the electric moment of a molecule from dielectric constant and density data at a single temperature, it is necessary to be able to evaluate the polarization by deformation. The latter may be defined as the limiting value that the optical polarization (obtained by means of the Lorentz–Lorenz formula) attains on passing to the limit for zero frequency when the orientation effect which would set in for smaller frequencies is disregarded. But this extrapolation cannot be carried out accurately with the dispersion measurements now at our disposal, so that the extrapolation to zero frequency cannot be used when *absolute* accuracy is necessary. From a practical standpoint, however, this aspect is entirely changed, for if we take non-polar molecules and compare the value of the dielectric constant with the square of the refractive index for the "D" line, the differences are found to be small. The method of the Lorentz–Lorenz formula will therefore be very satisfactory for the determination of the distortion contribution to the polarization except in the case when it is necessary to decide whether a molecule is but slightly polar or not polar at all. In the latter case there is considerable difference of opinion concerning the magnitude of the inaccuracy introduced. Thus Smyth[9] considers the difficulty to be a serious one, while the authors are of the opinion that even here the difficulty can have but little practical importance, especially now that it is possible to make very accurate determinations of the dielectric constant differences between that of the pure solvent and the extremely dilute solutions. An inspection of the data for the naphthalene and 2,6-dichloronaphthalene molecules shows that the difference between the total polarization of each, determined from dielectric constant studies, and the polarization due to deformation of each, calculated from the Lorentz–Lorenz formula using the refractive index for the "D" line, is so small as to be absolutely negligible, leaving no doubt that the polarity of each is zero.

It may be mentioned here that Morgan and Lowry,[10] in trying to account for the moment, $\mu = 0.7 \times 10^{-18}$ e. s. u., previously reported for the naphthalene molecule, have assumed the difficulty to be a result of the fact that this deformation part could not be calculated in the way described above. That this cannot be true is evident from the original data[7] which are reproduced in Table III. The only change that has been made is in the determination of P_2, which this time is simply calculated for each concentration of naphthalene in solution without any attempt being made to determine the limiting value.

TABLE III

DIELECTRIC CONSTANT AND DENSITY DATA FOR NAPHTHALENE SOLUTIONS IN CARBON BISULFIDE

f_1	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
1.000	1.2591	2.633	21.27	...
0.999	1.258	2.641	21.37	120
.994	1.255	2.646	21.55	66
.983	1.246	2.654	21.93	46
.973	1.240	2.663	22.25	45
.965	1.235	2.673	22.59	45
.935	1.225	2.680	23.30	42

If the last four values of P_2 had been used to determine the limiting value instead of having to make use of a value weighed by the first two values

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[9] Smyth, THIS JOURNAL, 51, 2051 (1929).

[10] Morgan and Lowry, *J. Phys. Chem.*, 34, 2385 (1930).

as well in the extrapolation there would have been little, if any, doubt that naphthalene was non-polar. The result of early experimental difficulties was quite often a molar polarization, and therefore an electric moment, which was somewhat high. The calculation of a moment for the anthracene molecule was not attempted[7] because it was realized that the solutions were too dilute for determinations of the dielectric constant differences with sufficient accuracy for the purpose.

Smyth, Morgan and Boyce[11] in presenting their result for the electric moment of monochlorobenzene ($\mu = 1.56 \times 10^{-18}$) make the statement "The value for the moment of monochlorobenzene agrees well with the figure 1.58×10^{-18} recently published by Höjendahl[12] and by Williams and Krchma[13] who, being unable to take into account the small quantity P_A, obtained a slightly high value." The value reported from this Laboratory was $\mu = 1.55 \times 10^{-18}$. The quantity P_A referred to is the atom polarization, which is ordinarily defined as the difference between the total induced polarization and that due simply to electronic shifts, that is, it is a quantity which measures the polarization due to the shifting of position of atoms and groups of atoms. Values of P_A have been determined by Errera[14] by making the assumption that when the molecules are held in the solid state they are unable to orient themselves in an applied field and therefore cannot contribute to the dielectric constant of a solid. The difference between the total polarization in the solid state and the electron polarization calculated from optical data should therefore be atom polarization. The assumption that molecules in solid substances are unable to orient themselves in an alternating field is hardly a safe one, for as Errera[15] himself has shown the dielectric constant of ice varies with the applied frequency. Furthermore, unpublished work from this Laboratory shows definitely that the dielectric constant of solid nitrobenzene changes with frequency. In all probability the orientation of molecules in the solid state will prove to be quite a general phenomenon and an excellent way in which to study it will be by means of dielectric constant determinations. This rotation of molecules in the solid state has recently been discussed from a theoretical point of view by Pauling.[16] For the problem at hand it is evident that care will have to be exercised in assigning a magnitude to P_A. It may also be claimed that other methods of determining it are not without difficulty. In this series of articles the molar refraction for the "D" line has been subtracted from the total polarization, and the electric moment has been calculated from the difference. This procedure certainly

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[11] Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928).

[12] Höjendahl, *Nature*, 117, 892 (1926).

[13] Williams and Krchma, THIS JOURNAL, 49, 1676 (1927).

[14] Errera, *Physik. Z.*, 27, 764 (1926).

[15] Errera, *J. phys.*, [6] 5, 304 (1924).

[16] Pauling, *Phys. Rev.*, 36, 430 (1930).

reduces any error caused by the failure to subtract the atom polarization to a quantity of little or no practical significance. The data for the electric moment of monochlorobenzene introduced at the beginning of this chapter and the data of Table II for naphthalene and 2,6-dichloronaphthalene demonstrate the truth of this statement.

The data of this section are also of interest in connection with the structure to be assigned to naphthalene and its derivatives. There is certain chemical evidence that the 2,6 and 2,7 positions are closer than the ordinary plane formula appears to indicate, and that the 1,8 positions have a relationship approaching that of an ortho compound.[17,18] This is interpreted to mean either that the two rings are completely folded over each other, or make a very small angle with each other. The data of Höjendahl[2] for α-nitronaphthalene, $\mu = 3.6 \times 10^{-18}$ e. s. u., 1,5-dinitronaphthalene, $\mu = 0.6 \times 10^{-18}$ e. s. u. and 1,8-dinitronaphthalene, $\mu = 7.1 \times 10^{-18}$ e. s. u., and the data of this article indicate that in these simpler compounds the two rings must be extended. The most important fact leading to this conclusion is the absence of a finite moment in the case of 2,6-dichloronitronaphthalene. If the rings were folded, either completely or in such a way as to make a small angle with each other, a finite moment would have to exist. If they were folded completely, that is, superimposed on one another, the moment should correspond almost identically with that of *o*-dichlorobenzene, for which $\mu = 2.3 \times 10^{-18}$ e. s. u.

The data of Höjendahl alone are probably insufficient to distinguish between a completely folded and a completely extended model if we assume with Höjendahl that the moment reported for 1,5-dinitronaphthalene should be zero, rather than the small finite value reported, $\mu = 0.6 \times 10^{-18}$ e. s. u. The latter value has resulted from experimental inaccuracy in the earlier work of the type referred to in the case of naphthalene itself. It is evident that if the rings were completely folded, the moment of the molecule would correspond to that of *p*-dinitrobenzene, which is known to be zero. The moment for 1,8-dinitronaphthalene is approximately, though not quite, twice that of a-nitronaphthalene. Considered vectorially, each nitro group is acting to produce its characteristic electrical dissymmetry in the same direction, instead of in opposite directions as in the case of 1,5-dinitronaphthalene. This result might have been expected either on the basis of a folded or extended structure. The situation may be compared with that of benzene itself in which it has been pointed out[4] that data for like para disubstituted benzenes are insufficient to determine whether or not the six carbon atoms lie in a plane, but when data for the corresponding symmetrically trisubstituted benzenes are considered the plane formula is definitely indicated.

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[17] Kaufler and Karrer, *Ber.*, 40, 3262 (1907).

[18] Raiford and Clark, THIS JOURNAL, 48, 483 (1926).

Discussion, Section B[19]

In one of the previous papers of this series[z0] electric moment data for cyclohexane and some of its simple derivatives were presented and discussed. It was stated that the extension of these studies to more complicated derivatives will be difficult and somewhat involved because of the possibilities of isomerism in these compounds. There should, for example, be four benzene hexachlorides. In addition to the more common *a*- and β-forms having melting points 157 and 310°, respectively, two other forms[z1] having melting points 112 and 129° have been prepared.

From theoretical considerations there should be four principal isomers, one in which all six chlorine atoms lie above the plane of the carbon atoms, one with five above and one below, one with four above and two below, and finally a symmetrical form with three above and three below.

X-ray data[a2] have shown that the β-isomer is the symmetrical form having the chlorine atoms evenly distributed above and below the plane of the carbon atoms. No definite conclusions have been drawn concerning the structure of the other three isomers, although attempts have been made by studying the trichlorobenzenes obtained when the various benzene hexachlorides are treated with alcoholic potassium hydroxide.[21]

In this work the α- and 8-isomers were prepared according to the method of Mathews[23] and their electric moments measured in benzene solutions. Their melting points agreed excellently with the values previously reported. Owing to the limited solubility of the 8-compound in benzene, a maximum concentration of only **0.3** mole per cent. could be obtained, so that the moment, 0.7×10^{-18} e. s. u., may be appreciably in error. However, the

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[19] Since the completion of this manuscript the authors have noted that Hassel and Naeshagen [*Tids. Kemi Bergvesen, 10,* **126–127** (1930)] have made similar measurements for these compounds. The agreement is excellent in the case of the a-derivative but not in the case of the @-derivative. For the α-compound there is reported $\mu = 2.20 \times 10^{-18}$ e. s. u., but for the @-compound the value $\mu = 0$ is insisted upon. There are given reasons why the moment should be zero, then the statement is made, "the measurement has been carried out and it was found that this is certainly the case." An inspection of the data is not convincing. The melting point of the compound used is given as 297° but the commonly accepted value for the pure substance is **310°.** The dielectric constant data are given not by recording the actual figures but by saying that the difference between the value for pure benzene and the value for a solution containing **1.2** g. per **100** cc. of benzene is less than **0.05.** The data have been collected in such a way that one would have to assume the dielectric constant value of the solution to be the larger. (The $\Delta\epsilon$ value intended should undoubtedly be **0.005.)** But in order for the electric moment of this molecule to be zero, the dielectric constant of the solutions must always be *less* than that of the pure benzene. Our As would be less than **0.005** for a solution of this same concentration, yet it corresponds to a moment, $\mu = 0.7 \times 10^{-18}$ e. s. u.

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

[21] Van der Linden, ***Ber.,*** 45, **231** (1912).

[22] Hendricks and Bilicke, THIS JOURNAL, 48, **3007 (1926).**

[23] Mathews, **J. *Chem. Soc.,* 59, 165 (1891).**

measurements were of sufficient accuracy to show that the moment is not zero as might have been expected on the basis of the x-ray structure reported for the solid material. It does not necessarily follow, of course, that because a substance is symmetrical as a solid it should also be symmetrical in the dissolved state. Thus this case is quite analogous to that of the symmetrical trinitrobenzene referred to in the introduction. The measurements were repeated in dioxane, in which the hexachloride was more soluble, and a value of 2.0×10^{-18} was obtained. This was evidently due to an influence of the solvent on the somewhat non-rigid structure of the benzene hexachloride.

If there be assumed for the a-compound a configuration having all six of the chlorine atoms on the same side of the plane of the carbon atoms (this seems justified by the work of van der Linden), it is possible to calculate the angle that the vector characterizing the carbon to chlorine linkage makes with the plane of the carbon atoms. Taking the value of each carbon to chlorine linkage as 2.3×10^{-18} e. s. u., its value in chlorocyclohexane, an angle of 9° is obtained. This is considerably smaller than the 55° angle which would be predicted on the basis of tetrahedral carbon atoms with no mutual repulsion between the chlorine atoms. The small angle, 9°, is interpreted to mean that there is powerful mutual interaction between the chlorine atoms, a fact which might have been predicted because of the number and size of the latter. Also, it further emphasizes the fact pointed out in other papers from this Laboratory that the electric moment of a molecule cannot be properly calculated without taking into account mutual attractions and repulsions between substituted atoms and groups.

Summary

The method of the binary liquid mixture has been used to determine the electric moments of the naphthalene, 2,6-dichloronaphthalene, a-benzene hexachloride and β-benzene hexachloride molecules. In the discussion it has been shown that in order to account for the experimental data there must be considered both the spatial configurations of these molecules and the mutual interactions between their polar substituents.

In the case of the substituted naphthalenes the data indicated an extended arrangement of the benzene rings rather than a partially or completely folded one. The data for the benzene hexachlorides did not show what might have been predicted, namely, that the form in which the six chlorine atoms were located on one side of the plane of the six carbon atoms of cyclohexane would be very strongly polar, while the form in which three chlorine atoms were located on either side of the plane would be completely non-polar. The explanation is undoubtedly to be found in mutual interactions between the substituents, the chlorine and hydrogen atoms.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF THE MICHIGAN STATE COLLEGE]

THE ELECTROMETRIC TITRATION OF URANIUM WITH CERIC SULFATE

BY DWIGHT T. EWING AND MRS. MABEL WILSON

RECEIVED MARCH 23, 1931 PUBLISHED JUNE 8, 1931

In a previous publication[1] it was shown that the electrometric titration curves for uranium and potassium permanganate, and potassium dichromate, had two inflection points. The first denoted the complete oxidation of trivalent uranium to the tetravalent form and the second point, the complete oxidation of the tetravalent form. Gustavson and Knudson[2] and Miiller and Flath[3] titrated uranium electrometrically, but did not note the first inflection point. In commenting on this point of difference it was correctly pointed out by Kolthoff and Furman[4] that the presence of carbon dioxide and the correct acidity must be obtained in order to form and titrate trivalent uranium. In our previous investigation we used a special titration cell designed to eliminate oxygen and the titration was only successful when made in an atmosphere of carbon dioxide or nitrogen.

Preparation of Solutions.—The ceric sulfate solution was prepared by the method that was used by Willard and Young.[5]

The ceric sulfate solution was standardized against 0.05 N sodium oxalate solution made from a Bureau of Standards product in a carefully calibrated flask, at 25.0°. This ceric sulfate solution was found to be 0.05326 *N*.

The uranium solution was prepared by dissolving 28.283 g. of uranyl acetate in a little distilled water containing 9.8 g. of sulfuric acid and carefully diluting to 2 liters.

The uranium solution was standardized by evaporating two 2-ml. portions of stock solution to dryness and then igniting to the oxide. From these data the normality of the uranium solution was found to be 0.07113.

An approximately 0.1 N solution of ferrous ammonium sulfate solution was prepared with an excess of free sulfuric acid. It was standardized against the ceric sulfate solution and was found to be 0.1041 N.

Apparatus.—The *e.* m. f. of the titration cell was determined with a potentiometer which read to one-half of a millivolt.

The titration vessel consisted of a 400-cc. beaker with a large cork stopper with six holes for the following pieces: a buret, a zinc reductor, a mechanical stirrer, an inlet for an inert gas and two electrodes. The standard

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[1] Ewing and Eldridge, THIS JOURNAL, 44, 1484 (1922).

[2] Gustavson and Knudson, *ibid.*, 44, 2756 (1922).

[3] Müller and Flath, *Z. Elektrochem.*, 29, 500 (1923).

[4] I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, New York, 1926, pp. 243–244.

[5] H. H. Willard and Philena Young. THIS JOURNAL, 50, 1322 (1928).

electrode was a tenth-normal calomel half cell, and a small bright platinum wire was used for the other electrode.

Experimental Procedure

1.06 ml. of concentrated sulfuric acid was added to 30 ml. of the uranium solution and evaporated almost to dryness. This was diluted to 50 ml., heated nearly to boiling and forced through a 50-cm. zinc reductor with nitrogen or carbon dioxide. The zinc reductor was washed with 2% sulfuric acid until the total volume of solution in the titrating vessel was 100 ml. This solution while warm was titrated with the standard cerium sulfate reagent. During this procedure nitrogen or carbon dioxide was run through continuously.

The first end-point was approached rather slowly and usually required about **3** ml. of the cerium solution. After each addition it was necessary to wait for a few moments for an equilibrium reading. After the first end-point was established, the cerium solution could be added quite rapidly until near the second end-point. The behavior of the reaction as the second end-point is approached is quite similar to that of any other cerium electrometric titration where equilibrium conditions must be carefully noted.

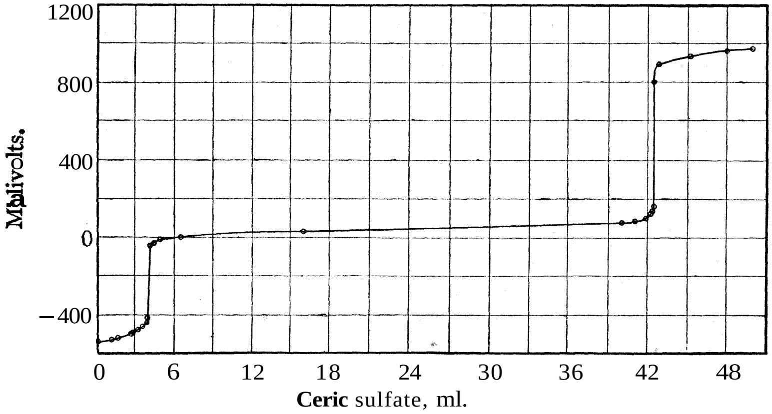

Fig. 1.

The volume of ceric sulfate represented by the difference between the two end-points was carefully computed, corrected for calibration errors, etc., and from this value the concentration of the uranium solution was found.

Graph 1 (Fig. 1) is typical of the results of many titrations which were made. In Table I are given the results of seven consecutive titrations.

Discussion of the Results

The stock solution of uranium used in this investigation was prepared from the acetate. Irregular results were obtained in the first titrations.

TABLE I

Total volume of solution titrated, 100 ml.; contained 2% sulfuric acid

Titration number	Uranium solution, ml.	Ceric sulfate, ml. By expt.	Ceric sulfate, ml. Calcd.	a/b
1	29.95	39.88	39.86	1.336
2	29.85	39.83	39.86	1.334
3	29.85	39.98	39.86	1.339
4	29.85	39.84	39.86	1.335
5	29.85	39.64	39.86	(1.327)
6	29.85	39.93	39 86	1.338
7	29.85	39.86	39 86	1.336
Mean		39.87		1.336

[a] Ml. of ceric sulfate solution. [b] Ml. of uranium solution.

In Experiment 5 trouble was encountered with the mechanical stirrer.

The second end-point was uncertain and the results low. This difficulty was not overcome until the acetate was removed. This was accomplished by evaporating the solution with sulfuric acid until the acetate had disappeared. The concentrated solution was diluted with water just previous to reduction.

The color of the freshly reduced acid uranium solution was a dark olive green and it was slightly opaque. Upon addition of ceric sulfate solution it gradually cleared and became of a very light green color at the first end-point. As oxidation proceeded the color became less intense and gradually changed to a greenish-yellow at the second end-point.

Due care must be taken in this titration to make certain that the e. m. f. measurements represent an equilibrium condition. Furman[6] in titrating ferrous sulfate allowed one to four minutes after each addition before making the e. m. f. measurements. In titrating uranium with cerium even more time was required for the e. m. f. reading, especially at the first end-point.

The initial e. m. f. of the reduced solution was usually -500 to -450 mv. This changed gradually about 100 mv. to the first end-point when an abrupt change of approximately 400 mv. was noted. A small fraction of a drop of ceric sulfate solution is sufficient to cause this abrupt change. The second end-point was also very definite and usually the addition of a small fraction of a drop of the ceric sulfate solution was sufficient to cause the e. m. f. to increase 500 or 600 mv.

Higher concentrations of sulfuric acid, 6, 15 and 30% by volume, were later titrated. The amount of uranium solution, the total volume and conditions of titration remained the same. In all cases both end-points were definite, and the amount of ceric sulfate used between end-points was the theoretical. Formerly reported titrations[1] stated that high acid concentrations caused the voltage to rise rapidly and the second end-point

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[6] N. H. Furman, THIS JOURNAL, 50, 755 (1928).

consequently disappeared. In all cases of the higher acid concentrations just mentioned, the shape of the curves remained the same, and all three corresponded closely to the curves obtained from the 2% titration data. The only noticeable effect was the time required for equilibrium to be established at the end-points. As the percentage of acid was increased, a longer time was required for equilibrium. This was particularly noticeable at the second end-point, which was fairly rapid in the 2% solution. In this respect the work of Gustavson and Knudson[2] has been confirmed.

Titration in Hydrochloric Acid Solution.—Hydrochloric acid may also be used in the titration of uranium with cerium sulfate. Titrations were made using 2, 4, and 6 *M* hydrochloric acid and a combination of 2 M for the first end-point, with an increase to 4 *M* immediately after reaching the first end-point.

In each case 30 ml. of the uranium solution was heated to boiling with half the acid, and put through the reductor. This was washed with the remainder of the acid in solution, making a total volume of 100 ml. for titrating. In each case more reduction to trivalent uranium was noted than in the case of the sulfuric acid titrations. The color of the reduced solution was a very dark red-brown and was opaque. Upon the addition of ceric sulfate, the color rapidly changed to the same olive-green noted in the case of sulfuric acid. Colors at the end-points were identical.

In no case was the titration with hydrochloric acid as satisfactory as with 2% sulfuric acid. The great difference in effect of these two acids on the titrations was that upon the change of voltage' at the end-points and the time required for equilibrium to be established.

Graph Number 2 gives a comparison between the deflections in voltage at the two end-points in the 2% sulfuric acid and in the 4 M hydrochloric acid titrations. It is noted that the rise in the e. m. f. at the first end-point in the hydrochloric acid solution is approximately 100 mv. and in the sulfuric acid solution the rise is 400 mv. At the second end-point the rise in the hydrochloric acid solution is 450 mv., which compares with a rise of about 675 mv. in the sulfuric acid solution.

In all cases where hydrochloric acid was used, the first end-point was too slow to be of practical use. In the 2 M solution, the first end-points covered about 400 mv., in the 4 *M*, 100–200 mv., and in 6 *M*, 50–75 mv. With higher acid concentrations, the time required for equilibrium was greater. This was also true of the sulfuric acid solutions, although it did not seem to affect the voltage greatly in case of the sulfuric acid solutions. In exact contrast to the first end-point, the stronger the hydrochloric acid, the sharper and quicker the second end-point. This is also in exact contrast to the second end-point when sulfuric acid was used. In 2 M hydrochloric acid, the equilibrium was very slow, and the change in voltage was approximately 300–400 mv.; in 4 M it was 400–500 mv. and more rapid;

in 6 *M*, which compared with 2% sulfuric acid, the change was 600 mv. and more rapid.

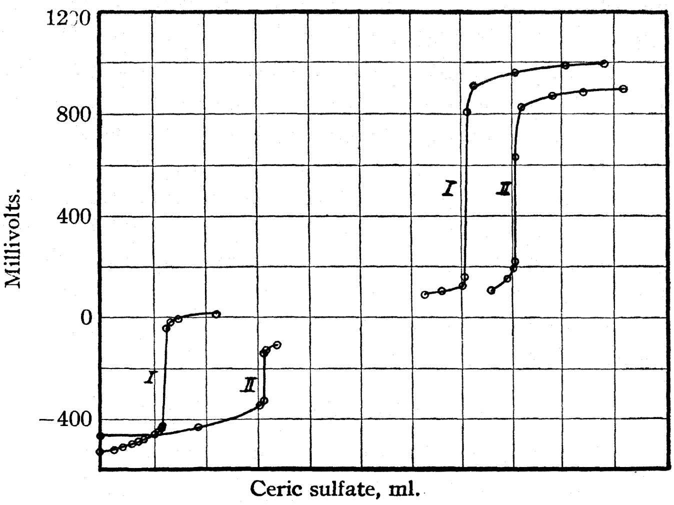

Fig. 2.—I, H_2SO_4, 2%; II, HCl, 4 *M*.

It was found that for hydrochloric acid solutions a concentration of about 2 *M* in hydrochloric acid gave the most definite e. m. f. change for the first end-point. For the second end-point the optimum concentration of hydrochloric acid seemed to be about 4 M.

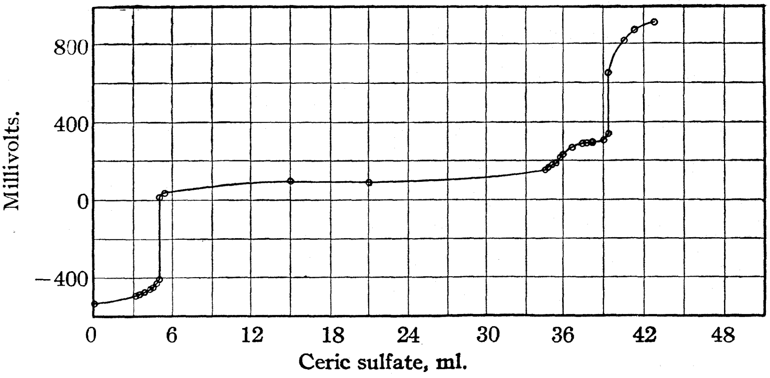

Fig. 3.

A few titrations were made with a combination of the uranium with ferrous ammonium sulfate. Thirty ml. of the uranium solution was prepared and reduced as in the 2% sulfuric acid titrations. Before washing the reductor, 5 ml. of the iron solution was added. The titration was performed in 100 ml. volume, 2% sulfuric acid.

Three end-points were obtained: one when trivalent uranium was oxidized to tetravalent, another when tetravalent was oxidized to hexavalent, and a third when the ferrous iron was oxidized to ferric iron. Because of the closely corresponding voltage of the second and third oxidations, it is advisable to plot also, Δmv./Δml., the change in millivolts per change in ml. This gave three definite end-points. The amount between the first and second corresponded closely to the theoretical amount of ceric sulfate necessary to oxidize the uranium present; and the amount between the second and third, very nearly to the amount required to oxidize the ferrous iron present. Graph Number **3** shows this titration.

Nitrogen was used to exclude the air from the cell during the titration. This is essential for titrating the small amount of trivalent uranium present in the reduced solution, due to the rapid oxidation of trivalent uranium in air, as shown by McCoy and Bunzel.[7]

Summary

1. When a hot acid solution of uranium sulfate is reduced in a Jones reductor and is titrated in an atmosphere of nitrogen with ceric sulfate as an oxidizing agent, two end-points are obtained. The amount of uranium oxidized between the two end-points corresponds exactly to the amount of uranium present. **A** 2% sulfuric acid of uranium sulfate gave satisfactory results.

2. Uranium acetate in hydrochloric acid solution, when treated in the same way, also gives two end-points, the difference between which is the amount of uranium present. A concentration of 2 M for the first and 4 M for the second gave the best results.

3. Sharper end-points were obtained for the titrations in sulfuric acid, and less time was required for the e. m. f. to come to equilibrium, than in hydrochloric acid. More consistent results were also obtained with 2% sulfuric acid.

4. Ferrous ammonium sulfate was added to the reduced 2% uranium solution and three end-points were obtained: (1) when trivalent uranium was oxidized to tetravalent, (2) when tetravalent was oxidized to hexavalent and (3) when ferrous was oxidized to ferric iron.

EAST LANSING, MICHIGAN

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[7] H. M. McCoy and H. H. Bunzel, THIS JOURNAL, **31**, 367 (1909).

[CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORIES, MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND PURDUE UNIVERSITY]

OXYCYANOGEN. I

BY HERSCHEL HUNT

RECEIVED MARCH 25, 1931 PUBLISHED JUNE 8, 1931

The field of inorganic free radicals contains, as is pointed out by Walden and Audrieth,[1] one piece of work, namely that of Lidov,[2] which must be substantiated or disproved before the properties of the radical CNO can be definitely established. Since no mention of Lidov's work is made by Birckenbach and Kellermann,[3] I thought it advisable to check this work before proceeding farther into the field.

Lidov did not hint that the substance with which he was dealing was a free radical. All evidence offered by him for the existence of a substance composed of carbon, nitrogen and oxygen hinges on density determinations of a gas. No chemical composition is proved by analysis. The electronic structure of OCN shows it to have an odd electron and hence we would expect it to be very active chemically unless polymerized. That such is not true of Lidov's substance is apparent since he prepared it in aqueous or alcoholic solutions without hydrolysis. He described his product as being a homolog of carbon dioxide, and names it oxan or monocyan.

Oxan is described as being a gas which polymerizes on standing, yet Lidov never obtained a greater density than 1.974 g./l. It is not decomposed by phosphoric acid or by temperatures up to 375°. It is precipitated by silver or barium ion and absorbed by an alkali. By long boiling with sodium hydroxide and zinc dust its salts will give ammonia. The nitrogen of beta-oxan is easily determined by burning it with magnesium powder.

The greatest care was taken to repeat most of Lidov's work, even in the most illogical cases, in order that I might definitely say that his work was correct or incorrect. The detailed results are as follows.

Paper Number 1.—A. In neutral solution, aqueous or alcoholic

$$2KCNO + H_2O_2 = K_2CNO_2 + H_2O + CNO \text{ (gas)}$$

The oxanate, K_2CNO_2, may be decomposed with phosphoric acid to give CNO also. The author found the following

$$KCNO + xH_2O_2 = KCNO + xH_2O + \frac{x}{2}O_2$$

The effluent gas supports combustion and is absorbed completely by alkaline pyrogallol. No precipitate was obtained by passing the gas into

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[1] Walden and Audrieth, *Chem. Reviews*, 5, 339 (1928).

[2] A. P. Lidov, *J. Russ. Phys.-Chem. Soc.*, 44, 527 (1909); 44, 529 (1909); *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 6, 185, 191, 194 (1912); THIS JOURNAL, 35, 132 (1913); *Rev. gén. chim.*, 16, 293, 310 (1914); "Tech. Inst. Charkov," Russia (Monograph) (1914).

[3] Birckenbach and Kellermann, *Ber.*, 58, 786 (1925).

barium hydroxide solution. The remaining salt was then decomposed by phosphoric acid as described and the gas evolved passed into barium hydroxide. The precipitate was washed and then digested with potassium hydroxide and aluminum dust. Not a trace of ammonia could be detected with Nessler's solution. When the Kjeldahl method failed to give ammonia, I also failed to get any Mg_3N_2 formed by burning the gas with magnesium.

B. In alkaline solution, aqueous or alcoholic

$$2KCNO + 2NaOH + H_2O_2 = K_2CNO_2 + Na_2CNO_2 + 2H_2O \text{ (corrected)}$$

I repeated this reaction, in a closed vessel, in dry, cold alcoholic solution. The hydrogen peroxide was added slowly but oxygen was persistently given off. The concentrated solution was decomposed with phosphoric acid. The resulting gases were passed into barium hydroxide solution. The barium salt was then boiled with aluminum dust in strong alkali, but no trace of ammonia was given off (Nessler test). Therefore it is quite evident that the evolving gases are carbon dioxide and nitrogen and not CNO. Lidov's trouble of having an extra amount of barium salt precipitated in the reaction flask, which he calls $BaCNO_3$, would have been overcome if he had allowed the gas to escape and pass into barium hydroxide solution instead of trying to precipitate the effluent gas in the reaction flask.

Paper Number 2.—(See part **5** of Number **3.)**

Paper Number 3.—A. Lidov claims that the familiar reaction

$$3NaOBr + CO(NH_2)_2 = CO_2 + N_2 + 2H_2O + 3NaBr$$

is not correct but that as we increase the dilution of the solution (alcoholic), we have more and more CNO formed. He supports this assumption by the meager evidence that he did not find the theoretical amount of carbon dioxide formed but a gas weighing (1.974, 1.945, 1.925, 1.921 and 1.911) g. per liter. "Further dilution, however, does not bring near the weight of the gas and the weight of a liter of pure oxan—1.875 g."

This titration was carefully repeated and the gases formed passed into barium hydroxide. The precipitate was tested for nitrogen content in the usual manner and was found to contain none.

B. Sodium cyanamide was claimed to give oxan on oxidation with hydrogen peroxide (perhydrol) or sodium hypobromite, very small quantities of nitrogen being liberated. However, I found the reactions to proceed as follows in aqueous solution

$$Na_2CN_2 + 3NaOBr = 3NaBr + Na_2CO_3 + N_2$$
$$Na_2CN_2 + 3H_2O_2 = Na_2CO_3 + 3H_2O + N_2$$

If the cyanamide or a cyanate is converted to an ammonium compound the strong oxidizing agents will oxidize it to free nitrogen, reducing agents giving ammonia. The sodium salts left were decomposed and the gas evolved proved to be pure carbon dioxide.

C. Other simple ways of preparing the gas are

(a) $2KCNO + H_2O_2 = K_2CNO_2 + CNO + H_2O$ (in water solution)

"There is always more or less potassium carbonate and ammonium carbonate formed," Lidov reports.

(b) $2KCNO + 2NaOH + H_2O_2 = K_2CNO_2 + Na_2CNO_2 + 2H_2O$ (in alcoholic solution in a hermetically closed vessel)

"No nitrogen is expelled and 15–20% extra Ba salt is precipitated." In checking these experiments I obtained the same results as described in paper I.

D. In this section properties of oxan salts are given. Lidov obtained his oxan salts, $BaCNO_2$, K_2CNO_2, etc., as shown in reactions above, but I was unable to separate any new salts.

E. By heating a mixture of KCNO and CuO to 375° in a stream of dry nitrogen, Lidov found

$$2KCNO + CuO = K_2CNO_2 + CNO + Cu$$

"That the reaction is really so, is confirmed as well by the weight of the gas expelled (1.900) by the heating, as by the weight of the gas produced from the remaining salts." I find the reaction to proceed as follows

$$2KCNO + 3CuO + N_2 = K_2CO_3 + CO_2 + 2N_2 + 3Cu$$

when everything is carefully dried and protected from water vapor. Otherwise I find

$$4KCNO + 3H_2O + 3CuO + N_2 = 2N_2 + 2NH_3 + 3Cu + 2K_2CO_3 + 2CO_2$$

The expelled gases in the former reaction were passed through barium hydroxide. No trace of nitrogen was found in the precipitate. No evidence of CNO_2, or CNO_3, as reported, was found. (No oxidizing salt was left in the tube.)

F. When Lidov used oxygen instead of nitrogen, as in V, he found

$KCNO + CuO + O_2 = K_2CNO_2 + CNO + CO_2 + Cu +$ (a heavier gas, 2.590, precipitated with Ba^{++})

I found the simple conditions

$$4KCNO + 2CuO + 3O_2 = 2K_2CO_3 + 2CuO + 2N_2 + 2CO_2$$

which is in accord with all Dumas' determinations.

G. "Of the Formation of Oxan by the Reciprocal Action of Nitrogen Dioxide with Charcoal." Lidov learned in the following year that he was using nitric oxide and not nitrogen dioxide (see paper No. 6).

"The simplest way of obtaining oxan ... if we judge by weight of the gas" is to pass NO (not NO_2) over charcoal at 150°. "If the solution of sodium hydroxide, which has absorbed the gas, is immediately decomposed by phosphoric acid, in most cases pure oxan, if we judge by weight, is obtained." I followed Lidov's explicit directions for the best method of getting the pure gas (see part VII of paper 3 and paper 6) and absorbed it in alkali as stated. It was then precipitated as the Ba salt and carefully washed to get rid of any nitrates or nitrites. It was then decomposed by phosphoric acid, the evolved gas passed through a vapor trap and then through long tubes of phosphorus pentoxide and finally frozen out in a liquid air trap. The density of the gas was determined as described by Schumb and Gamble.[4] The gas was found to have a density of 1.9693 g. per liter, which is within 0.4% of the determined density of carbon dioxide ("International Critical Tables," Vol. III, p. 1). The gas was allowed to stand for several days and its density determined at two-day intervals. No polymerization takes place as evidenced by the various determinations.

June	17	19	21	23	25
Density	1.9693	1.9693	1.9693	1.9693	1.9693

These latter experiments disprove Lidov's sole argument for the existence of a gas, CNO, homologous with CO_2.

Paper Number 4.—Since there is no evidence for the formation of the salts described in this paper by the given methods, I will not try to explain how he obtained the peculiar properties listed. Perhaps the compounds listed will have the properties described, but I have proved that such compounds cannot be prepared by the methods given.

Paper Number 5.—By passing nitrogen dioxide over charcoal at room temperature and collecting the gas in alcoholic sodium hydroxide, Lidov did not obtain oxan but beta-oxan, ONC. In repeating this work with carefully prepared gases and solutions, and pure dry sugar charcoal, I obtained a mixture of $C_2H_4NaNO_2$, $NaNO_2$ and Na_2CO_3, the two former occurring in the first few hours of reaction and the last after fifteen to twenty hours. My organic salt was identified by its reactions and properties identical to those listed for $C_2H_4NaNO_2$. The mixture on decomposition gave no gas of the nature of CNO, only oxides of nitrogen and carbon. The first-named compound will explain the explosive properties of beta-oxan salts.

Paper Number 6.—The foregoing experiments show that Lidov was dealing with impure carbonates in this paper, and not new compounds. By treating the solution mixture described in Paper 5 with ferric chloride, Lidov obtained a ferric salt which he called iron beta-oxanate, I found simply ferric hydroxide, the explosive properties being due again to $C_2H_4NaNO_2$.

Passing pure nitrous oxide over charcoal at 150° gave only carbon dioxide and nitrogen and not CNO as claimed by Lidov.

Paper Number 7.—A review of previous work with a few new methods of preparing oxan, such as heating phosphorus pentoxide and urea.

Papers Number 8 and 9.—To confirm the contents of these two papers, namely, that CNO is a product of all combustions in air along with carbon dioxide and carbon monoxide, and of respiration of animals, would prove all

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[4] Schumb and Gamble, THIS JOURNAL, 52, 4302 (1930).

Dumas' determinations inaccurate and calorific values subject to error. It would proclaim a new property of nitrogen, which has been proved not to be possible by thousands of able chemists, namely, the ability to support combustion. Therefore I wish to point out the fallacies of Lidov's writings.

Summary

1. The author has shown that $(CNO)_x$ cannot he obtained by any of the methods described by Lidov.

3. He has proved that salts, such as Na_2CNO_2, $Fe(NCO)_3$ or $BaCNO_2$, cannot be prepared as described.

3. He has shown that Lidov's peculiar observations are due to inaccurate work. This is particularly true of the density determinations.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. IV. THE GLYCOLS

BY C. P. SMYTH AND W. S. WALLS

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In the lirst paper[1] of this series the effect upon the resultant electric moment of the molecule produced by separating the component moments by a carbon chain of varying length was investigated, the complex $-COOC_2H_5$ group being placed at each end of the chain. In the present investigation the simpler $-OH$ group has been attached to the carbon chain. The low solubility of the glycols in the non-polar liquids, benzene and heptane, usually used as solvents in the determination of electric moments, has made it desirable to use 1,4-dioxane, which has been employed by Williams for a similar purpose.[2] Williams found values for the moments of chlorobenzene, chlorocyclohexane, diethyl o-phthalate, and water measured in dioxane in good agreement with the values obtained in other ways. It was feared, however, that the glycols might form addition products with the dioxane which would lead to incorrect values for the moments. In order to test the possibility of such errors, *n*-butyl alcohol, which had been thoroughly investigated in the vapor state[S] and in solution in other solvents,[4] was measured in dioxane. The monohydric alcohol would be expected to resemble to some extent, at least, the glycols in the possible formation of addition products and, therefore, in the error in the moment arising from such formation. The resemblance should be close in the case of the long-chain glycols.

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[1] Smyth and Walls, THIS JOURNAL, 53,527 (1931).

[2] Williams, *ibid.*, 52,1838 (1930).

[3] Miles, *Phys. Rev.*, 34,964 (1929).

[4] Smyth and Stoops, THIS JOURNAL, 51,3312 (1929).

Preparation of Materials

The refractive indices and densities of the pure liquids, which give evidence of the purity of the materials, are listed in Table I. Other criteria of purity are given under each substance below.

1,4-Dioxane.—1,4-Dioxane from the Eastman Kodak Company, m. p. 9.5–10.5°, was dried over sodium and fractionally distilled; b. p. 100.5–100.7°.

***n*-Butyl Alcohol**,---n-Butyl alcohol from the Commercial Solvents Corporation was refluxed over freshly ignited calcium oxide and fractionally distilled three times; b. p 117.2–117.4'.

Ethylene Glycol.—Material from the Carbide and Carbon Chemicals Corporation was fractionally distilled under reduced pressure and the middle fraction collected. This fraction was dried over anhydrous sodium sulfate, decanted and twice fractionally distilled; b. p. 197.2–197.3°.

Propylene Glycol.—Material from the Eastman Kodak Company, b. p. 85–86' (10 mm.), was fractionally distilled under reduced pressure, dried over anhydrous sodium sulfate, decanted and twice redistilled; b. p. 104° (32 mm.).

Trimethylene Glycol.—Material from the Eastman Kodak Company, b. p. 123–125° (30 mm.), was twice fractionally distilled under reduced pressure. The middle fraction was dried over anhydrous sodium sulfate, decanted and twice fractionally redistilled under reduced pressure; b. p. 127° (33 mm.).

Hexamethylene Glycol.—Material kindly loaned to us by Dr. Wallace H. Carothers of E. I. du Pont de Nemours & Company, b. p. 145–147° (13 mm.), was twice fractionally crystallized and allowed to stand in an evacuated desiccator; m. p. 42.8°.

Decamethylene Glycol.—Material loaned by Dr. Carothers was crystallized from hot, dried benzene, washed twice with cold benzene and carefully dried in an evacuated desiccator; m. p. 72.2°.

Experimental Results

The densities and dielectric constants of these solutions were measured with the apparatus and methods previously employed,' a wave length of 1000 meters being used in the dielectric constant determinations. The refractive indices for the D sodium line and the densities of the pure liquids determined for use in the calculation of the molar refractions MR_D and as criteria of purity are listed in Table I. Similar measurements on the solutions of the solids made possible the calculation of MR_D, the values of which are listed in Table II. In Table I the first column gives the mole fraction c_2 of the butyl alcohol or the glycol in the dioxane solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ and the densities d of the solutions and the polarizations P_2 of the polar substance. P_2 is calculated by means of the usual equations

$$P_{12} \quad \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} \text{ and } P_2 \quad \frac{P_{12} - P_1}{c_1} + P_1$$

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 extrapolation of the P_2–c_2 curve to infinite dilution, that is, $c_2 = 0$, gives the value of P_∞ at the absolute temperature T, from which the electric moment μ is calculated by means of the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

The absolute values of the moments are probably a little high because of the neglect of the atomic polarization P_A.

TABLE I

REFRACTIVE INDICES AND DENSITIES OF THE PURE LIQUIDS

	n_D^{20}	n_D^{25}	d_4^{25}	d_4^{50}
1,4-Dioxane.	1.42290	1.42032	1.0311	1.0027
n-Butyl alcohol.	1.39922	1.39727	0.8060[5]	0.7867[5]
Ethylene glycol..	1.43180	1.43055	1.1099	1.0923
Propylene glycol.	1.43291	1.43143	1.0328	1.0138
Trimethylene glycol.	1.43965	1.43832	1.0503	1.0344

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			n-Butyl Alcohol			
0.00000	2.306	2.251	1.0311	1.0027	(25.91	25.85 = P_1 of 1,4-dioxane)
.01927	2.391	2.321	1.0263	0.9981	88.2	80.3
.02893	2.430	2.355	1.0238	.9957	86.1	79.5
.03023	2.439	2.362	1.0236	.9955	87.2	80.5
.06606	2.606	2.507	1.0145	.9866	87.2	81.7
.07914	2.675	2.563	1.0112	.9834	88.0	82.1
.11647	2.876	2.729	1.0018	.9744	88.5	82.4
			Ethylene Glycol			
0.02181	2.480	2.405	1.0325	1.0042	121.7	115.3
.04475	2.676	2.580	1.0339	1.0059	120.2	114.4
.05309	2.745	2.638	1.0345	1.0065	118.4	112.1
.08938	3.105	2.956	1.0366	1.0090	117.7	112.0
.10838	3.317	3.143	1.0377	1.0102	117.3	111.8
.13227	3.598	3.383	1.0394	1.0122	115.7	110.3
			Propylene Glycol			
0.02311	2.484	2.410	1.0313	1.0029	123.7	118.5
.03782	2.606	2.519	1.0312	1.0030	124.0	118.7
.06184	2.815	2.701	1.0311	1.0031	123.1	117.2
.07692	2.964	2.834	1.0311	1.0032	123.8	118.3
			Trimethylene Glycol			
0.01068	2.408	2.340	1.0316	1.0033	149.5	139.1
.02455	2.542	2.458	1.0320	1.0037	146.5	137.8
.04267	2.725	2.619	1.0324	1.0043	144.3	136.2
.06356	2.955	2.821	1.0328	1.0051	143.0	135.3
.08037	3.155	2.992	1.0332	1.0057	142.0	134.2
.10385	3.453	3.250	1.0337	1.0064	140.2	132.9

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[5] Value taken from measurements of Smyth and Stoops, Ref. 4 on the *same* material.

Table II (Concluded)

c	ϵ		d		P_2	
	25°	20°	25°	50°	25°	50°
Hexamethylene Glycol						
0.00980	2.397	2.330	1.0306	1.0024	161.6	150.9
.02563	2.546	2.460	1.0292	1.0012	160.1	150.3
.04354	2.725	2.615	1.0278	1.0002	160.0	150.4
.06313	2.938	2.795	1.0262	0.9990	160.5	150.
Decamethylene Glycol						
0.00645	2.366	2.304	1.0297	1.0014	184.0	174.7
.01183	2.414	2.348	1.0282	1.0002	182.3	174.6
.02290	2.517	2.434	1.0254	0.9977	182.2	171.8
.02744	2.562	2.470	1.0241	0.9967	183.3	171.3

Table III

Refractions, Orientation Polarizations and Electric Moments

	MR_D	$P_\infty - MR_D$		$\mu \times 10^{-18}$	
		25°	50°	25°	50°
OC_4H_8O	21.63	4.28	4.22	(0.45)	(0.47)
n-C_4H_9OH	22.15	68.3	59.1	1.81	1.75
$HO(CH_2)_2OH$	14.47	108.3	101.9	2.28	2.30
$CH_3CH(OH)CH_2OH$	19.08	105.0	100.0	2.25	2.28
$HO(CH_2)_3OH$	19.02	130.0	121.0	2.50	2.51
$HO(CH_2)_6OH$	32.7	128.1	118.1	2.48	2.48
$HO(CH_2)_{10}OH$	51.3	132.6	123.6	2.52	2.54

Discussion of Results

The values given for 1,4-dioxane under $P_\infty - MR_D$ are the differences between the polarizations of the pure liquid and the refraction. As the unknown atomic polarization P_A is disregarded in the calculation of the moment, the result merely shows that the value of the moment is not far from zero. Williams[6] reports a decrease in the polarization of dioxane with decreasing concentration in dilute benzene solution, which seems curious in view of the small or zero moment of the molecule. However, his value of P_∞, 26, is in excellent agreement with the values in Table II for P_1, which might be expected to be practically identical with P_∞ in this case. Williams calculates a value, $\mu = 0.4 \times 10^{-18}$, but concludes that the moment "can differ but slightly, if at all, from zero." The apparent symmetry of the molecule would lead one to expect a small or zero moment.

The values of P_2 for n-butyl alcohol in Table II show a minimum, as do those for the alcohol in benzene solution[4] in the same region of temperature and concentration. The values at 25° are 3 or 4 units higher than those at the same concentrations in benzene solution, probably because of a slightly high value used for P_1 in the latter, while the polarizations in the two solvents at 50° differ from one another by less than one unit. In both solvents the minimum in the P_2–c_2 curve at such low concentrations makes

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[6] Williams, This Journal, 52, 1831 (1930).

difficult an accurate extrapolation to obtain P_∞. The value of the moment found in dioxane solution at 25° is a little high, but that at 50° is in excellent agreement with the mean value, 1.74×10^{-18}, obtained from the benzene solutions. As benzene is the most generally used solvent and as this value of the moment is in fair agreement with the value, 1.65×10^{-18}, found by Miles[3] for the vapor, dioxane appears to be an adequate solvent for the alcohol. As the glycols should resemble the monohydric alcohols in their action upon the solvent, it may be concluded that dioxane solutions of the glycols should give satisfactory values of the moments. The previously mentioned work of Williams gives further justification for the conclusion.

The moment found for ethylene glycol is much higher than the value 1.5×10^{-18} obtained by Williams[7] from measurements in benzene solution. However, the very low solubility of the glycol in benzene renders it difficult to obtain an accurate value in this solvent. It had been hoped that some of the higher glycols would prove sufficiently soluble in benzene to render measurements possible for comparison with those in dioxane, but the insolubility was such that no accurate determination could be made.

The moment of a monohydric alcohol is, in the main, the resultant of the moments of two doublets, one in the line of the C–O bond and the other in that of the H–O bond.[8] By empirical methods, Eucken and Meyer[9] have calculated the moment of the former doublet as 0.7×10^{-18} and that of the latter as 1.6×10^{-18}. The method is necessarily somewhat arbitrary, the moments of ethyl ether and of water being used for the calculation and the two oxygen valences being assumed to act at an angle of 110° to one another. When these assumptions, together with the assignment of a moment, 0.4×10^{-18}, to the H–C bond, are used to calculate the moment of a monohydric alcohol, the value obtained, 1.61×10^{-18}, agrees satisfactorily with those observed, which, for the most part, lie between 1.65×10^{-18} and 1.70×10^{-18}. Calculation further shows that the resultant of the C–O and H–O moments, 1.52×10^{-18}, should make an angle of 84° with the direction of the C–O bond. This angle has been suggested as the reason for the absence of induced moments along the carbon chains of the alcohols as shown by the absence of increase in the moment of the alcohols with increase in the number of carbons.

The resolution of the two C–O and the two H–O moments in ethylene glycol is a complicated matter because the angle between the two resultants, 1.52×10^{-18}, of the C–O and H–O moments is variable as the result of the rotation about the C–O and C–C bonds. Moreover, there is a small mutual inductive effect of the moments in the two halves of the molecule upon one another. In view of these complexities which cannot be treated

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

[8] *Cf.* **Smyth**, THIS JOURNAL, 46, 2151 (1924).

[9] **Eucken** *and* Meyer, *Physik. Z.*, **30**, 397 (1929).

accurately, it seems best to attempt to obtain merely a rough idea of the magnitude of the resultant moment. It has been shown that the resultant of the C–O and H–O moments acts nearly at a right angle to the direction of the C–O bond, which makes an angle to that of the C–C bond. If the total resultant moment in each half of the molecule is taken equal to that of a monohydric alcohol, 1.7×10^{-18}, and assumed to act at right angles to the C–C bond and if all positions of one moment relative to the other around the C–C bond are assumed to be equally probable, the average moment found for the molecule should be $1.41 \times 1.7 \times 10^{-18} \times \sin 90° = 2.4 \times 10^{-18}$.[10]

When the doublets are close together, as in ethylene and propylene glycol, their considerable mutual potential energies tend toward a minimum by bringing the doublets as far as possible into opposition to one another and so reducing the resultant moment. As would be expected, the replacement of a hydrogen in ethylene glycol by a methyl group to form propylene glycol has a negligible effect upon the moment as it does not alter the positions of the hydroxyl groups relative to one another. This should not be the case, however, if the replacement of the hydrogen by methyl produced any considerable change in the energies of the other bonds. Similarly, practically identical values were found by Gross[11] for the moments of ethylene chloride, 1.86×10^{-18}, and propylene chloride, 1.85×10^{-18}. When the doublets are more widely separated as in trimethylene glycol, their mutual potential energies are less and, indeed, appear to be so small as to have a negligible effect upon the positions of the doublets relative to one another. This is evident in the higher moment found for trimethylene glycol and in the fact that the further separation of the hydroxyl groups in hexamethylene and decamethylene glycol has no apparent effect upon the moment. The rough value 2.4×10^{-18} calculated for the moment of ethylene glycol is evidently of the right order of magnitude for it lies between those of the glycols in which the hydroxyls are on adjacent carbons and those in which the hydroxyls are more widely separated.

It is of interest now to consider qualitatively the effect of the valence angles of the carbons and the possible bending of the carbon chains. Of the dihydroxybenzenes, only the ortho compound, catechol, has been measured,[12] the moment found being 2.16×10^{-18}, a value higher than that for phenol, 1.70×10^{-18},[13] by an amount slightly less than the difference between ethylene glycol and the monohydric alcohols. The angle between the two C–O valences in catechol is fixed at 60°, while in ethylene glycol it may vary from 40 to 180°. The moments of the ethers of the

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[10] *Cf.* the calculations on the dicarboxylic acid esters (Smyth and Walls, Ref. 1).

[11] Gross, *Z. physik. Chem.*, [*B*] 6, 215 (1929).

[12] Weissberger and Sangewald, *Physik. Z.*, 30, 792 (1929).

[13] Williams, *ibid.*, 29, 174 (1928); Smyth and Morgan, THIS JOURNAL, 49, 1030 (1927).

dihydroxybenzenes are smaller because the C–O moment is smaller than the H–O but the valence angles involved and the dependence of the moments upon these angles should be much the same. o-, *m*- and p-dimethoxybenzene have the moments 1.31, 1.58 and 1.81 X 10^{-18}, respectively, while o-, m- and *p*-diethyoxybenzene have the values 1.37, 1.70 and 1.76 X 10^{-18}.[12] The moments of the ortho compounds may be somewhat lowered by the mutual inductive action of the moments and by the tendency of their mutual potential energies to reach a minimum by bringing the doublets as far as possible into opposition to one another. Lowering due to these causes should be slight, if not negligible, in the meta compounds where the separation of the doublets is greater, and certainly negligible in the para compounds. Although this lowering of the moment reduces the significance of the differences between the ortho, the meta and the para compounds, it would appear that the moment increases as the angle between the lines joining the oxygens to the ring carbons increases from approximately 60 to 120, to 180°.

The fact has been cited in the first paper of this series[1] that dimethyl *o*-phthalate has a moment *2.5* X 10^{-18}, while that of dimethyl terephthalate is 2.2 × 10^{-18}, that is, when the two $-COOCH_3$ groups are attached to the ring in such a way that the group bonds make an angle of about 60° with one another, the moment is a little higher than when the group bonds point in opposite directions. This behavior was contrasted with that of the substituted benzenes in which the substituent could be regarded as giving rise to a single moment in the plane of the ring. In such cases the behavior is very different, as illustrated by the moments of the dichlorobenzenes, the ortho compound having *a* moment, *2.25* X 10^{-18}, the meta, 1.48 X 10^{-18} and the para, 0.[14] The behavior of the di-ethers is in even more marked contrast to that of the dichlorobenzenes for the change of moment with change in the angle between the group bonds is different not only in magnitude but also in direction.

Evidently, rotation around the C–O bonds makes possible so many different orientations of the hydroxyl moments relative to one another in a dihydroxy compound that the angle between the C–O bonds does not have a large effect upon the moment. When to this is added the effect of the rotation about the C–C bonds in the glycols, it appears that lengthening of the carbon chain between the two hydroxyls should have little effect upon the resultant moment once the hydroxyls are so far removed from one another that the mutual potential energies of their doublets are small. The marked increase in moment observed when the number of carbons between the hydroxyl groups is increased from two to three may result in **part** from change in the angles between the C–O bonds because of the valence angles of the added carbon, but is probably due mainly to the

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[14] Smyth, Morgan and Boyce, This Journal, 50, 1536 (1928).

greater distance between the doublets, which permits freedom of rotation and orientation relative to one another and renders negligible the lowering of the moments by mutual inductive action. Further lengthening of the chain should have little effect unless it should give rise to bending to form a ring-like structure. Unfortunately, the tetra- and pentamethylene glycols, which should be most apt to form a ring structure, have not been secured for measurement. In spite of the smallness of the effect of the angle between the C–O bonds upon the moment, it would seem that any very pronounced bending of the carbon chain might cause noticeable differences between the moments of molecules possessing chains of different lengths. Certainly, if any one molecule were so bent as to bring its hydroxyl groups into contact with each other, its moment would be materially different from those in which such proximity between the hydroxyl groups did not occur.

The difference between the value found for hexamethylene glycol and that for decamethylene glycol, though slightly greater than the probable experimental error, is too small to be significant. The differences between all the values found at 25° and those at 50° are no greater than the experimental error, although measurement over a wide temperature range should show an increase in the moments of ethylene and propylene glycol if they are low because of the mutual potential energies of their doublets. If there were any pronounced ring formation in the longer molecules, they might be expected to be affected by change of temperature and show a change of moment such as was found for diethyl succinate.[1] It may be concluded that the moments of the glycols give no indication of ring formation in the molecule or of very pronounced bending of the carbon chain, although they do not preclude the possibility of some bending of the chain.

Summary

The dielectric constants and densities of n-butyl alcohol and of five glycols have been measured in solution in 1,4-dioxane at 25° and at 50° and the refractive indices of the substances in the pure liquid state or in solution have been determined.

The data have been used to calculate the electric moments of the molecules and the agreement of the value for n-butyl alcohol with that obtained by other methods is regarded as evidence of the correctness of the results for the glycols.

Because of rotation around the bonds the relative positions of the two hydroxyl groups in the molecule do not have large effects upon the moment, but the absence of any significant difference in moment between trimethylene, hexamethylene and decamethylene glycol is regarded as indicating that there is no very pronounced bending of the carbon chain.

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THE STRUCTURE OF GROUPS XO_3 IN CRYSTALS

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In this paper will be presented the general results of a series of x-ray investigations which have been carried out with the object of determining the structures of radicals XO_3 in crystals.

Previously it was generally believed that the structures of the groups XO_3 were different principally in the absolute dimensions, *i. e.*, that they all were built like the CO_3-group with the cation situated in the center of an equilateral triangle formed by the 3 oxygens. In 1928 I was able to show from an examination of the atomic arrangement in $KBrO_3$ that the BrO_3 group had the shape of a low trigonal pyramid.[1] As a consequence of this result I classified the groups XO_3 in two classes: one including the co-planar groups and the other including all pyramidal groups. From considerations to be given later I referred to class 1 the $(NO_3)^{-1}$-, $(CO_3)^{-2}$- and $(BO_3)^{-3}$-groups; to class 2 the groups $(PO_3)^{-3}$, $(SO_3)^{-2}$, $(ClO_3)^{-1}$, $(AsO_3)^{-3}$, $(SeO_3)^{-2}$, $(BrO_3)^{-1}$ and $(SbO_3)^{-3}$. The empirical material upon which this classification was founded was very meager; my later investigations have, however, confirmed my predictions completely.

At present we have x-ray data on the following groups: $(NO_3)^{-1}$, $(CO_3)^{-2}$, $(BO_3)^{-3}$, $(ClO_3)^{-}$, $(SO_3)^{-2}$, $(BrO_3)^{-1}$, $(AsO_3)^{-3}$ and $(SbO_3)^{-3}$. In the following section I will describe the experimental results for the individual groups.

Experimental Data on the Structure of the Individual Groups XO_3

NO_3 Group.—Sodium nitrate and lithium nitrate are the two crystals which have given the most reliable data on the NO_3 group. In the first place the atomic arrangement is characterized by only one degree of freedom, and in the second place the oxygens have a large effect on the intensities of reflection, so their positions can be determined with accuracy.

According to the symmetry of the space group the NO_3 radical in these two crystals is planar with nitrogen in the center of an equilateral oxygen triangle. The dimensions of the group were determined as

$NaNO_3$[2]	N–O, 1.22 Å.	O–O, 2.11 Å.
$LiNO_3$[3]	N–O, 1.25 Å.	O–O, 2.17 Å.

We have reason to believe that the NO_3 group will not be influenced very much by the surrounding atoms in the lattices because of the strength

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[1] W. H. Zachariasen, *Norske Vid. Akad. Skr. Oslo*, No. 4, p. 90 (1928).

[2] R. W. G. Wyckoff, *Phys. Rev.*, 16, 149 (1920).

[3] W. H. Zachariasen, Ref. 1, p. 53.

of the bonds inside the group. V. M. Goldschmidt[4] has suggested that the dimensions of the group should be greater in compounds containing small cations; e. g., we should expect to find a larger NO_3 group in lithium nitrate than in sodium nitrate. Definite proof of the effect of Goldschmidt's contrapolarization is, however, still lacking. If such an effect exists, it must at any rate be small.

Due to the small scattering power of nitrogen it has been impossible to prove definitely that the NO_3 group always is a planar group. It seems, however, justifiable to assume that the NO_3 group will possess the same structure in all compounds (small deformations may of course be present in some compounds).

CO_3 Group.—In carbonates with calcite structure a planar CO_3 group follows from the space group symmetry. The dimensions of the group are found to be the same as for the NO_3 group within the limits of error. Wyckoff[5] determined from calcite:

$CaCO_3$	C–O, 1.23 Å.	O–O, 2.13 Å.

For the struciure of the CO_3 group in other compounds the same considerations that were given for the NO_3 group will be valid.

W. L. Bragg[6] has determined the dimensions of the CO_3 and the NO_3 groups also from the refractive indices of crystals with calcite or aragonite structure. In the CO_3 group he finds, in agreement with the x-ray data, C–0 1.25 Å. For the NO_3 group, however, he calculated N–O 1.10 Å., which is in definite disagreement with the x-ray determinations 1.24 Å. This result is not suprising when we consider that the center of the oxygen atom determined according to these two methods need not be identical.

BO_3 Group.—Indirect evidence that the BO_3 group is analogous to that of the carbonate group we have from the fact that the two compounds, dolomite, $CaMg(CO_3)_2$, and nordenskjöldine, $CaSn(BO_3)_2$, are isomorphous. Only one x-ray determination of the BO_3 group exists, namely, from the compd $Be_2(BO_3)(OH)$ (the rare mineral hambergite). The atomic arrangement in hambergite is characterized by twenty-one degrees of freedom, so the accuracy necessarily is not very great. A conscientious determination of the parameters led to a planar BO_3 group, however. This result combined with the indirect evidence should be sufficient proof of the analogy to the NO_3 and CO_3 groups. The dimensions of the BO_3 group from hambergite are

$Be_2(BO_3)(OH)$[7]	B–0, 1.35 Å.	O–O, 2.35 Å.

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[4] V. M. Goldschmidt, *Geochem. Vert. Ges. VIII Norske Vid. Akad. Skr.* No. 2, p. 64 (1926).

[5] Wyckoff, *Am. J. Sci.*, 50,317 (1920).

[6] W. L. Bragg, *Proc. Roy. Soc.* (London), **A105**, 370 (1924); **106**, 346 (1924).

[7] W. H. Zachariasen, *Z. Krist.*, 76,289 (1931).

ClO_3 Group.—The earlier x-ray investigations on sodium chlorate led to very divergent structures of the ClO_3 group. Kolkmeijer, Bijvoet and Karssen[8] found Cl–O 0.93 Å., O–O 1.56 Å.; Dickinson and Goodhue,[9] Cl–O 1.43, O–O 2.34 Å.; Vegard[10] Cl–O 1.85 Å., O–O 1.17 Å. The two former sets of values result in nearly planar groups, while Vegard's ClO_3 values lead to an extremely acute trigonal pyramid. I have determined the atomic arrangement in sodium chlorate with the greatest care, using absolute intensity measurements and applying two-dimensional Fourier analysis of the electron distribution.[11] My results were in fairly good agreement with those of Dickinson and Goodhue, but differ in one essential point. My observations show definitely that the ClO_3 group is not planar, but has the shape of a low trigonal pyramid.

From an investigation on potassium chlorate, which has an atomic arrangement completely different from sodium chlorate, I have also determined the structure of the ClO_3 group, making use of the same experimental methods.[12] These two independent determinations of the ClO_3 group agree very well

$KClO_3$	Cl–O, 1.48 Å.	O–O, 2.38 Å.	*h*, 0.50 Å.
$NaClO_3$	Cl–O, 1.48 Å.	O–O, 2.38 Å.	*h*, 0.48 Å.

h being the displacement of chlorine out of the oxygen plane.

SO_3 Group.—Recently Mr. Buckley and I have determined the atomic arrangement in sodium sulfite.[13] Our results for the SO_3 group are

Na_2SO_3	S–O, 1.39 Å.	O–O, 2.24 Å.	h, 0.51 Å.

It is to be remarked that the dimensions of the SO_3 group in sodium sulfite probably are too small due to the fact that the sodium atoms surround the group in an unsymmetrical way. If the SO_3 group is surrounded by the neighboring ions in a more symmetrical way (as is the case for the ClO_3 group in sodium chlorate and potassium chlorate), we might expect dimensions more close to those of the ClO_3 group.

BrO_3 Group.—The structure of the BrO_3 group was determined from the atomic arrangement in potassium bromate. The results obtained were

$KBrO_3$	Br–O, 1.68 Å.	O–O, 2.76 Å.	h, 0.56 Å.

AsO_3 Group and SbO_3 Group.—The crystal lattices of arsenic trioxide and antimony trioxide were determined by Bozorth.[14] The lattice can be considered as composed of molecules As_4O_6 or Sb_4O_6. As the coordination numbers are 3 and 2, each molecule is built up of 4 AsO_3

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[8] Kolkmeijer, Bijvoet, Karssen, *Proc. Roy. Acad.* Amsterdam, *23,* 644 (1921).

[9] Dickinson and Goodhue, THIS JOURNAL, 43,2045 (1921).

[10] L. Vegard, *Z. Physik,* 12, 289 (1922).

[11] Zachariasen, Z. *Krist.,* 71, 517 (1929).

[12] Zachariasen, *ibid.,* 71, 501 (1929).

[13] Zachariasen and Buckley in press in *Phys. Rev.*

[14] Bozorth, THIS JOURNAL, 45,1621 (1923).

or SbO_3 groups, each oxygen being divided between two groups. It is thus not correct to speak of the radicals AsO_3 and SbO_3 existing in these lattices, but only about groups of the said composition.

Bozorth's results for the structure of the groups were

As_2O_3	As–O, 2.01 Å.	O–O, 3.28 Å.	h, 0.67 Å.
Sb_2O_3	Sb–O, 2.22 Å.	O–O, 3.62 Å.	h, 0.75 Å.

Among important radicals XO_3 for which experimental data are lacking we have $(PO_3)^{-3}$ and $(SeO_3)^{-2}$.

Considerations on **the** Structure of Groups **XO_3**.—The experimental data at once suggest the classification of the groups introduced by the **author**.[15] The groups examined are divided between the two classes in the following way: Class 1, planar groups, BO_3, CO_3, NO_3; Class 2, pyramidal groups, SO_3, ClO_3, AsO_3, BrO_3, SbO_3.

The following regularity exists: if we consider the groups to have the valence usually ascribed to them (indicated throughout the paper), the number of valence electrons in the groups of class 1 is 3×8; in the groups of class 2 the number of valence electrons is $3 \times 8 + 2$. This feature is so striking that it seems natural to seek the cause of the differentiation in planar and pyramidal structures in the number of the valency electrons.

It is not surprising to find that the symmetry of the group has to be correlated with the number of valence electrons. A rigorous explanation of the rule cannot, however, be given until a wave-mechanical treatment of such groups has been carried out. In the meantime we must be content with rough approximations.

It is well known that the greater part of the inorganic non-metallic crystal structures can be treated successfully by introducing the conception of ions, ionic dimensions and polarizability. The results obtained from this point of view may be considered as an approximation to the correct ones. It would be incorrect to consider the bonds within the radicals dealt with here to be of a purely ionic character; therefore we have to take into account also the deformations taking place in the electron clouds of the ions.

Let us consider the ClO_3 group as an example. The constituents are Cl^{+5} and O^{-2}. The polarizability is related to the mole refraction by the well-known expression

$$R = \frac{4\pi}{3} N\alpha$$

α is again defined by the relation $m = \alpha F$, where m is the moment induced in an atom under the influence of the force F. The moment we must consider to be due to a displacement of the centers of the positive and negative charges in the atom. Practically this will mean a displacement

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[15] Zachariasen, *Norske Vid. Akad. Skr. Oslo, No. 4*, p. 136 (1928).

of the core relative to the center of the outer electron shell. If there are v valence electrons and if the amount of displacement is d, we have

$$m = dxv \text{ or } d = \frac{3RF}{4\pi Nve}$$

i. e., the displacement is proportional to the molar refraction, and inversely proportional to the number of valence electrons. It is evident therefore that the polarizability constants do not give us directly the degree of deformation in the outer electron shell.

The molar refraction values for O^{-2} and Cl^{+5} are 3.3 and 1.5 cc.[16] If we consider that oxygen has an outer shell of 8 electrons while chlorine has only 2, we derive from our result above that deformation on the outer shell is greatest for Cl^{+5}. It has been shown that groups with a polarizable central ion will have an unsymmetrical structure, so that a pyramidal ClO_3 group is just what we should expect.[17] The deformations taking place are easy to picture. The field intensity due to the three oxygen ions will polarize the chlorine ion, and in such a way that the outer electron density (the two valence electrons) is pushed away from the oxygens. The chlorine ion on the other hand will to some extent attract the electron density corresponding to the valence electrons of oxygen. The relative displacement of core and valence electrons is, however, much greater in the Cl^{+5} ion both because of the stronger force acting upon it and also because of the small number of valence electrons.

As a final result we obtain a ClO_3 group which roughly can be pictured as a tetrahedral arrangement; three of the corners are occupied by oxygen ions, the center by a Cl^{+7} ion and the fourth corner by the two valence electrons of chlorine. If this tetrahedron were accurately regular and if we could consider the ions and the two electrons to be point charges, the center of the positive and negative charges would coincide. It has, however, been definitely shown that unsymmetrical molecules have a permanent dipole moment. The observed moment is very small and corresponds to only a few hundreths of an Ångström unit displacement between the centers of the negative and positive charges. For rough considerations of the structure of such groups we may therefore disregard this displacement. The conception of a tetrahedral ClO_3 group as presented above would give the following relation between the oxygen–oxygen distance (a) and the height h of the Cl^{+7} core above the plane of the oxygens

$$h = \frac{a}{12}\sqrt{6} \qquad (1)$$

From x-ray determination we will obtain the position of the Cl^{+7} core, as the two valence electrons have no detectable effect on the scattering power. The centers of the oxygens fixed by the same method on the

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[16] From paper submitted to *Phys. Rev.*

[17] Van Arkel and de Boer, *Ree. trav. chim.*, 47,593 (1928).

other hand must correspond very closely to the center of electron density as the valence electrons in this case have **an** appreciable effect. The experimentally determined values of h and a are thus within the limits of error identical with those of Equation (1). In the table is shown how closely the relation I holds for all the groups examined, so that there seems to be justification for the conception of tetrahedral groups.

Group	a	h	$\frac{a}{12}\sqrt{6}$	r
SO_3	2.24	0.51	0.46	1.39
ClO_3	2.38	.49	.49	1.48
AsO_3	3.28	.67	.67	2.01
BrO_3	2.76	.56	.56	1.68
SbO_3	3.62	.75	.74	2.22

The picture given for the structure of pyramidal groups XO_3 must not be taken too literally. To say that the two valence electrons of Cl^{+5} lie at the fourth corner of the tetrahedral structure is naturally incorrect, and must be interpreted as meaning a concentration of electron density in that region. If we use interpretations of that kind, I believe that the picture can be considered as an approximation toward the true distribution of electron density in the group.

In a following paper[16] I am trying to locate the positions of the displaced electrons in the ClO_3 group from the strength of the birefringence in potassium chlorate. The result of that calculation supports the considerations given here.

A Relation between the Symmetry of Groups and Molecules XY_2, XY_3 and the Number of Valence Electrons

In the previous section we found that groups $(XO_3)^{-m}$ had a co-planar structure if the total number of valence electrons was 24 (3 X 8), while the groups were pyramidal if there were 26 (3 X 8 + 2) valence electrons in the group.

A more general formulation of this empirical rule will now be considered. We will confine ourselves to groups and molecules of the form XY_2 and XY_3, in which all atoms Y are chemically identical and are related to atom X in the group in an identical way. Furthermore, we will make the restriction that the atomic numbers are relatively small.

The existing reliable observations then show:

$$\text{A group or molecule}\left\{\begin{matrix}(XY_2)^{-m}\\(XY_3)^{-m}\end{matrix}\right.\text{ is }\left\{\begin{matrix}\text{co-linear}\\\text{co-planar}\end{matrix}\right.\text{ if }\left\{\begin{matrix}\Sigma v = 2p\\\Sigma v = 3p\end{matrix}\right.$$

Σv is the total number of valence electrons in the group or molecule; p represents the number of valence electrons in the inert gas following atom Y in the periodic system. If, on the other hand, the relation between Σv and p takes the form $\left\{\begin{matrix}\Sigma v = 2p + \Delta\\\Sigma v = 3p + \Delta\end{matrix}\right.$ the group or molecule is $\left\{\begin{matrix}\text{angular}\\\text{pyramidal}\end{matrix}\right.$.

Because these rules have been derived from empirical data, we may with reason use it as a guiding principle until an exact formulation on the basis of wave mechanics can be given, or until we have experimental evidence that the rule does not hold.[18]

In the following table I have listed a number of groups and molecules according to the kind of structure which should be expected if the rule holds.

TABLE I

Co-linear	Angular
CO_2, ON_2, CS_2	SO_2, NO_2, SH_2, OH_2, OO_2 ? (ozone)
$(NN_2)^-$, $(HF_2)^-$	$(NO_2)^-$
Co-planar	**Pyramidal**
SO_3, BH_3, BF_3, BCl_3, AlF_3	NH_3, PH_3, AsH_3, PF_3, PCl_3
$(BO_3)^{-3}$, $(CO_3)^{-2}$, $(NO_3)^-$	$(OH_3)^+$, $(PO_3)^{-3}$, $(SO_3)^{-2}$, $(ClO_3)^-$
	$(AsO_3)^{-3}$, $(SeO_3)^{-2}$, $(BrO_3)^-$

Mr Ziegler in this Laboratory is at present working on the crystal structure of sodium nitrite. The investigation is not quite completed yet, but his results so far do not seem to be compatible with a co-linear $(NO_2)^-$ group.

Groups XO_2 for which $\Sigma v = 2 \times 8 + 2$ can be pictured as an equilateral triangle. The center of the triangle will be occupied by the core of the central ion, two of the corners by oxygens and the third corner by the two displaced valence electrons. The angle between the two cation–oxygen bonds would thus be 120 degrees.

Since the above paper was written, valuable contributions to the quantum mechanical treatment of shared electron bonds have been made by Slater[19] and Pauling.[20]

Pauling has applied the theory on groups XO_3 with the following results. For groups XO_3 of class 2 in my notation he finds that the angle between the X–O bonds is $109^1/_2$ (the tetrahedral angle), in excellent agreement with the experimental results I have obtained. In groups of class 1, however, the central atom according to Pauling is oscillating with a very small amplitude perpendicular to the oxygen plane, again in accordance with the results of this paper.

There are thus two ways of interpreting the structure of groups XO_3, which both lead to the same result: one being the conception of shared electron bonds (naturally in the quantum mechanical treatment), the other being the conception of ions and their deformation in the field of the surrounding ions. These two methods of attack are dualistically related to each other.

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[18] It is to be remarked that the above rule for the structure of groups XY_2 and XY_3 can be deduced directly from considerations of ions and their polarizability.

[19] Slater, Phys. *Rev.*, **37**, 481 (1931).

[20] Pauling, THIS JOURNAL, 53, 1367 (1931).

Summary

The general results concerning the structure of groups XO_3 in crystals are given. The groups are found to be of two kinds, one kind of groups has a co-planar structure, the other a low pyramidal structure. In the following table *a* denotes the oxygen to oxygen distance; *r* the cation to oxygen distance and h the displacement of the cation out of the plane of the oxygens.

Co-planar groups

	a	F
$(BO_3)^{-3}$	2.35 Å.	1.35
$(CO_3)^{-2}$	2.13	1.23
$(NO_3)^{-}$	2.14	1.23

Pyramidal groups

	a	r	b
$(SO_3)^{-2}$	2.24	1.39	0.51
$(ClO_3)^{-}$	2.38	1.48	.49
$(AsO_3)^{-3}$	3.28	2.01	.67
$(BrO_3)^{-}$	2.76	1.68	.56
$(SbO_3)^{-3}$	3.62	2.22	.75

It is pointed out that groups $(XO_3)^{-m}$ are co-planar if the number of valence electrons in the groups is 3×8, while a pyramidal arrangement seems to be connected with $3 \times 8 + 2$ valence electrons. An explanation of the formation of the asymmetrical groups in terms of ions and their polarizability is given. The displacement h is related to the oxygen–oxygen distance *a* by the expression $h = (a/12)\sqrt{6}$. This relation suggests a simple picture of the pyramidal groups; they can be considered as tetrahedral groups, with three of the corners occupied by oxygen ions, the center by the cation core and the fourth corner by two displaced electrons.

It is shown that the symmetry of groups $(XY_2)^{-m}$ and $(XY_3)^{-m}$ can be correlated with the number of valence electrons. The result is expressed in the following rule: A group or molecule $\left\{\begin{matrix} XY_2 \\ XY_3 \end{matrix}\right.$ is $\left\{\begin{matrix} \text{co-linear} \\ \text{co-planar} \end{matrix}\right.$ if the number of valence electrons in the group or molecule (Σv) can be expressed by $\left\{\begin{matrix} \Sigma v = 2p \\ \Sigma v = 3p \end{matrix}\right.$, *p* being the number of valence electrons in the inert gas following atom Y in the periodic system. If the number of valence electrons has to be written in the form $\left\{\begin{matrix} \Sigma v = 2p + \Delta \\ \Sigma v = 3p + \Delta \end{matrix}\right.$ the group or molecule is $\left\{\begin{matrix} \text{angular} \\ \text{pyramidal} \end{matrix}\right.$.

CHICAGO, ILLINOIS

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

THE VOLUMETRIC ESTIMATION OF FLUORINE BY MEANS OF CEROUS NITRATE

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Among the compounds which have been employed in the gravimetric determination of fluorine are: calcium fluoride,[1] barium fluoride,[2] lanthanum fluoride,[3] thorium fluoride[4] and lead chlorofluoride.[5] While good results have been reported in most cases, none of the gravimetric methods seems to possess the accuracy and general applicability that are necessary for a standard determination.

Omitting acidimetric titrations of hydrofluoric and fluosilicic acids, a list of volumetric procedures includes the methods of Hempel and Scheffler,[6] Wagner and Ross,[7] Penfield,[8] de Boer,[9] Steiger[10] and Merwin,[11] Guyot[12] and Greeff[13] and Fairchild.[14] The first three mentioned involve the evolution of silicon tetrafluoride which is either measured or absorbed and determined acidimetrically. Such procedures possess the advantage of being applicable in the presence of phosphates, but have the disadvantage that their accuracy depends to no small degree upon the skill and experience of the analyst. The method of de Boer depends upon the fact that the color produced by a zirconium solution when treated with sodium alizarin sulfonate is bleached by fluoride ions but not by other halogens at low acid concentrations.

The Steiger–Merwin and Guyot–Greeff methods are probably the two most widely used at the present time. The former involves the removal of the yellow color from a hydrogen peroxide titanium solution by fluorides, while the latter consists in the formation of FeF_6^{---} ion when ferric chloride is added to a fluoride solution, the indicator according to Greeff being SCN^-. Critical studies of these two procedures have been made by Fresenius[15] and by Treadwell and Köhl,[16] who employed

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[1] Berzelius, *Pogg. Ann.*, 1,169 (1824).

[2] Rose, *Ann.*, 72, 343 (1849).

[3] Meyer and Schulz, *Z. angew. Chem.*, 38,203 (1925).

[4] Pisani, *Comfit. rend.*, 162,791 (1916).

[5] Starck, *Z. anorg. Chem.*, 70, 173 (1911).

[6] Hempel and Scheffler, *ibid.*, 20,1201 (1899).

[7] Wagner and Ross, *J. Ind. Eng. Chem.*, 9, 1116 (1917).

[8] Penfield, *Z. anal. Chem.*, 21,120 (1882).

[9] De Boer, *Chem. Weekblad*, 21,404 (1924).

[10] Steiger, THIS JOURNAL, 30,219 (1908).

[11] Merwin, *Am. J. Sci.*, 28, 119 (1909).

[12] Guyot, *Compt. rend.*, 71,273 (1870).

[13] Greeff, *Ber.*, 46,2511 (1913).

[14] Fairchild, *J. Wash. Acad. Sci.*, 20,141 (1930).

[15] Fresenius, Schröder and Frommes, *Z. anal. Chem.*, **73**, 65 (1928).

[16] Treadwell and Köhl, *Helv. Chim. Acta*, 9,470 (1926).

the potentiometer as an end-point indicator for the ferric chloride titration. In a more recent modification of the Guyot–Greeff method, Fairchild added an excess of ferric chloride to the fluoride solution, estimating the excess of ferric chloride by the addition of potassium iodide and titration of liberated iodine by means of thiosulfate. Good results were obtained when the variables, temperature, time and concentration were carefully controlled. Although very satisfactory under the proper conditions, the limited ranges of these two methods and the existence of several variables affecting their accuracy make the development of better procedures for the analysis of fluorides highly desirable.

Trivalent Cerium as a Precipitant.—The use of lanthanum acetate as a precipitant for fluoride ions by Meyer and Schulz suggested to us possibilities in the use of cerium. Attempts at a gravimetric separation of cerous fluoride were, however, unsatisfactory on account of the gelatinous character of the precipitate. What results were obtained indicated a high degree of adsorption on the surface of the cerous fluoride. This was borne out by further attempts to obtain a potentiometric end-point without filtration.

A Back Titration Method.—Since the gravimetric separation of cerous fluoride proved to be impracticable due to adsorption, a volumetric modification was investigated. It was hoped that the error introduced in the gravimetric method by adsorption might be eliminated in the volumetric procedure.

Materials.—The sodium fluoride which was used as a primary standard was prepared by adding an excess of hydrofluoric acid to sodium bicarbonate, the fluoride thus formed being dried and finally fused in platinum. The reagent quality hydrofluoric acid was specially purified for the above preparation by repeated distillation. Sodium fluoride obtained by this method gave a clear water solution. The purity of this salt was checked by conversion to the sulfate.

White reagent quality cerous nitrate was'used in these experiments. Samples of this material were ignited to the oxides and the cerium content determined by Metzger's bismuthate method[17] and the method of Lenher and C. Meloche.[18] The results of these analyses showed the residue to consist of 98.6% CeO_2. The remainder of the sample was found to be oxides of the rare earths. Calculations indicate that in the case of the largest samples reported in the table error due to rare earth content is not greater than 0.0002 g. (about 0.00003 g. of NaF per 10 cc. of the titrating solution used). This is due to a proximity of molecular and atomic weights. Correction for impurities was therefore neglected.

Method.—The proposed method involved the addition of an excess of a known cerous nitrate solution to a neutral solution of sodium fluoride, and titration of the excess cerium by means of potassium permanganate, according to the method of Lenher and C. Meloche. This method depends upon the equations

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[17] Metzger, THIS JOURNAL, 31, 523 (1909).

[18] Lenher and C. Meloche, *ibid.*, **38**, 66 (1916).

$$6Ce(NO_3)_3 + 2KMnO_4 + 4H_2O = 4Ce(NO_3)_4 + 2Ce(OH)_4 + 2KNO_3 + 2MnO_2$$

and

$$Ce(NO_3)_4 + 4H_2O = Ce(OH)_4 + 4HNO_3$$

An excess of zinc oxide is added to take care of the nitric acid produced.

Before application of the permanganate titration to the indirect determination of fluoride, it was necessary to test the accuracy of the cerium determination. Table I contains a few typical results obtained by the direct titration of cerous nitrate solutions with permanganate. The titrations were made in the usual way in the presence of zinc oxide at a temperature of 80°. The addition of 0.5–1.0 g. of zinc sulfate to the solution aided materially in the coagulation of the precipitate. In this and in all subsequent work the concentration of stock solutions was carefully checked by weighing the residues resulting from the evaporation of measured volumes.

TABLE I

Stock solution of $Ce(NO_3)_3$—10 cc. = 0.0377 g. of CeO_2

(a) Using macroburet			(b) Using microburet		
CeO_2 added, g.	CeO_2 calcd., g.	Vol. of sample, cc.	CeO_2 added, g.	CeO_2 calcd., g.	Vol. of sample, cc.
0.0302	0.0301	50	0.00152	0.00160	50
.0151	.0150	50	.00114	.00110	50
.0075	.0075	50	.00076	.00071	50
.0038	.0035	50	.00076	.00068	50
			.00076	.00065	50

An examination of data indicates that under optimum conditions an agreement of 0.0001 g. of CeO_2 may be expected. Since this represented a satisfactory value, the method was next applied to the estimation of excess Ce^{+++} in the fluoride titration.

The Indirect Titration of Fluorides—A neutral solution of sodium fluoride having a volume of about fifty cubic centimeters was treated with an excess of a known solution of cerous nitrate. The solution was then heated to about 80°, 0.5 g. of zinc oxide was added and the titration was made with $N/40$ potassium permanganate. Instead of titrating the solution to the first detectable change of color in the supernatant liquid, the precipitated MnO_2, CeF_3 and $Ce(OH)_4$ were removed by means of a Gooch crucible slightly before the equivalence point was reached. The filtrate was then reheated, a slight excess of zinc oxide was added and the titration with permanganate completed. Filtration was necessary at this point since it was discovered that otherwise an over-titration was obtained due to adsorption of MnO_4^- ion.

Using this method it was possible to detect quantities of fluoride ranging from 0.1 to 0.001 g. with an accuracy of about 0.0003 g. Characteristic results are given in Table II.

Although exhibiting a fair degree of accuracy, this procedure is rather cumbersome and difficult for one not familiar with it. The color and

TABLE II

RESULTS OF EXPERIMENTS

NaF added, g.	NaF found, g.	Volume of sample, cc.	NaF added, g.	NaF found, g.	Volume of sample, cc.
0.1502	0.1502	50	0.0108	0.0108	50
.1502	.1502	50	.0072	.0070	100
.0719	.0722	50	.0072	.0072	100
.0108	.0108	50	.0072	.0072	100

extent of coagulation of the precipitate give some indication of the point at which filtration should be made, but this cannot usually be determined without two or three trials upon fluoride solutions of equal concentration. This necessitates the use of aliquots. It is important that the filtration be performed as close to the equivalence point as possible, since the error due to adsorption is then at a minimum. Ions such as phosphate and oxalate which precipitate cerium interfere with the determination. This includes hydroxyl ion since if the PH be greater than the value resulting from the buffering effect of ZnO, $Ce(OH)_3$ will be precipitated.

Direct Titration.—In the search for a better scheme of analysis it was decided to try adsorption indicators, hoping that a direct titration with cerium would be possible. Samples of fluoride were titrated with cerous nitrate at room temperature, using a variety of indicators. Among these two were discovered which exhibited a color change at the stoichiometric point: ampho magenta and diiodophenylsulfonephthalein. After trying various concentrations of the phenolsulfonephthalein, the end-point (from a reddish-brown to a yellow) was not thought to be sufficiently sharp to warrant further investigation.

Ampho Magenta as an Indicator.[19]—The ampho magenta in a concentration of 20 mg. to a liter was found to give a very satisfactory indication of the equivalence point at which it changed from a deep blue to a less intense purple. Results using this indicator are given in Table III.

TABLE III

20 Cc. of solution containing the indicator was used in all cases. Stock solution of $Ce(NO_3)_3$—10 cc. = 0.0401 g. of CeO_2

(a) Using macroburet Stock NaF — 10 cc. = 0.1502 g.		(b) Using microburet Stock NaF — 10 cc. = 0.0015 g.	
NaF added, g.	NaF found, g.	NaF added, g.	NaF found, g.
0.1502	0.1503	0.00075	0.00081
.1502	.1502	.00075	.00084
.0451	.0452	.00075	.00074
.0451	.0454	.00075	.00064
.0300	.0300	.00075	.00074
.0150	.0150		

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[19] Ampho magenta was obtained from the National Aniline and Chemical Company and was described by them as made by diazotizing *p*-aminoethylacetanilide and coupling with 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

The accuracy of this determination is seen to be about 0.0001 g. of sodium fluoride under the best conditions. Although more dilute solutions of magenta were tried, the end-point seemed most satisfactory at the concentration given. A very slight decrease in the sharpness of the color change was observed in the case of the smaller quantities of fluoride.

Methyl Red as an Indicator,—Kurtenacker and Jurenka[20] have recently published a procedure involving the use of methyl red as an indicator for the titration of fluorides with cerous nitrate. Samples of sodium fluoride were analyzed according to their procedure and very satisfactory results obtained. Titrations were made at a temperature of 80° *as* recommended. The results are given in Table IV.

TABLE IV

Stock solution $Ce(NO_3)_3$—10 cc. = 0.0401 g.

Using macroburet		Using microburet	
Stock solution NaF—10 cc. = 0.1502 g.		Stock solution NaF—10 *cc.* = 0.0015 g.	
NaF added, g.	NaF found, g.	NaF added, g.	NaF found, g.
0.1502	0.1505	0.00075	0.00071
.1502	.1500	.00075	.00071
.0300	.0297	.00030	.00044
0300	.0298	.00030	.00023
.0300	.0296	.00030	.00022

These results exhibit an accuracy of about 0.0001, with the microburet and 0.0004 g. with the macroburet. It will be noticed that the procedure is satisfactory for the detection of quantities of fluoride amounting to less than a milligram.

It was impossible to compare these values with those of Kurtenacker and Jurenka, since similar data were not published by them. Although claiming an ability to detect a few milligrams of fluorides, Kurtenacker and Jurenka reported difficulty in obtaining results in agreement with the theoretical values based upon the cerium content of the solution added in the titration. A deviation of as much as 4% was reported in some cases. Our results were not in agreement with these findings since no such discrepancy was observed.

The anomalous results obtained by Kurtenacker and Jurenka may possibly be explained in the following manner. The change of the methyl red at the end-point was apparently attributed by them to hydrolysis of the cerous nitrate, the nitric acid liberated causing a change of PH. In case the end-point is due to a change of PH, it would seem logical to run a blank titration in order to determine what excess of cerous nitrate was necessary to change the color of the indicator. When an aqueous solution of the indicator was titrated with the standard cerous nitrate solution, 2.5 cc. was required to change the color of the methyl red. No color change occurred under similar circumstances with the ampho ma-

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[20] Kurtenacker and Jurenka, *Z. anal. Chem.*, 82,210 (1930).

genta. If, however, fluoride is present, the titration with cerous nitrate gives a color change with the indicator when an equivalent amount of cerous nitrate has been added to the fluoride. When quantities of cerous nitrate which were insufficient to convert the indicator to the acid form were titrated with a sodium fluoride solution, the color of the methyl red gradually changed from yellow to red and at the equivalence point the solution again became yellow. The addition of excess cerium or excess fluoride now caused a change, respectively, from yellow to red or from red to yellow. From this point on the end-point was reversible. Thus it seems likely that in the presence of Ce^{+++} ions, precipitated cerous fluoride preferentially adsorbs indicator and in the presence of fluoride ions, the cerous fluoride preferentially adsorbs fluoride.

No end-point was obtained in the presence of sulfate ion either in the case of the ampho magenta or in the case of the methyl red. Attempts at varying the P_H resulted either in the precipitation of cerous hydroxide or in a change of the color of the indicator. In addition to sulfate ions, in general, any ion such as phosphate or oxalate capable of precipitating cerium will interfere with the determination.

Summary

An indirect method and two direct methods for the volumetric estimation of fluorides with cerous nitrate are given. Neutral solutions must be used in all cases.

The indirect method consists of adding a known excess of cerous nitrate to a fluoride solution and determining the excess cerium by means of a back titration with permanganate. This method is not recommended because it is cumbersome and the chance for error is relatively large.

The direct methods involve the titration of neutral fluoride solutions with cerous nitrate using methyl red and ampho magenta as indicators. These methods are very satisfactory for ordinary quantities of fluoride. The methyl red seems to be slightly better in the case of the smaller samples. Explanation of the indicator change on the basis of adsorption seems plausible.

MADISON, WISCONSIN

[Contribution from the Chemical Laboratory of the University of Illinois]

THE INTERACTION BETWEEN NITROGEN TRICHLORIDE AND NITRIC OXIDE AT −150°. III. INTERACTION OF NITRIC OXIDE AND CHLORINE AT −80 AND AT −150°

By William Albert Noyes

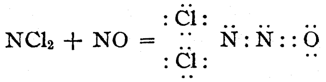
Received April 8, 1931 Published June 8, 1931

In the papers already published[1] it has been shown that at −80 and −150° nitric oxide reacts with nitrogen trichloride chiefly in accordance with the equations

$$\text{At } -80^\circ \qquad 2NO + NCl_3 = N_2O + NOCl + 2Cl$$
$$\text{At } -150^\circ \qquad 3NO + NCl_3 = N_2O + 2NOCl + Cl$$

The difference in conduct of the compounds at the two temperatures was explained by assuming that the primary reactions, in both cases, are expressed by the equations

$$NO + NCl_3 = NOCl + NCl_2$$



$$NCl_2 + NO = \begin{matrix} :\ddot{Cl}: \\ \because \\ :\underset{\cdot\cdot}{\ddot{Cl}}: \end{matrix}\ \ddot{N}:\ddot{N}::\underset{\cdot\cdot}{\ddot{O}}$$

The difference in conduct at the two temperatures was explained in the second paper by assuming that the dichlorodinitrogen oxide formed in the second reaction is so unstable at −80° that it decomposes at once to nitrous oxide and chlorine, while at −150° it is sufficiently stable to yield a second atom of chlorine to the nitric oxide before it decomposes. It was also assumed that nitric oxide reacts more rapidly with dichlorodinitrogen oxide than it does with chlorine at −150°.

As it has not been possible to isolate either of the intermediate products, nitrogen dichloride and dichlorodinitrogen oxide, it has seemed desirable to obtain further evidence for their existence. This has been accomplished in three ways: by studying the reaction between chlorine and nitric oxide at −80, −150 and −180°; by using purified carbon tetrachloride instead of the mixture of chloroform and carbon tetrachloride as the solvent for the nitrogen trichloride; and by an improved technique in carrying out the reaction and in separating the products formed.

Chlorine and Nitric Oxide at −80, −150 and −180°.—Eight to ten grams of carbon tetrachloride was frozen on the inner wall of the bulb shown in Fig. 2 of the last paper.[2] After immersing the bulb in liquid air, from 0.4 to 1.4 g. of chlorine was introduced through the long capillary tube of a small bulb in which it was weighed. The chlorine condensed and froze on the surface of the carbon tetrachloride. In the experiments at −80° the chlorine liquefied and ran to the bottom of the bulb when it

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[1] Noyes, This Journal, 50, 2902 (1928); 52, 4298 (1930).

[2] Noyes, *ibid.*, 52, 4299 (1930).

was warmed to that temperature or during the reaction with nitric oxide. In all experiments an excess of chlorine was used. In the first experiments the nitric oxide was completely converted to nitrosyl chloride within a few hours. In later experiments a rough determination of the rate of combination was made.

At —80°, 1.403 g. of chlorine (39.5 mg.-atoms) and 36.3 mg.-moles of nitric oxide were used. After thirty-three minutes from the beginning of the introduction of the nitric oxide only 7% of the latter was recovered uncombined.

At —150°, 1.402 g. of chlorine (39.5 mg.-atoms) and 35 mg.-moles of nitric oxide were used. In thirty-five minutes from the beginning of the introduction of the nitric oxide, 81% of the gas was recovered uncombined.

At —180°, 20.9 mg.-atoms of chlorine was frozen on the walls of the bulb without the use of carbon tetrachloride. After an hour and a half 67% of the nitric oxide was recovered uncombined. As some combination doubtless took place during the fractional distillation carried through the U-tubes to separate the nitric oxide from the chlorine and nitrosyl chloride, the combination which had occurred at —180° must have been less than 33% in one hour and a half.

Because of the difference in the physical conditions at —80 and at —150°, the results give only a rough approximation as to the rates of reaction at these two temperatures but the experiments show conclusively that nitric oxide and chlorine combine much more rapidly at —80 **than** at —150°.

To secure further evidence for the course of the reaction, thirteen new experiments have been carried out at —150° and nine at —80°, using carbon tetrachloride as the solvent for the nitrogen trichloride.

At the close of the reaction the bulb in which it was carried out contained six or seven substances: nitrogen, which boils at —196°; nitric oxide, which boils at —150.3'; nitrous oxide, which boils at —89.4'; chlorine, which boils at —33.6'; nitrosyl chloride, which boils at —5.4'; nitrogen trichloride, which distils easily with carbon tetrachloride; and carbon tetrachloride, which boils at 76.8°.

It has been found advisable to carry out the operations in such a manner that by using an excess of nitrogen trichloride and waiting until the reaction is complete before distilling the products, no nitric oxide is left in the mixture to be distilled.

The U-tube, H,[2] which was connected to the set of U-tubes by rubber tubing in the experiments previously described, was replaced by a smaller U-tube sealed to the end of the system. This had a capacity of 18 cc. and was connected to a manometer, drying towers and a mechanical pump. When the system was exhausted and the connection between the drying towers and the pump was closed, on allowing the air in the

U-tube to pass into the system four times the manometer rose 30 mm. Hence 1 mm. on the manometer corresponded to 2.4 cc. of air. By allowing the nitrogen present at the end of an experiment to pass through the U-tube, immersed in liquid air to remove other gases, the rise of the manometer gave a rough determination of the amount of nitrogen present. This was always small in satisfactory experiments. It may have been present in the nitric oxide used or may have been formed by the decomposition of a little of the nitrogen trichloride.

The distillation of the other substances through the series of U-tubes is best carried out in a rather high vacuum and many tedious experiments have been tried and many analyses of products have been made to secure a quantitative determination of the course of the reactions.

In carrying out the separation the reaction bulb was at first surrounded with carbon dioxide snow in acetone while most of the nitrous oxide distilled into the first U-tube surrounded with liquid air. The nitrous oxide was then distilled to the second tube, also surrounded with liquid air. The liquid air was replaced around the first U-tube and an acetone bath at $-50°$ placed around the reaction bulb. After a time the liquid air around the first U-tube was transferred to the third, the nitrous oxide in the second allowed to distil into that and the carbon dioxide–acetone mixture placed around the first tube. When a considerable part of the chlorine and nitrosyl chloride had distilled into the first U-tube, the reaction bulb was allowed to warm up slowly and the distillation of the chlorine and nitrosyl chloride continued till the latter was completely removed from the bulb as shown by the disappearance of the red color. The connection between the reaction bulb and the U-tubes was then closed and the nitrogen trichloride remaining in the former was later determined by methods which have been described. A little of the trichloride which distilled into the U-tubes with some carbon tetrachloride was unavoidably lost.

By distilling the nitrous oxide rather rapidly through the six U-tubes, using two Dewar cylinders containing liquid air, one with carbon dioxide snow and acetone and one with acetone at $-50°$, it was possible to bring the nitrous oxide into the last, 18-cc. U-tube, with only a little chlorine and nitrosyl chloride. By allowing this gas to evaporate into an empty bottle connected with a second bottle containing water, the water displaced from the latter gave a means of determining the number of moles of gas which had been condensed. The chlorine and nitrosyl chloride were absorbed in dilute sodium hydroxide. By determining the amounts of chlorine and nitrogen in aliquot portions of the solution the number of moles of each could be calculated. By subtracting the sum of these from the total moles of gas the moles of nitrous oxide were given.

In the experiments with chlorine and nitric oxide, it was necessary to use two empty bottles between the 18-cc. U-tube and the bottle of water because the heat of the reaction between the nitric oxide and the oxygen of the air caused the nitrogen dioxide and tetroxide formed to mix with the air of the first bottle. The mixture, cooled as it passed into the second bottle, remained in the lower part of that, displacing only air to the bottle containing water.

After removing the nitrous oxide as described above, the residue of chlorine, nitrosyl chloride and carbon tetrachloride was distilled back to the first two U-tubes and the fractionation was repeated to concentrate the chlorine and nitrosyl chloride in the 18-cc. tube with only a little of the carbon tetrachloride. From this the two were distilled into a solution of sodium hydroxide and the chlorine and nitrogen were determined in the latter. The following reports of two experiments illustrate the degree of separation sometimes secured. The results are given in mg.-atoms and moles.

DEGREE OF SEPARATION OF SUBSTANCES PRESENT AFTER REACTION

Temp., −80". **Initial** mg.-moles NCl_3, 13.6; **NO,** 23.3

	N_2O fraction	NOCl fraction	NCl_3 fraction	Total
N_2O **recovered** (mg.-moles)	8.1	..	...	8.1
Cl recovered (mg.-atoms)	2.2	12.5	1.1	15.8
NOCl **recovered** (mg.-moles)	0.6	12.5	...	13.1
NCl_3 **recovered** (mg.-moles)	...	..	2.9	2.9

Temp., −150°. Initial mg.-moles NCl_3, 18.4; **NO,** 35.3

	N fraction	N_2O fraction	NOCl fraction	NCl_3 fraction	Total
N (mg.-atoms)	1.6	...	...	...	1.6
N_2O	...	9.6	...	...	9.6
Cl	...	1.0	8.7	1.4	11.1
NOCl	...	0.3	21.8	...	22.1
NCl_3	...	...	...	7.2	7.2

Two experiments at −80° and three at −150° have been selected for the final report. The results were as follows.

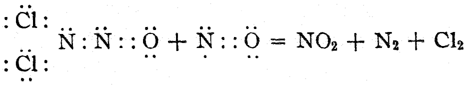
MOLECULAR AND ATOMIC RATIOS BETWEEN NITROGEN TRICKLORIDE, NITRIC OXIDE AND THE REACTION PRODUCTS

t, °C.	NCl_3	NO	N	N_2O	NOCl	Cl
− 80	1	2.18	...	0.76	1.48	1.23
− 80	1	2.49	0.2	.86	1.57	1.25
−150	1	3.15	.15	.86	1.97	0.99
−150	1	3.38	.20	.82	2.20	.67
−150	1	3.59	.05	.85	2.39	.61

A further explanation of these results will be given later.

In one experiment at −150°, a slight leakage of air caused the formation of some blue nitrogen trioxide, N_2O_3. This evidently reacted later with chlorine, forming nitrogen tetroxide and dioxide, N_2O_4 and NO_2. These were separated quite completely by fractional distillation through the

U-tubes. This result made it seem possible that dichlorodinitrogen chloride may react with nitric oxide to form nitrogen dioxide, nitrogen and chlorine



$$\overset{:\ddot{\mathrm{Cl}}:}{\underset{:\ddot{\mathrm{Cl}}:}{\ddot{\mathrm{N}}:\ddot{\mathrm{N}}::\ddot{\mathrm{O}}}} + \ddot{\mathrm{N}}::\ddot{\mathrm{O}} = \mathrm{NO_2} + \mathrm{N_2} + \mathrm{Cl_2}$$

To test this possibility, three experiments ware carried through at −150° and 9 g. of the mixture of nitrosyl chloride and chlorine obtained was carefully fractionated for the presence of nitrogen dioxide. The ratio of nitrogen to chlorine in the last portion was 1:0.985 The amount of nitrogen dioxide present, if any, must have been very small.

Structure of Nitrous Oxide.—In the first paper[1] the electronic formula, $:\mathrm{N}:::\overset{+}{\mathrm{N}}:\ddot{\mathrm{O}}:^{-}$, was proposed as probable. R. Mecke[3] and C. P. Snow[4] think that a linear formula with the oxygen between the two nitrogen atoms is indicated strongly by the infra-red spectra and the fact that the molecule has no electrical moment or only a very small one. In addition to the reasons given in the first paper, four facts about the chemical conduct of nitrogen seem inconsistent with such a formula.

(1) Nitrogen trioxide, N_2O_3, nitrogen tetroxide, N_2O_4, and nitrogen pentoxide, N_2O_5, in which nitrogen atoms are held together by oxygen atoms, dissociate very easily, nitrogen trioxide almost completely, below zero.

(2) Lochte, Noyes and Bailey[6] have shown that a double covalence between two nitrogen atoms in 2,2′-azobispropane, $(CH_3)_2CH:N::N:CH(CH_3)_2$, is much more stable than a double covalence between carbon and nitrogen in the isopropyl hydrazone of acetone, $(CH_3)_2CH:NH:N::C(CH_3)_2$. The stability of nitrous oxide, which dissociates only slightly even at 500°,[6] also points very strongly toward a union between the nitrogen atoms rather than to one between nitrogen and oxygen

(3) The electronic structure of N—O—N should be, in accordance with the rules for shared electrons,[7] $:\ddot{\mathrm{N}}:\ddot{\mathrm{O}}:\ddot{\mathrm{N}}:$. K. F. Schmidt[8] has assumed a compound of similar structure, $:\ddot{\mathrm{N}}:\mathrm{H}$, as an intermediate in many reactions of hydrazoic acid, N_3H, but it is so reactive that it has not been isolated. If nitrous oxide has the structure suggested, it should also be very reactive. The comparative indifference of carbon monoxide weakens this argument, however.

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[3] R. Mecke, *Z. Physik.*, 64, 173 (1930). A little earlier, Z. *physik. Chem.*, [B] 7, 114 (1930), he suggested the formula N≡N=O, for chemical reasons.

[4] C. P. Snow, *Proc. Roy. Soc.* (London), [A]128,294 (1930).

[5] Lochte, Noyes and Bailey, THIS JOURNAL, 44,2557 (1922).

[6] Berthelot, *Compt. rend.*, 77,1448 (1874).

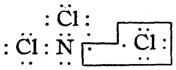
[7] Noyes, *Z. physik. Chem.*, 130,323 (1927)

[8] K. F. Schmidt, *Ber.*, 57,704 (1924).

(4) The formula N—O—N implies that both the trivalent nitrogen of the nitrogen trichloride and the bivalent nitrogen of nitric oxide have been changed to univalent nitrogen. Both chlorine and nitrogen trichloride are powerful oxidizing agents and such a result seems very improbable. The electronic formula of these papers represents one of the nitrogen atoms of nitrous oxide as trivalent and the other as quinquevalent. The quinquevalent nitrogen atom has one polar valence. This seems to be true of all quadrivalent or quinquevalent nitrogen atoms. This is clearly recognized for ammonium salts by everyone who does not claim that polar valences are not true valences. The parachors show that it is also true for nitro compounds, nitric acid, etc., which have a semipolar oxygen atom.

The discrepancy between the interpretations of the chemical and the physical evidence for the structure of nitrous oxide should lead us to hold our minds open for the present. Possibly some form of the old formula, which is, electronically,  $\underset{:\dot{O}:}{:N::N:}$, may reconcile the two views.

R. G. W. Norrish[9] has recently found a photochemical reaction between nitrogen trichloride and chlorine which he explains by assuming that nitrogen dichloride is formed. The action of light on chlorine splits it into neutral atoms having odd electrons. Heat alone has the same effect at high temperatures:



Norrish's work offers very welcome support for the explanations offered in these papers.

Small losses of nitrogen, oxygen and chlorine were observed in nearly all experiments. Whether this was merely due to errors in the difficult and complicated technique involved or whether it may be due to other reactions or other compounds which have not been discovered is worthy of careful consideration by other experimenters who may find better methods of approach to the problem. It is not the intention of the author to continue the experiments further at the present time.

Summary

1. It has been shown that in the presence of carbon tetrachloride, nitric oxide and chlorine combine rather rapidly at $-80°$, much more slowly at $-150°$ and, in the absence of any solvent, very slowly at $-180°$.

2. By means of experiments with a solution of nitrogen trichloride in carbon tetrachloride, further evidence has been obtained in support of the hypothesis that the primary reaction with nitric oxide gives nitrosyl

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[9] J G. A. Griffiths and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A130**, 608 (1931).

chloride and nitrogen dichloride; that the dichloride combines with nitric oxide to form dichlorodinitrogen oxide; that this compound decomposes very rapidly at –80° but that it is sufficiently stable at –150° to yield a second chlorine atom to nitric oxide before it decomposes; and that this reaction is much more rapid than the combination of nitric oxide and chlorine at that temperature.

3. The rather rapid combination of nitric oxide with chlorine at –80° explains the excess of nitric oxide used and the excess of nitrosyl chloride found as compared with those required by the equation given. It also explains the deficiency of chlorine. The excess of nitric oxide and nitrosyl chloride and deficiency of chlorine at –150° may be explained in the same way or by supposing a further reaction of nitric oxide with a hypothetical monochlorodinitrogenoxide.

4. No satisfactory evidence was obtained that nitrogen dioxide is formed in the reactions studied.

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THE POSSIBILITY OF BIMOLECULAR ASSOCIATION REACTIONS

BY LOUIS S. KASSEL

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It seems to have been first pointed out by Herzfeld[1] that the recombination of atoms to form a diatomic molecule could not be a bimolecular process, but must occur either on the walls or at triple collisions; Herzfeld calculated the mean life of the molecules which could result from simple collisions and obtained values of the order of 10^{-12} sec.; such a time is scarcely greater than the rather indefinite duration of a collision, which has, of course, exact meaning only after an arbitrary definition has been given. The details of this calculation might be changed slightly if it were to be repeated in the light of more recent knowledge, but the result would surely be unchanged. Furthermore, there is a considerable body of experimental material, all of which shows that diatomic molecules are not ordinarily formed at binary collisions.

There has been some tendency to generalize this statement and say that no bimolecular association reaction is possible, or at least that it will occur with only a negligible rate.[2] Now it is certainly true that bimolecular association reactions can occur, because this process is the reverse of unimolecular decomposition, and there are known some dozen reactions which are of this type, beyond any reasonable doubt. Such an argument

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[1] Herzfeld, Z. *Physik*, 8, 132 (1922).

[2] This view has been frequently expressed by H. S. Taylor and recently by Taylor and Emeléus, THIS JOURNAL, 53, 562 (1931). It has been held by numerous other workers also.

has been, and still remains, of a rather academic character, because of the known unimolecular reactions not one leads to a measurable equilibrium at the temperatures of the rate measurements; it is true that the dissociation of nitrogen tetroxide is very probably a unimolecular reaction, but this hypothesis does not have a shred of experimental evidence to support it. The study of polymerization processes in hydrocarbon vapors which has been made at Princeton during the last few years is making association reactions accessible to reaction-rate studies; fairly recently Pease[3] has presented rather definite evidence that under suitable circumstances the polymerization of ethylene is a second order reaction. The question whether such a reaction can have a true bimolecular mechanism thus becomes of real interest. It will be shown in the present paper that such a mechanism is perfectly possible, at least on general theoretical grounds.

From a practical consideration the reason why a diatomic molecule cannot be formed at a binary collision is that the energy of the reaction, which is necessarily greater than the heat of dissociation, cannot be removed from the molecule's only bond. For although it may possibly be emitted as radiation, or stored either as electronic or as rotational energy, detailed analysis shows that the probability of any of these occurrences is very small; hence, except at a minute fraction of all collisions, the molecule formed must dissociate immediately. That is to say, if a diatomic molecule has enough energy to dissociate, it will do so at once; there is, in the reverse case, no time lag between activation and reaction. Since it is upon the existence of such a time lag that the possibility of unimolecular reaction rests, we know experimentally that for more complex molecules there is such a time lag. The order of magnitude of this lag can be computed from experimental data without reference to any detailed theory of unimolecular reaction, because in any case it must be, on the average, not much different from the mean free time at pressures such that the reaction is just beginning to deviate from a first order course. In most cases, the time lags found in this way are of the order of 10^{-9} to 10^{-7} sec. A complex molecule, once formed at a binary collision, may then be stabilized at any subsequent collision within this period; the stabilizing molecule may thus have been, in some cases, as much as 0.01 cm. distant at the instant of formation of the complex; such a process can hardly be considered a triple collision.

We must next consider the second objection to such a process; this is that in the large majority of binary collisions no complex can be formed because of quantum restrictions. This objection also seems to disappear upon analysis. The restrictions which have to be considered are the conservation of energy, of momentum and of angular momentum, to-

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[3] Pease, THIS JOURNAL, 52, 1158 (1930); 53, 613 (1931).

gether with the quantization of rotation and of vibration. It has already been shown by Beutler and Rabinowitsch[4] that the quantum mechanical uncertainty principle completely destroys the restriction based on the conservation of angular momentum and the quantization of rotation This principle will at the same time relax somewhat the restriction arising from conservation of momentum, though it is not clear just how this is to be treated. There remains to be considered the possibility of satisfying at once the conservation of energy and the vibrational quantum conditions. Now it must be remembered that the quantum states in which we are interested are not real stationary states, because they have finite mean lives; this has the important result that they do not possess sharply defined energy; the relation between the mean life and the vagueness in the energy is given by the well-known equation

$$\tau = h/\Delta E \tag{1}$$

There will thus be a finite chance that the energy available for the vibrational degrees of freedom will lie within some quantum state. It is important to try to form some estimate of the actual magnitude of this chance, and to do this we need to know how closely the vibrational states are spaced. Consider a molecule with s vibrational degrees of freedom and a total of n quanta of energy distributed among them. If all of the associated frequencies are different, then each distribution will have a different total energy; it is well known that the number of such distributions is

$$\frac{(n + s - 1)!}{n!\,(s - 1)!} \tag{2}$$

Now, since the various frequencies are all different, there will not be any simple relation between the total energy of a distribution and the number of quanta which it involves; that is, there will be pairs of states such that the one with more quanta has less energy. Nevertheless, it seems that no great error will be made in taking the total number of distributions whose energy is between that of n and $n + 1$ mean quanta as given by (2). Numerical tests in several cases, for moderate values of n and s, always gave divergences in the direction of slightly greater numbers than predicted by (2). By using (2) in connection with an estimated (or assumed) mean quantum for the molecule concerned, we are able to calculate the average spacing between energy levels; this may be combined with the average width of energy levels to give the fraction of energy values within a given range which correspond to a quantum state. We shall proceed to make such calculations.

The most satisfactory energy unit for these purposes is the reciprocal second—that is, the energy of the quantum with unit frequency; this value is equal to 6.55×10^{-27} ergs, or about 10^{-10} cal./mole. Suppose

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[4] Beutler and Rabinowitsch, *Z. physik. Chem.*, 8B, 231 (1930).

that the heat of reaction plus the heat of activation is 10^{15} sec.$^{-1}$, or about 100,000 cal./mole. If we take the rather large value of 10^{14} sec.$^{-1}$ for the mean energy of a vibrational quantum, we will then have $n = 10$; the value will in most cases be rather larger than this, but we purposely begin with an unfavorable case. The value to be used for s is $3(m - 2)$, where m is the number of atoms in the molecule being formed; to allow for the fact that all of the vibrational states may not have different frequencies, we take a somewhat smaller value; thus a molecule with 10 atoms might have $s = 24$; we shall make the calculations for $s = 6$. 8 and 10. Taking $s = 6$, we see by (2) that the number of different energy levels with 10 quanta will be $15!/5! \times 10! = 3003$; these states are within an energy range of 10^{14} sec.$^{-1}$, so that the mean distance between adjacent states is 3×10^{10} sec.$^{-1}$; this is rather larger than the width of a level, and under such circumstances only a small fraction of all collisions could result in reaction. With $s = 8$, however, we find a mean spacing of 5×10^{9} sec.$^{-1}$, and with $s = 10$ we get 10^{9} sec.$^{-1}$. If we use instead of $n = 10$ the more likely value $n = 15$, and keep $s = 10$, we find for the mean spacing a value 8×10^{7} sec.$^{-1}$. If we push the values of n and s anywhere near the upper limits of plausibility, we obtain values for the mean distance between levels much less than the mean width of a level as determined from the time lag. It is thus possible that in some cases any energy value will correspond to some quantum state, while in other cases the chance for such a correspondence may be 0.1, 0.01 or even less. As a general rule, we should expect that the chance for correspondence would increase with the complexity of the molecule being formed, though the influence of specific factors will probably be a great one. This calculation tells us nothing, of course, about the efficiency with which reaction will occur even when all the energy and quantum conditions are satisfied.

We may consider in a little more detail the application of these ideas to Pease's work on ethylene polymerization. This reaction is second order between 2.5 and 10 atm.; at 1 atm. there is some evidence for a rate less than that predicted by the second order equation. The energy of activation determined from the temperature coefficient is given by Pease as 35,000 cal.; when this value is used in the simple expression $Ze^{-E/RT}$ to calculate the reaction rate, a value is found about 2000 times that observed. Pease interprets this as meaning that only in $^1/_{2000}$ of the collisions can the energy **and** quantum conditions be satisfied. He gives also an interpretation suggested by Taylor; this is that every collision which supplies the necessary reaction energy leads to formation of an unstable complex which either dissociates spontaneously, or survives until it colloids with a molecule of ethylene, whereupon it may be stabilized or may be destroyed; if the odds in favor of destruction are 2000:1, this mechanism gives a reaction which will be second order at high pressure, but will deviate when the pressure is low enough, and will give the correct absolute rate. The interpretation which the present writer would suggest is of an intermediate nature. There does not seem to be sufficient evidence to decide how the low efficiency is apportioned between a low yield for the formation of the dissociable complex and a low yield for the stabilization process; if the formation of the complex has a low yield, however, this need not necessarily be blamed on the necessity of satisfying a quantum condition, as Pease has suggested; in the decomposition of nitrogen dioxide, a bimolecular reaction which is not an association, the rate is only about $^1/_{200}$ of that calculated in the usual way from the activation energy and recent work by Hartel and Polanyi[5] furnishes other examples of low efficiencies. We thus suppose that collisions which are able to supply the necessary activation energy result, with an unknown efficiency, in formation of a complex which is capable of spontaneous dissociation; this complex may, however, be stabilized by collision with a molecule of ethylene; here again the process may not be 100% efficient; the product of the two efficiencies is about $^1/_{2000}$. The experiments do not supply any evidence in favor of a specific effect of ethylene in stabilization; it is quite probable, however, that ethylene and the reaction product, butene, are more efficient than inert gases, because in almost all unimolecular reactions it has been found that the reacting substance and its decomposition products are more effective in maintaining the rate than are indifferent gases; this means, of course, that the efficiency of energy transfer at collision is greater. If the second order reaction rate falls off at a pressure as high as one atmosphere in this case, then the mean time lag between formation of a complex and its dissociation is about 3×10^{-10} sec., and the mean width of a quantum state 3×10^9 sec.$^{-1}$. With a value this large, it should be easy for the energy and quantum conditions to be satisfied. The distance of the stabilizing molecule at the instant of formation of the complex would then be rather smaller than usual, about 10^{-5} cm. Even in this case, however, it would seem an exaggeration to speak of the event as a triple collision.

Summary

Calculations have been presented to show that the formation of complex molecules by a bimolecular association process should be possible at a considerable fraction of all collisions so far as the conservation laws and the quantum conditions are concerned. The polymerization of ethylene appears to be an example of such a reaction.

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[5] Hartel and Polanyi, *Z. physik. Chem.*, **11B**, 97 (1930).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 9]

THE ANHYDROUS LOWER BROMIDES OF ZIRCONIUM

BY RALPH C. YOUNG

RECEIVED APRIL 23, 1931 PUBLISHED JUNE 8, 1931

The present paper is the second[1] of a series dealing with a general study of the lower anhydrous bromides of the elements of the titanium family, and considers the preparation and properties of the lower bromides of zirconium.

The lower chlorides of zirconium were prepared by Ruff and Wallstein,[2] who allowed aluminum powder to react with zirconium tetrachloride in an evacuated tube in the presence of aluminum chloride as a catalyst. On account of the oxide of aluminum in the powder and because of the method of introducing the reactants into the reaction tube, resulting in hydrolysis, the product obtained by Ruff and Wallstein after sublimation of the unchanged zirconium tetrachloride and aluminum chloride was inevitably rendered impure by aluminum oxide and zirconium oxide.

In order to prevent hydrolysis and oxidation as far as possible, it was planned to prepare the bromides by a method which would enable one to obtain the product without the necessity of transfer from one apparatus to another and also by a method which would not require the placing of the reactants in that part of the apparatus in which the products would be collected

The general procedure adopted for the preparation of zirconium tribromide consisted essentially of the passing of zirconium tetrabromide with hydrogen over aluminum metal (wire) in a hot tube and of quickly chilling the volatile products of the reaction upon a tube kept cold by a current of water. The apparatus was so devised that the products could then be transferred in the presence of an inert gas to a tube joined to the reaction tube and the *former* tube could then be drawn nut and sealed. The procedure and results in detail are described below, after a consideration of the preparation and degree of purity of the zirconium tetrabromide used.

Zirconium tetrabromide was prepared from zirconium dioxide which had been shown by analysis to be free from impurities other than hafnium. Nitrogen saturated with bromine was allowed to pass through a 30-mm. Pyrex tube filled with an intimate mixture of four parts of dry sugar charcoal to one of dry zirconium dioxide, the tube being heated in a combustion furnace to the temperature at which the glass begins to soften. The zirconium tetrabromide sublimed and was collected at the end of the

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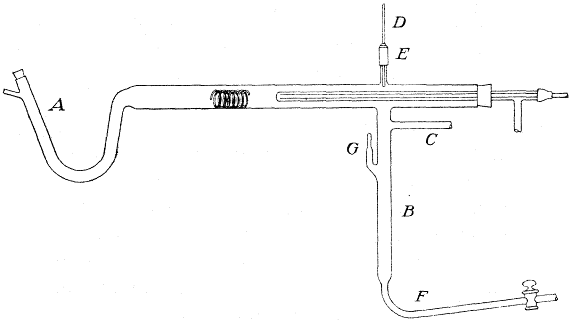
[1] Young with Sehumb, THIS JOURNAL, 52,4233 (1930).

[2] Ruff and Wallstein, *Z. anorg. allgem. Chem.*, 128, 96 (1923).

tube. The crude material was purified by sublimation in *vacuo,* the white product obtained was analyzed for zirconium by the selenious acid method, and found to be pure. The bromine was determined separately as silver bromide.

Anal. Calcd. for $ZrBr_4$: Zr, **22.20;** Br, 77.79. Pound: Zr, **22.30,** 22.33; Br, 77.68, 77.76.

Preparation of **Zirconium Tribromide.**—Referring to Fig. 1, at A, 30 g. of zirconium tetrabromide was introduced into the curved 22-mm. Pyrex tube which had been sealed directly to the larger (28 mm.) horizontal Pyrex tube. A current (about 200 cc. per min.) of dry, oxygen-free hydrogen was passed through the apparatus which, after the air had been displaced, was heated in a hinged-type electric furnace until the temperature of the furnace measured a minimum of 450°. Then the zirconium tetrabromide was slowly volatilized by means of a free flame and as it passed with the hydrogen through the furnace reacted in part with aluminum wire placed in the tube so that the wire would be in the center of the furnace. The wire consisted of four concentric coils, each coil 5 cm. long, of No. 18 wire, the diameter of the largest coil being 18 mm. The total weight of aluminum was 14 g. The cooling tube through which the water circulated was 9 mm. in diameter and extended to within approximately one inch of the wire. It was noted that satisfactory results were obtained only when this distance was carefully observed. A black to blue mass collected on the cold tube. Some of the aluminum bromide formed was carried by the hydrogen into the tube B and out the smaller tube C. The metal at the end farthest from the cold tube became incandescent during the reaction. Some of the zirconium tetrabromide was reduced to zirconium metal which alloyed with the aluminum.



Pig. 1.—Apparatus for the preparation of zirconium tribromide.

After all the zirconium tetrabromide had been volatilized in about one-half to three-quarter hour, the furnace was cooled to room temperature and dry carbon dioxide was substituted for the hydrogen. Tube C was closed and the cooling tube was partially withdrawn through the cork stopper. Part of the product usually clung to the tube, and sometimes it was necessary to use the glass rod D, which could be worked up and down in the tube E, to dislodge it and break the large pieces into smaller ones which would be able to enter tube B. Thick-walled rubber tubing connecting the apparatus with the drying train allowed the apparatus to be tipped so that all the product could be made to enter B, after which it was sealed just below side tube C.

The contents of the tube were now shaken to the end opposite the stopcock and the tube containing aluminum bromide, zirconium tetrabromide and reduced product was placed in a furnace and evacuated while being heated. About 6 cm. of the large tube was allowed to protrude beyond the furnace and after the temperature had reached approximately 140°, the aluminum bromide began to condense in the cold end. After the temperature had reached 200° the tube was sealed at F and the temperature raised to 290° and held there while the tube was gradually withdrawn from the furnace so that the zirconium tetrabromide which collected in the tube at the end of the furnace would not cause the tube to crack. It was noticed that a blue color always developed where aluminum bromide was in contact with zirconium tetrabromide.

Heating at 290° was continued until no more sublimate formed in the tube just outside of the furnace. In determining this fact, the tube was withdrawn from the furnace a distance of 1 cm., thus presenting a clear and transparent surface. If at the end of fifteen minutes a coating of zirconium tetrabromide formed, the tube was pushed back 1 cm., thus causing the compound to be volatilized forward and after thirty minutes a second test was made as before. About sixteen hours were required for the complete removal of the aluminum bromide and zirconium tetrabromide.

After the volatile products had been sublimed to the cold end of the tube, the furnace was allowed to cool to room temperature and the small tube G was connected by means of thick-walled tubing to a source of dry nitrogen and the narrow part of the tube *G* was broken thus allowing the gas to enter. The large tube was then sealed just beyond tube G and then tube G also was sealed. The sample now was in a sealed tube in an atmosphere of nitrogen and appeared as a blue-black powder. Crystalline form could not be distinguished with a magnification of 300 diameters.

The tube was filed at the tip, weighed, the tip was broken and the sample weighing approximately 0.5 g. introduced at once into ice water. The reaction was vigorous; a yellow to orange solution was formed, hydrogen was evolved and the color faded and disappeared completely in about five minutes. The solution was filtered and the gray to black residue was ignited. Dilute ammonium hydroxide solution was added to the filtrate and the precipitated hydrous oxide of zirconium was also ignited. The bromide contained in the filtrate from this precipitate was determined as silver bromide. The results of careful investigation showed that the dark insoluble matter amounting to as much as 5% of the sample (which after ignition proved to be zirconium dioxide) could be accounted for by the presence of a small amount of zirconium metal and of zirconium dibromide in the original reaction product. It was found that zirconium dibromide. the preparation of which will be given later, reacts so violently with water even at 0° that some zirconium dioxide is produced directly. The fact that, in the analysis, the zirconium was higher than the theoretical for zirconium tribromide and the bromine lower indicated that zirconium dibromide was present and the fact that the insoluble matter was dark showed the presence of zirconium metal.

To avoid the presence of zirconium metal and zirconium dibromide in the sample, the following procedure was adopted. In the preparation of the tribromide a great excess of the tetrabromide was allowed to accumulate in the product; the usual proportion would be 25 g of zirconium tetrabromide to 0.5 to 1.0 g. of the reduced material The tube with contents after being evacuated as described above was sealed and heated for eight hours at 300° in the center of a long electric sleeve with the view of converting any zirconium metal and zirconium dibromide to the tribromide.

$$3ZrBr_4 + Zr \longrightarrow 4ZrBr_3$$
$$ZrBr_4 + ZrBr_2 \longrightarrow 2ZrBr_3$$

Tests had been carried out to show that the first of these reactions **will take** place and it had been shown previously that the second reaction proceeds in the case of the titanium bromides.

After the eight hours' heating at 300°, the aluminum bromide and unchanged zirconium tetrabromide were sublimed away from the reduced product and the resulting sample was analyzed as described. The water insoluble matter now amounted to only a milligram in a 0.2-g. sample, the solution being clear and transparent.

Anal. Calcd. for $ZrBr_3$: Zr, 27 55; Br, 72.45. Found: Zr, 27.79, 27.77; Br, 72.35, 72.27.

The zirconium tribromide with the dibromide and metal eliminated appeared as a blue-black powder similar in color to the tribromide of titanium. When subjected to a slight amount of hydrolysis it took on a brown appearance and upon further hydrolysis turned red.[3] It dissolved in water to give a yellow to orange colored solution which was acid to litmus and evolved hydrogen. The color faded quickly. On the addition of the compound to a cold dilute solution of ammonium hydroxide, an orange precipitate was formed which persisted only momentarily.

In the formation of a 0.5-g. sample of the tribromide, **3** to 5 g. of aluminum hromide was obtained; the aluminum metal gained in weight slightly due to the substitution of some zirconium metal for the aluminum. Larger yields of the tribromide were obtained by volatilizing the tetrabromide more slowly. The production of 1 g. was the maximum obtained in one hour.

As a test of its reducing power small samples were added to the following dilute solutions arranged in order of increasing difficulty of reduction: sodium chromate, ferric chloride, bismuth chloride, copper chloride, titanium tetrabromide, stannous chloride and zinc sulfate. The change from yellow to green in the first case showed that chromium had been reduced from valence 6 to valence **3.** A blue precipitate formed on the addition of potassium ferrocyanide in the second test solution proved that ferric iron had been reduced to ferrous. Metallic bismuth was obtained in the third test; a precipitate of cuprous chloride in the fourth. A violet color formed in the test with titanium bromide indicated reduction to trivalent titanium. Negative results were obtained with stannous chloride and zinc sulfate. Since zirconium tribromide caused the evolution of hydrogen from water—due to hydrolysis, the solution is acid—the molal reduction potential of Zr^{+++}/Zr^{++++} can be approximately placed as above that of hydrogen but below that of tin.

Other reducing substances were tried in place of aluminum in the preparation of zirconium tribromide. Iron wire reacted with the zirconium tetrabromide to produce the lower bromides and ferrous bromide.

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[3] Ruff and Wallenstein[2] describe the trichloride of zirconium as brown in color Inasmuch as the tribromide and trichloride of titanium and the tribromide of zirconium have all been found to be blue-black in color, it seems possible that the brown color of the trichloride of zirconium prepared by these authors was due to partial hydrolysis.

The product, however, was freed from the latter with great difficulty. An alloy of zirconium and aluminum was successfully used. Magnesium metal produced a much larger percentage of the dibromide than did aluminum.

Zirconium tetrabromide is insoluble in carbon tetrachloride, benzene, and ethyl bromide and the metals mercury, aluminum, and silver caused no reducing action, when added to the tetrabromide in the presence of these liquids, even when heated to the boiling point of the liquid. In solvents in which the salt did dissolve, such as glacial acetic acid, acetic anhydride, and acetone there was no indication of any tribromide formation by the reducing action of the metals given above.

Considerable effort was made to reduce zirconium tetrabromide with hydrogen alone by use of the hot–cold tube principle and a resistance-wound silica tube as the reaction tube, which was heated to 1100°. No evidence of reduced product was obtained, nor did any reaction occur when the tube was heated to such a temperature that the silica softened in spots.

Zirconium Dibromide.—The preparation of the dibromide of zirconium involved heating the tribromide. obtained in the evacuated tube as previously described, to a temperature at which decomposition into the dibromide and tetrabromide took place and of keeping the material at that temperature until decomposition was complete.

$$2ZrBr_3 \rightleftharpoons ZrBr_4 + ZrBr_2$$

After all the unchanged zirconium tetrabromide had been evolved from the tribromide as already described, the temperature of the furnace was gradually raised and at 310° the tetrabromide began to deposit again at the end of the furnace, but very slowly. The rate increased as the temperature was further raised. At 350° from ten to fifteen hours were required to decompose a 0.5-g. sample of zirconium tribromide and at 390° about six hours.

In appearance the dibromide is a lustrous black powder. It was obtained in an atmosphere of nitrogen in a sealed tube exactly as in the case of the tribromide. On exposure to the air the dibromide catches fire. It was therefore introduced into ice water saturated with nitrogen by breaking the tube under water. As the water vapor came in contact with the solid there was a very vigorous reaction, part of the solid became incandescent and hydrogen was liberated.[4]

There was in this case considerable dark gray to white insoluble residue consisting mainly of the oxide of zirconium with a very small amount

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[4] J. H, de Boer and J. D. Fast[5] in an article on the preparation of pure metals of the titanium group through the thermal decomposition of their iodides briefly mention the preparation of the dibromide of zirconium by the action of zirconium tetrabromide on zirconium metal. They however report the dibromide of zirconium as reacting slowly with water to give off hydrogen, and as forming an orange colored solution which slowly decolorized. The analyses given differ considerably from the theoretical.

[5] J. H. de Boer and J. D. Fast, *Z. anorg. allgem. Chem.*, **187**, 177 (1930).

of zirconium metal, which caused the dark appearance of the oxide. In the analysis of a sample of the dibromide weighing 0.1745 g., 0.0283 g. of zirconium dioxide was obtained on ignition of the water-insoluble material and 0.0604 g. was obtained on ignition of the precipitate formed by addition of ammonium hydroxide solution to the filtrate from the water-insoluble matter. The total zirconium calculated from these two weights gives a percentage of zirconium of the sample as 36.41%, the theoretical percentage of zirconium in zirconium dibromide being 36.18. Since the percentage of bromine determined as silver bromide corresponded with that required for the dibromide, it is evident that not all of the zirconium dibromide dissolves as zirconyl bromide but that part of the compound reacts with the water to form zirconium dioxide with the formation of hydrogen bromide and liberation of hydrogen.

$$ZrBr_2 + H_2O \longrightarrow ZrOBr_2 + H_2$$
$$ZrBr_2 + 2H_2O \longrightarrow ZrO_2 + H_2 + 2HBr$$

Anal. Calcd. for $ZrBr_2$: *Zr*, **36.33;** Br, 63.67. Found: *Zr*, 36.41, **36.34;** Br, **63.98, 63.45.**

If the decomposition of zirconium tribromide is carried out at too high a temperature, considerable zirconium metal will be formed due to the reaction $2ZrBr_2 \longrightarrow ZrBr_4 + Zr$. This takes place very slowly at 350° but does go on as the somewhat dark appearance of the zirconium dioxide before ignition indicates. At temperatures of 400° and above, the decomposition of the dibromide proceeds quite rapidly. One sample heated at 410° for twenty-four hours gave, on analysis, 44.5% of zirconium and 57.2% of bromine.

Summary

Anhydrous zirconium tribromide has been prepared by the reduction of the tetrabromide with aluminum in an atmosphere of hydrogen in the hot-cold tube. Appropriate apparatus and manipulation are described. The compound is a blue-black powder which dissolves in water with the evolution of hydrogen, producing a yellow to orange colored solution, the color of which quickly disappears. Trivalent zirconium was found capable of bringing about the following reductions: $CrO_4^{=}$ to Cr^{+++}, Fe^{+++} to Fe^{++}, Bi^{+++} to Bi, Cu^{++} to Cu^{+}, TiO^{++} to Ti^{++} and $2H^{+}$ to H_2. Negative results were obtained in the attempts to reduce stannous chloride.

The dibromide of zirconium is formed by the decomposition of the tribromide at 350°, the tetrabromide being formed at the same time. Zirconium dibromide is a lustrous black powder which catches fire in the air and reacts with water so vigorously as to cause incandescence even in an atmosphere of nitrogen. Hydrogen is evolved and considerable dioxide of zirconium is formed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY (No. 656) AND OF VASSAR COLLEGE]

THE QUINHYDRONE ELECTRODE. III.

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Introduction

The first papers of this series[1] were concerned chiefly with the reproducibility in 0.1 N hydrochloric acid of the quinhydrone half-cell prepared under varying conditions from different pieces of the same sample of metal. While metals of different ages, sizes, and compositions were used, no intercomparisons between the different series of electrodes were reported. Therefore, except in the case of those series of electrodes which were made up of odd pieces of metal of unknown history, no conclusions could be drawn as to whether the age, size, and composition of the metal base affects the actual value of the potential difference developed or, whether as long as the electrodes are inert with respect to the solutions used, the potentials developed are the same. It is the object of this paper, then, to present the results obtained from an intercomparison not only of the electrodes of different ages, sizes, and compositions used in the first papers of this series but also of electrodes of gold, gold-plated platinum, and graphite not reported upon heretofore. Upon no point in connection with the quinhydrone electrode has there been such a divergence in opinion among earlier investigators as upon the substance to be used as the base of the electrode.

Materials and Apparatus

The materials and apparatus used have been described in the first and second papers of this series with the exception of the following new electrodes:

Gold Electrodes.—Small *Wires* (approximately *0.38* mm. in diameter and **1.5** cm. in length). ***Series Au,*** Nos. *7–12,* six pieces of new 24K gold purchased from Baker and Co. ***Series Am–Au,*** Nos. **7–12,** six pieces of new 24K gold purchased from American Platinum Works. ***Series B–Au,*** Nos. *7–12,* six pieces of new 24K gold purchased from **J.** Bishop and Co. ***Series C–Au,*** Nos. **7-12** six pieces of new 24K gold purchased from Sigmund Cohen. *Large Wires* (approximately *1* mm. diameter, *2* cm. length). ***Series Au,*** Nos. 1–6, ***Series Am–Au,*** Nos. 1–6, ***Series B–Au,*** Nos. 1–6, ***Series C–Au,*** Nos. 1–6, six pieces in each series of new 24K gold purchased from Baker and Co., American Platinum Works, Bishop and Co., and Sigmund Cohen, respectively. In each case the electrodes prepared were of the type heretofore described as short electrodes.

Gold–Plated Electrodes.—Wires (approximately **1** mm. diameter, **2** cm. length). ***Series G-P Nos. 1-12:*** for this series two platinum electrodes were selected from each of the A, B, and Pt series, and six new platinum electrodes were made from a sample of new C. P. platinum wire furnished by Baker. The electrodes were plated with a potas-

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[1] Morgan, Lammert and Campbell, THIS JOURNAL, 53, **454, 597 (1931).**

sium cyanide solution, approximately 2 g. in 100 cc. water, in which some 24K gold was dissolved by electrolysis. A gold anode and three volts were used and the plating continued for some time after the platinum was covered. For one set of data the time was five minutes, for another ten, the electrode being turned during the electrolysis. The plate was perfectly adherent in all cases, although on those electrodes which were plated for the longer time the gold was somewhat darker in color.

***Foils.—Series** G-P_{11}* (approximately 1 X 1 cm.) and ***Series** G-P_{12}* (approximately 1 X 2 cm.). For these series two of the platinum electrodes series P_{11} and P_{12} were chosen at random and plated by the method just described.

Graphite Electrodes (approximately 2.6 mm. diameter; 2 cm. length). —The lead was removed from 4B Venus pencils made by the American Pencil Company. About one cm. from one end of a three cm. length the lead was ringed with the wax-like substance "piecein" (purchased from Schroder and Ehlers) in the same manner that sealing-in-glass is used. The graphite was then pushed into a length of glass tubing of somewhat greater diameter than the lead while the piecein was still soft, until the ring of piecein was partly in the tube and partly out. More piecein completed the seal, the joint being "wiped" before the substance hardened. The glass tube was then filled with mercury through which connections were made to the potentiometer system.

Because of the sealing wax used for these electrodes the cleansing procedure was modified to some extent. In the first place while the piecein is not attacked by dilute acids, even when in contact with them for many hours, nor by dichromate cleaning mixture over a short time, it is attacked to some extent by cleaning mixture if allowed to stand in it overnight. It is only slightly soluble in cold alcohol. For this reason the graphite electrodes were short-circuited, pair by pair, and immersed in the cleaning mixture for about five minutes, after which they were rinsed hastily in alcohol and dried with purified air.

Procedure and Results

Our procedure for the measurements reported in this paper did not, in general, differ from that reported in the first two papers of this series except that in the case of the intercomparisons, rather than placing six electrodes of one series in one electrode vessel, we placed one pair of each of three series in each vessel. The potential differences between the two like electrodes were measured until the difference was constant, and then the potential differences between all possible combinations of electrodes, taken pair by pair, were measured.

Gold Electrodes.—In view of the fact that the investigators[2] who express a definite preference for gold or gold plate as a metal base for the quinhydrone electrode, particularly in body fluids, outnumber those[3] who state a preference for platinum, and in view of the fact that of the other group[4] who report equally successful results with either gold or

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[2] La Mer and Parsons, *J. Biol. Chem.*, 57,613 (1923); Corran and Lewis, *Biochem. J.*,18, 1358 (1924); Mislowitzer, *Biochem. Z*, *159,* 77 (1925); Liu, *ibid.,* 185,242 (1927); Watson, *Ind. Eng. Chem.,* 19, 1272 (1927); Snyder, *J. Agr. Research,* 35, 825 (1927); Halton and Fisher, *Cereal Chemistry,* 5,445 (1928).

[3] Meeker and Oser, *J. Biol. Chem.,* 67, 307 (1926); Grossmann, *Biochem. J.,* 21, 267 (1927); Pennycuick and Best, *J. Chem. Soc.,* 131,551 *(1928).*

[4] Haber and Russ, *Z. physik. Chem.,* 47, 257 (1904); Biilmann, *J. Soc. Leather Trades Chem.,* 5, 27 (1921); La Mer and Baker, THIS JOURNAL, 44,1954 (1922); Conant

platinum, La Mer and Baker make the distinction that while the potentials are the same with either gold, gold plate, or platinum, gold and gold-plated platinum give sharper readings, we did not feel satisfied to confine our investigation to the samples of gold reported in the first paper. Most of the gold electrodes reported upon in that paper were made from 24K gold supplied by Baker and Co., the small and large wires Series Au and the foils Series G_{11}, G_{12}, G_{13}, G_{22} and G_{23}. The source and purity of the larger wires Series St was unknown and the Series L & N were gold electrodes supplied by Leeds and Northrup Co. The foils and the L & N electrodes gave excellent results, although a few inexplicably erratic results were obtained with the foils. The small gold wires were extremely erratic and unreliable and the larger wires, while fairly good, were also somewhat erratic. Therefore wires of the same size and specifications were obtained from three other companies and the electrodes already described prepared. Wires were selected rather than foils since it was among the wires that the greatest differences in reproducibility appeared. A comparison of their reproducibility in air and in nitrogen follows in Table I. Results for the Series Au are included since many beyond those reported in the first paper have been obtained.

Among the small wires (7–12) the series Am-Au and B-Au were much more readily reproducible than the Series Au which continued to be erratic, although, like the Series Au, Am-Au, B-Au and C-Au gave cells of much smaller current capacities than the platinum wires of the same size The C-Au series, however, gave results more nearly like the Au series although neither the averages, ranges, nor average deviations were quite as large.

Among the large wires (1–6), on the other hand, the Au series gave the lowest averages, ranges and average deviations. The values for all three of the other series were not only higher than the large wires of the Au series but were higher than the small wires of the same series, although the range on the bridge wire over which there was no deflection on the galvanometer was always greater with the small wires.

All in all, then, there seems to be no doubt that, in so far as our results in 0.1 N hydrochloric acid are typical, wire electrodes of small surface made of 24K gold from any source are likely to be extremely erratic in their behavior and that in systems where its presence does not cause difficulty platinum is greatly to be preferred. In the first place, platinum can be sealed into the glass directly whereas gold must be welded to platinum; in the second place, the gold is easily alloyed with mercury,

and Fieser, *ibid.*, 45, 2194 (1923); Clark, *Chem. Reviews*, 2, 127 (1926); Parker and Greer, *Trans. Am. Electrochem. Soc.*, 49, 451 (1926); Rosanov, *Zhurnal Exptl. Biol. Med.*, *10*, 141 (1928); Gesell, *Am. J. Physiol.*, 87, 1 (1928); Meeker and Reinhold, *J. Biol. Chem.*, *77*, 505 (1928); Kolthoff, *Z. physiol. Chem.*, 144, 259 (1925); Cullen, *J. Biol. Chem.*, 83,535 (1929).

TABLE I

Comparison of the Potential Differences Obtained after Sixty Minutes in 0.1000 N Hydrochloric Acid Solution Saturated with Quinhydrone between Electrodes Made of 24K Gold from Different Sources. Solutions Stirred in Air and with Nitrogen; Electrodes Short-circuited and Dried in Air

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying operations between measurements	Av potential diff., volt	Ranges of diff., 0 000000 to . volt	Av dev., mv.	Number results discarded in average
Small wires							
Air Au, 7–12	**6**	**129**	**9**	0.000069	0.000640	0.069	0
Nitrogen Au, 7–12	**6**	**41**	**5**	.000068	.000410 (.004510)	.074	2
Air Am-Au, 7–12	**6**	**63**	**6**	.000012	.000089	.014	0
Nitrogen Am-Au 7–12	**6**	**58**	**5**	.000004	.000036	.004	0
Air B-Au, 7–12	**6**	**88**	**8**	.000004	.000058	.008	0
Nitrogen B-Au, 7–12	**6**	**98**	**10**	.000006	.000130	.008	0
Air C-Au, 7–12	**6**	**101**	*7*	.000048	.000400	.052	0
Nitrogen C-Au, 7–12	**6**	**120**	**12**	.000027	.000380	.031	0
Large wires							
Air Au, 1–6	**6**	205	13	.000012	.000066	.010	0
Nitrogen Au, 1–6	**6**	106	11	.000005	.000041	.005	0
Air Am-Au, 1-6	**6**	94	8	.000020	.000150	.016	0
Nitrogen Am-Au. 1–6	**6**	110	9	.000015	.000210	.012	0
Air B-Au, 1–6	**6**	111	11	.000035	.000940 (.001880)	.040	2
Nitrogen B-Au. 1–6	**6**	128	9	.000015	.000580	.019	0
Air C-Au, 1–6	**6**	135	10	.000019	.000170	.016	0
Nitrogen C-Au 1–6	**6**	139	10	.000026	.000170	.022	0

a contamination which greatly alters the potential difference of the electrode; in the third place, a cell prepared with platinum wires has a larger current capacity than a cell prepared with the same size gold wire; and in the fourth place, the gold electrodes exhibit a capriciousness in behavior which is extremely annoying. On the other hand, it is to be noted that the effect of nitrogen upon the gold electrodes is not as definite as upon the platinum electrodes. While the effect of oxidizing agents upon the electrode is a matter still under investigation and will be reported upon at some future date, it seems probable that the reproducibility of the electrode is not altered to the same extent by the presence or absence of oxidizing agents when gold is used as when platinum is used. This fact may account for the disagreement among earlier investigators as to the metal to be used.

As to the cause of the variability of the gold electrodes, we have as yet no explanation to offer. There seem to be at least two effects of the metal upon the cells constructed. One effect is upon the current capacity; cells constructed with platinum wires of a given size have greater current capacities than those with gold of the same size; for other conditions being the same there is with the smaller electrodes a greater range on the bridge over which there is no deflection of the galvanometer of the type we are using (Leeds and Northrup Type 2500 c). With a more sensitive galvanometer of the type 2285Å, however, this range becomes much smaller.

The second effect is upon the reproducibility of the electrode potentials and may be catalytic in nature. This effect may be a combination of more than one catalytic effect, one possibly involving the quinone–hydroquinone equilibrium and the other involving some reaction with the oxygen, possibly oxidation of the quinone. Since the results with platinum are very much improved with nitrogen, it seems probable that the platinum catalyzes the reaction with oxygen more effectively than the gold. On the other hand, since the large electrodes of both kinds give much better results than the small it seems probable that the metal is instrumental in bringing the quinhydrone system to equilibrium.

We have worked for some time on the theory that gold electrodes which were contaminated with even very small amounts of mercury exhibit an erratic behavior but we can find no connection between their behavior and such contamination. Electrodes which we knew to be alloyed with mercury never improved until the mercury was removed, whereas the electrodes, which we have described as erratic, would give quite consistent results, then one or more inexplicably large potential differences, and then become quite normal. Furthermore some gold electrodes were consistently good throughout the entire research.

Gold–Plated Electrodes.—Enough investigators[6] have used gold-plated electrodes to make it seem advisable to include some work on these in this paper.

Biiimann and Jensen[5] found greater deviations between the potentials of quinhydrone half-cells prepared with gold-plated electrodes than with polished platinum electrodes. Biilmann[5] states that while there are solutions in which platinum cannot be used, and in which gold plate may be used, platinum gives, when it can be used, more precise results. He states further that a concentration of quinhydrone sufficient to give exact potentials with bare platinum electrodes will not give exact potentials with gold-plated electrodes.

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[5] Biilmann, *Ann. chim.*, [9] 15, 109 (1921); *J. Soc. Leather Trades' Chem.*, 5, 27 (1921); La Mer and Baker, THIS JOURNAL, 44, 1954 (1922); Conant and Fieser, *ibid.*, 45, 2194 (1923); Kolthoff, *Z. physiol. Chem.*, 144, 259 (1925); Cullen and Biilmann, *J. Biol. Chem.*, *64*, 727 (1925); Robinson, *ibid.*, 66, 811 (1925); Biilmann and Jensen, *Bull. soc. chim.*, 41, *151* (1927); Biilmann, *ibid*, 41, 213 (1927); Clark, *Chem. Reviews*, 2, *127 (1926)*; Watson, *Ind. Eng* Chem, 19, 1272 (1927); Cullen and Earle, *J. Biol Chem*, 76, 565 (1928); Halton and Fisher, *Cereal Chem*, 5, 445 (1928); Cullen, *J. Biol. Chem.*.*83*,*535* (1929).

In our experience the gold-plated electrodes give results in air similar to the gold electrodes until they become scratched, with the exception of the foils, which do not give as good results as the gold foils. These electrodes differ from the gold electrodes, however, in that their reproducibility improves in nitrogen. As soon as the electrode is scratched it must be replaced, since a very small scratch seems to change greatly the potential developed. This seems strange in view of the fact that a platinum and a gold electrode may be connected and treated as one electrode and the potential of this combination found not to differ from a single platinum or gold electrode by any amount greater than the latter differ from each other or other platinum or gold wires. Furthermore, we find no difference in reproducibility in those gold electrodes which are prepared with some platinum exposed to the solution from those prepared in such a way that all the gold is covered, and finally, the L & N electrodes which have given such consistently good results throughout the entire investigation have more platinum exposed to the solution at the ends of the gold wire than was exposed by the scratch on a foil.

Our results for the gold-plated electrodes are collected in Table II. The results obtained from electrodes known to be scratched were not included in the average. The electrodes were deplated and tested as platinum electrodes after the results in the table were obtained. Since they were in every case normal it was evident that the results were characteristic of the gold plate and were not due to electrodes faulty in construction.

Table II

Comparison of the Potential Differences Obtained After Sixty Minutes in 0.1000 N Hydrochloric Acid Solution Saturated with Quinhydrone between gold-plated Electrodes; Solutions Stirred in Air and with Nitrogen; Electrodes Dried in Air; Electrodes Short-Circuited

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying operations between meas.	Av. potential diff., volt	Ranges of diff. 0.000000 to .... volt	Av. dev., mv.	Number of results discarded in average
Air **G-P**	12	52	**4**	0 000024	0.000101	0.017	0
Nitrogen G-P	12	72	4	000011	.000079	010	0
Air G-P$_{11}$	2	10	*3*	.000012	.000026	.017	0
Nitrogen G-P$_{11}$	2	11	4	.000003	.000009	.003	0
Air G-P$_{12}$	**2**	13	3	.000032	.000150	.032	0
Nitrogen G-P$_{12}$	2	12	4	.000002	.000016	.002	0

Unless the conditions in other solutions differ greatly from those in 0.1 N hydrochloric acid, we can see no advantage in using gold-plated electrodes and a number of disadvantages. In the first place, the electrodes possess most of the disadvantages of the gold electrodes to which are added the disadvantages that the plating is troublesome, that the plate is fragile, and that the electrodes are not as reproducible as the gold.

Finally, as we shall see in Table IV of this paper, the potentials of the gold-plated electrodes deviate from the potentials obtained with other metals to a far greater extent than they do with any other metals. Of course, it is possible that some special conditions of plating may give far better results but as soon as the reproducibility of an electrode depends upon a method of metal deposition, an uncertainty arises, creating a situation similar to the one which exists with respect to the hydrogen electrode, and removes one of the greatest advantages of the quinhydrone electrode, that of simplicity. Our experience very nearly corroborates that of Biilmann, who took some five or six hours to plate his electrodes. We found the gold-plated electrodes sensitive to the oxygen of the solution, however, and suspect that our more rapidly deposited plate was rougher and hence catalyzed the oxygen reaction more readily. If gold plate must be used for some reason (although we cannot foresee any condition under which gold welded to platinum would not be preferable), we suggest that it be plated very slowly.

Graphite Electrodes.—Except for the work of Flexner and Barron,[6] we are not aware of any attempt having been made to use a carbon electrode as the base of the quinhydrone half-cell. Flexner and Barron report two results in 0.1 N hydrochloric acid, one (0.38835 volt) obtained when a quinhydrone half-cell prepared with carbon was measured against a saturated calomel cell, the other (0.3886 volt) when the half cell was prepared with gold plate They state that the purity of the carbon is unimportant, the rods of a carbon arc lamp or the core of a lead pencil giving identical results.

We prepared a series of carbon electrodes using arc carbons, some carbon electrodes of different cross sections found in the laboratory, and some graphite electrodes prepared from different lead pencils. The carbons were connected directly to the potentiometer wires with binding posts; the cores of the lead pencils were sealed as already described into glass tubing with picein.

While the lead pencil graphite cores gave promising results from the first, all of the other forms of carbons gave poor results. Moreover, it was observed that when these carbons were immersed in the same electrode vessel with a pair of platinum or gold electrodes, not only did the potentials of the carbon electrodes differ from one another, but the potentials of the platinum electrodes also differed greatly from one another even after they had given low potential differences before the carbon electrodes were introduced. This observation suggests that the carbons absorbed material from the solution, which fact affected not only the potentials of the carbon electrodes but of the others in the same vessel. Graphite not being wetted by water as is carbon and not absorbing ma-

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[6] Flexner and Barron, THIS JOURNAL, 52, 2773 (1930).

terial to the same extent, could be expected to yield more readily reproducible potentials.

We tried a number of pencil leads but were most successful in sealing in the 4B Venus pencil leads, possibly fortuitously. possibly because the leads were corrugated on the surface. At any rate, as we wished to examine the properties of these electrodes before we compared the lead from different sources and of different degrees of hardness, we selected from the lot those electrodes which had good seals and had given good results, which happened to be those carrying the 4B Venus leads. It is our present plan to try other forms of graphite after we have seen whether the electrode proves of enough value to justify such a research.

Our results for these electrodes are collected in Table III.

Table III

Comparison of the Potential Differences Obtained after Sixty Minutes in 0.1000 *N* Hydrochloric Acid Solution Saturated with Quinhydrone between Graphite Electrodes. Solutions Stirred in Air and with Nitrogen; Electrodes Dried in Air; Electrodes Short-Circuited

	Electrodes in series	Values in average	Identical cleaning and drying operations between meas.	Av. potential diff., volt	Ranges of diff. 0.000000 to .... volt	Av. dev.. mv.
Air 4 B	**14**	**86**	**12**	**0.000005**	**0.000033**	**0.005**
Nitrogen 4 B	**14**	**256**	**22**	.000032	.000620	.038

These lead pencil electrodes have been in constant use for four or five months, and cleaned and measured many times. Prepared in the way we have described, they seem to be just as rugged as the gold or platinum electrodes and to lend themselves to the same cleaning treatments. They resemble the gold electrodes in that the results obtained in air are always as satisfactory and frequently more satisfactory than those obtained in nitrogen. This suggests that they will not be as sensitive to oxidizing agents as platinum and consequently may be more valuable in determinations in body fluids. Electrodes of the size we used give cells with a sufficiently large current capacity to be used with the Type K potentiometer and 2500 ***e.*** galvanometer; the region on the wire over which there is no current deflection is small and of about the same magnitude as that observed with the large platinum wires and much less than the gold. They are, of course, unaffected by mercury and are so readily available and so simply and cheaply constructed that they have everything to recommend them. They differ from the gold and the platinum in that the initial potential difference between two electrodes is usually higher but this large difference rapidly disappears and they soon behave in a manner quite similar to the metal electrodes.

It is our plan to try other samples of graphite. It seems quite possible that excellent micro electrodes might be prepared with blocks of graphite, indentations in which hold the liquid–quinhydrone mixture.

Comparison of the Potential Differences Developed in the Quinhydrone Half-Cell by Different Electrode Substances.—In Table IV are collected the results of a rather extended comparison of the potentials developed by electrodes of different compositions, 24K gold, c. p. platinum, platinum–10% iridium alloy, platinum–10% rhodium alloy, gold-plated platinum, and graphite, of different sizes, ages, and sources in air and in nitrogen. While in our earlier papers we showed that the precision of the quinhydrone half-cell is very great, we hope in this table to give some idea of the probable accuracy among the results obtained in different laboratories. In this table ate given only the results of the intercomparisons between electrodes of different series; for the results within any one series the reader is referred to the tables given in the first two papers of this series and to the tables given in the first part of this article. The signs of the potential differences of the cells are reported in this table, the sign being given to the first mentioned electrode. When the average deviation is of the same order of magnitude as the average potential difference, it seems probable that a sign in any direction does not represent an actual difference of potential developed but merely a deviation; when however, the average potential difference is in one direction and is larger than the average deviation, we have considered that there was an actual difference in potential developed with the two metals.

TABLE IV

COMPARISON OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 N HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN ELECTRODES FROM DIFFERENT SERIES, MADE FROM METALS OF DIFFERENT COMPOSITIONS, SIZES AND AGES. SOLUTIONS STIRRED IN AIR AND WITH NITROGEN: ELECTRODES DRIED AND SHORT-CIRCUITED

Electrode series	Number of electrodes inter-compared	Values in average	Identical cleaning and drying operations between meas.	Average potential diff.. volt	Ranges of diff. 0.000000 to .... volt	Average dev.. mv.
			Comparison of Metals			
Small Wires						
Air B–Au_{7-12} os. Au_{7-12}	12	44	3	±0.000016	0.000100	0.016
Nitrogen B–Au_{7-12} *vs.* Au_{7-12}	12	47	3	± .000043	.000370	.058
Air C–Au_{7-12} *vs.* Au_{7-12}	12	44	3	± .000012	.000100	.014
Nitrogen C–Au_{7-12} *vs.* Au_{7-12}	12	46	3	± .000040	.000410	.058
Air B–Au_{7-12} *vs* C–Au_{7-12}	12	100	6	± .000010	.000056	.011
Nitrogen B–Au_{7-12} *vs.* C–Au_{7-12}	12	106	6	± .000028	.000490	.037
Air Au_{7-12} *vs.* Pt_{7-12}	12	26	2	± .000018	.000041	.010

Table IV *(Continued)*

Electrode series	Number of electrodes inter-compared	Values in average	Identical cleaning and drying operations between meas.	Average potential diff., volt	Ranges of diff 0 000000 to volt	Average dev., mv.
Air B–Au$_{7-12}$ *vs.* Pt$_{7-12}$	12	56	3	±0.000025	0.000068	0.013
Nitrogen B Au$_{7-12}$ *vs* Pt$_{7-12}$	12	58	3	± .000014	.000090	.011
Air C–Au$_{7-12}$ *vs.* Pt$_{7-12}$	12	56	3	± .000020	.000055	.010
Nitrogen C–Au$_{7-12}$ *vs* Pt$_{7-12}$	12	54	3	± .000029	.000400	.033
Large Wires						
Air Pt$_{1-6}$ *vs* A$_{1-6}$	12	48	2	± .000007	.000024	.005
Nitrogen Pt$_{1-6}$ *vs.* A$_{1-6}$	12	48	2	– .000002	.000010	.002
Air Pt$_{1-6}$ *vs.* B$_{1-6}$	12	48	2	± .000008	.000024	.005
Nitrogen Pt$_{1-6}$ *vs.* B$_{1-6}$	12	48	2	± .000003	.000011	.003
Air A$_{1-6}$ *vs.* B$_{1-6}$	12	48	2	± .000006	.000023	.003
Nitrogen A$_{1-6}$ *vs.* B$_{1-6}$	12	48	2	± .000002	.000005	.002
Air Am–Au$_{1-6}$ *vs.* A$_{1-6}$	12	38	3	± .000039	.000087	.019
Nitrogen Am–Au$_{1-6}$ *vs* A$_{1-6}$	12	38	2	± .000025	.000200	.026
Air B–Au$_{1-6}$ *vs.* Au$_{1-6}$	12	44	4	± .000016	.000070	.015
Nitrogen B -Au$_{1-6}$ *vs.* Au$_{1-6}$	12	36	2	± .000004	.000015	.002
Air C–Au$_{1-6}$ *vs.* Au$_{1-6}$	12	47	4	± .000010	.000090	.008
Nitrogen C–Au$_{1-6}$ *vs.* Au$_{1-6}$	12	36	2	± .000009	.000100	.012
Air B–Au$_{1-6}$ *vs.* C–Au$_{1-6}$	12	84	7	± .000018	.000063	.013
Nitrogen B–Au$_{1-6}$ *vs* C–Au$_{1-6}$	12	80	5	± .000012	.000100	.012
Air B$_{1-6}$ *vs.* Au$_{1-6}$	4	8	2	± .000006	.000014	.004
Air Pt$_{1-6}$ *vs.* Au$_{1-6}$	4	16	2	± .000015	.000030	.006
Nitrogen Pt$_{1-6}$ vs. Au$_{1-6}$	4	16	2	± .000002	.000006	.002
Air Pt$_{1-6}$ *vs.* St$_{1-6}$	12	52	2	± .000011	.000035	.006
Nitrogen Pt$_{1-6}$ *vs.* St$_{1-6}$	12	48	2	± .000002	.000014	.002
Air Pt$_{1-6}$ *vs.* B–Au$_{1-6}$	12	52	3	± .000030	.000110	.024
Nitrogen Pt$_{1-6}$ *vs.* B–Au$_{1-6}$	12	47	3	± .000012	000038	.008
Air Pt$_{1-6}$ *vs.* C–Au$_{1-6}$	12	56	3	± .000032	000100	.022
Nitrogen Pt$_{1-6}$ *vs.* C–Au$_{1-6}$	12	44	3	± .000013	.000045	.010
Air Pt$_{1-6}$ *vs.* Rh$_{1-6}$	12	52	3	– .000012	.000044	.008
Nitrogen Pt$_{1-6}$ *vs* Rh$_{1-6}$				± .000002	.000013	

TABLE IV (*Continued*)

Electrode series	Number of electrodes intercompared	Values in average	Identical cleaning and drying operations between meas.	Average potential diff., volt	Ranges of diff. 0.000000 to .... volt	Average dev., mv.
Air Pt$_{1-6}$ vs. Ir$_{1-6}$	12	52	3	−0.000044	0.000076	0.014
Nitrogen Pt$_{1-6}$ vs. Ir$_{1-6}$	12	56	3	± .000002	.000011	.002
Air Rh$_{1-6}$ vs. Ir$_{1-6}$	12	52	3	− .000035	.000075	.014
Nitrogen Rh$_{1-6}$ vs. Ir$_{1-6}$	12	56	3	± .000001	.000010	.002
Air Pt$_{1-6}$ vs. G-P	4	4	1	− .000029	.000045	.014
Nitrogen Pt$_{1-6}$ vs. G-P	4	1	4	− .000001	.000003	.001
Air A$_{1-6}$ vs. G-P	4	8	2	− .000026	.000030	.002
Air B$_{1-6}$ vs. G-P	4	8	2	− .000034	.000052	.009
Air Au$_{1-6}$ vs. G-P	4	8	2	− .000033	.000049	.011
Foils and special wires						
Air D vs. P$_{12}$	8	29	2	± .000002	.000005	.002
Nitrogen D vs. P$_{12}$	8	32	2	± .000001	.000005	.001
Air I vs. P$_{22}$	8	32	2	± .000005	.000013	.003
Nitrogen I vs. P$_{22}$	8	32	2	± .000001	.000003	.001
Air D vs. G$_{12}$	8	28	2	± .000004	.000012	.004
Nitrogen D vs. G$_{12}$	8	32	2	± .000001	.000006 (.000014)	.001
Air P$_{12}$ vs. G$_{12}$	8	28	2	± .000003	.000008	.002
Nitrogen P$_{12}$ vs. G$_{12}$	8	32	2	± .000001	.000005	.001
Air L & N vs. G-P$_{11}$	4	16	3	− .000047	.000108	.045
Nitrogen L & N vs. G-P$_{11}$	4	6	2	± .000006	.000008	.002
Air L & N vs. G-P$_{12}$	4	16	3	− .000115	.000250	.095
Nitrogen L & N vs. G-P$_{12}$	4	8	2	− .000067	.000120	.046
Comparison of Metals and Graphite 4B						
Nitrogen 4B vs. Au$_{1-6}$	12	64	2	− .000026	.000090	.012
Air 4B vs Am–Au$_{7-12}$	12	60	4	± .000012	.000090	.014
Nitrogen 4B vs. Am–Au$_{7-12}$	12	48	2	± .000003	.000024	.004
Air 4B vs. Am–Au$_{1-6}$	12	88	6	± .000016	.000110	.010
Nitrogen 4B vs. Am–Au$_{1-6}$	12	78	6	± .000018	.000210	.016
Air 4B vs. St$_{1-6}$	12	43	3	± .000015	.000028 (.000150)	.005
Nitrogen 4B vs. St$_{1-6}$	12	40	3	± .000007	.000042	.006
Air 4B vs. A$_{1-6}$	12	48	4	± .000045	.000071	.011
Nitrogen 4B vs. A$_{1-6}$	12	56	4	± .000024	.000100	.022
Air 4B vs. Pt$_{1-6}$	8	10	2	± .000028	.000060	.011
Nitrogen 4B vs. Pt$_{1-6}$	12	120	8	± .000030	.000190	.023
Air 4B vs. G-P	4	6	2	± .000049	.000079	.020
Nitrogen 4B vs. G-P	4	4	1	− .000002	.000007	.002
Air 4B vs. G$_{11}$	4	16	2	± .000003	.000007	.002

TABLE IV (*Concluded*)

Electrode series	Number of electrodes inter-compared	Values in average	Identical cleaning- and drying operations between meas.	Average potential diff., volt	*Ranges* of diff. 0.000000 to .... volt	Average dev., mv.
Nitrogen 4B *vs.* G_{11}	4	16	2	±0.000005	0.000012	0.005
Air 4B *vs.* L & N	8	34	4	± .000007	.000024	.005
Nitrogen 4B *vs.* L & N	8	24	2	± .000009	.000019	.006
Comparison of sizes						
Air O *vs.* P_{23}	8	40	2	+ .000014	.000048	.008
Nitrogen O *vs.* P_{23}	8	32	2	.000000	.000002	.000
Nitrogen Pt_{1-6} *vs.* P_{13}	6	8	2	± .000002	.000002	.001
Air Am–Au_{7-12} *vs.* L & N	8	34	4	± .000010	.000090	.013
Nitrogen Am–Au_{7-12} *vs.* L & N	8	24	2	± .000005	.000020	.004
Air Am–Au_{7-12} *vs.* G_{11}	4	16	2	− .000004	.000010	.003
Nitrogen Am–Au_{7-12} *vs.* G_{11}	4	16	2	± .000001	.000002	.001
Air St_{1-6} *vs.* Au_{1-6}	4	16	2	+ .000004	.000012	.003
Nitrogen St_{1-6} *vs.* Au_{1-6}	4	16	2	+ .000002	.000006	.002
Air St_{1-6} *vs.* Am–Au_{1-6}	12	44	3	± .000010	.000033	.008
Nitrogen St_{1-6} *vs.* Am–Au_{1-6}	12	40	3	± .000009	.000032	.007
Air St_{1-6} *vs.* G_{12}	8	32	2	± .000008	.000020	.005
Nitrogen St_{1-6} *vs.* G_{12}	8	32	2	± .000003	.000010	.002
Nitrogen Au_{1-6} *vs.* G_{13}	6	8	2	− .000004	.000006	.002
Air Au_{1-6} *vs.* G_{22}	8	32	2	± .000004	.000008	.003
Nitrogen Au_{1-6} *vs.* G_{22}	8	28	2	± .000002	.000012	.003
Air G-P_{11} *vs.* G-P_{12}	4	16	3	± .000143	.000245	.064
Nitrogen G-P_{11} *vs.* G-P_{12}	4	12	1	± .000013	.000025	.008
Comparison of Sizes and Metals						
Air Pt_{1-6} *vs.* G_{12}	8	32	2	± .000011	.000023	.005
Nitrogen Pt_{1-6} *vs.* G_{1-2}	8	32	2	± .000002	.000007	.002
Air St_{1-6} *vs.* Pt_{1-6}	12	52	2	± .000011	.000035	.006
Nitrogen St_{1-6} *vs.* Pt_{1-6}	12	48	2	± .000002	.000014	.002
Air L & N *vs.* A_{1-6}	4	8	2	− .000012	.000014	.002
Air L & N *vs.* G-P	8	8	2	− .000038	.000038	.001

The following conclusions may be drawn from the results in this table. The small (Au, 7–12, Am–Au, 7–12, B–Au, 7–12, and C–Au 7–12) and large (Au, 1–6, Am–Au, 1–6, B–Au, 1–6, C–Au, 1–6 and St, 1-6) gold wires from different sources do not differ from each other to any greater extent than they differ among themselves. The reproducibility of the quinhydrone half-cell prepared with gold electrodes is not, in general, improved in nitrogen.

The large C. P. platinum wires (A, 1–6, B, 1–6, Pt, 1–6) give practically the same differences of potential no matter what the source or the age of the platinum. Quinhydrone electrodes prepared with these wires are reproducible with great precision, particularly when the solution is stirred with nitrogen.

When the large gold and platinum wires are compared, the average potential differences are of the same order of magnitude as the average deviations and are no larger than the differences among the gold electrodes measured by themselves, from which it may be concluded that, within the limits of experimental error, gold and platinum electrodes develop the same potential difference in the quinhydrone half-cell.

When, however, the C. P. platinum (Pt 1–6) and platinum–10% iridium (Ir 1–6) and platinum–10% rhodium (Rh 1–6) alloys are intercompared, the C. P. platinum is negative to the alloy in air and more negative to the iridium alloy than to the rhodium alloy Quite consistently the rhodium alloy is negative to the iridium alloy. In nitrogen these differences disappear almost entirely, although there are a few more negative results than positive.

Other actual differences in potential developed appear when the large C. P. platinum (A, 1–6, B, 1–6, Pt, 1–6) or gold (Au, 1–6) wires are compared with the gold-plated wires (G-P). Here again the C. P. platinum and 24K gold are negative to the gold-plate and again the difference disappears in nitrogen.

Among the foils and longer wires (L & N) all electrodes, old and new, seem to give the same potential differences and with great precision with the exception of the gold plates. Again the gold wires, in this case L & N, are negative to the gold plate.

The potential differences obtained with the graphite electrodes (4B) deviate from those obtained with gold or platinum wires. but the deviations are both positive and negative. They give, however, with great precision, the same results as the gold foils (G_{11}) and long wires (L & N).

An intercomparison of sizes indicates that there is no difference in the potential developed, but merely the difference in range and deviation expected of the smaller wires from the previous results.

Of course, there is the possibility in an intercomparison such as this, when electrodes being compared are in the same vessel, that if the effect of the electrode substance is catalytic in nature, a small electrode, for instance, will be affected by the presence in the vessel of a large electrode. While an effect on the gold and platinum electrodes was obvious in the vessels containing the carbon electrodes, in other cases the electrodes seem to retain their own characteristics regardless of the properties of their neighbors. Any catalytic effect seems to be upon the medium immediately surrounding the electrode.

The results given in this paper indicate that, in so far as results obtained in 0.1000 N hydrochloric acid are typical, an investigator in one laboratory may select either gold, platinum, or graphite for the base of a quinhydrone electrode and expect the potential of such an electrode to agree with that obtained in another laboratory with the same precision with which electrodes prepared from different samples of the same metal or graphite agree. Further work in other solutions will be reported in another paper.

We are greatly indebted to the Special Research Fund of Columbia University for a grant for this work and to Miss Margaret Campbell, who, as research assistant, made the measurements and compiled the results for this paper.

Summary

A study has been made of the comparative potential differences obtained for the quinhydrone electrode in 0.1000 *N* hydrochloric acid when prepared with metals and graphite of different sizes, ages, sources and compositions, from which study the following conclusions may be drawn.

1. Gold electrodes, from whatever source, are likely to give erratic results unless the electrode is a foil or wire as large or larger than 1 sq. cm.
2. Gold electrodes give cells of lower current capacities than do platinum electrodes of the same size under the same conditions.
3. Very satisfactory quinhydrone electrodes may be prepared from the graphite core of a lead pencil but not from lamp carbons, etc., since the latter seem to absorb the electrolyte, affecting not only their own potentials but the potentials of any metal electrodes immersed in the same solution.
4. The reproducibility of gold-plated electrodes is not as satisfactory as either gold, platinum or graphite.
5. The reproducibility of quinhydrone electrodes prepared with gold or with graphite is not in general improved in nitrogen, whereas that of electrodes prepared with c. p. platinum, platinum–iridium, platinum–rhodium alloys, or with gold-plated platinum is very decidedly improved.
6. 24K gold and c. p. platinum develop, within the limits of the reproducibilities possible with different samples of the same substance, the same potential differences, no matter what the size, age or source of the substance. Lead pencil graphite also seems to develop the same potential difference, although that from only one source has been thoroughly tested.

Platinum–10% iridium, platinum–10% rhodium alloys and gold-plated electrodes do not develop the same potentials, the c. p. platinum or 24K

gold being negative to the alloys and plate. This difference, however, disappears almost entirely if the solution is stirred with nitrogen.

Further work in other solutions and on the effect of oxidizing agents is in progress.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

MOLECULAR AND ACTIVATED ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE SURFACES

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In a recent communication,[1] the rapidly accumulating data relative to the variation of adsorption and heats of adsorption of gases on numerous surfaces with variation in temperature and pressure as well as data on the velocities with which adsorption and desorption equilibria are attained have been collected and analyzed. The data have been shown to be a necessary consequence of a modified theory of adsorption which differs from the classical theory in the introduction of the concept of activation energy into adsorption processes. On classical theory, the activation energy of adsorption is zero and that for desorption is X, which is identical in magnitude with the usual heat of adsorption. The modification proposed is to require an activation energy, E, for adsorption and, consequently, an activation energy, E + X, for desorption processes. This introduction of the activation energy concept does not change the theoretical equilibrium value for adsorption in its dependence on λ. On the other hand, the individual rates of adsorption and desorption will decrease exponentially as E increases, so the rate of attainment of equilibrium may vary within wide limits which will be dependent upon the magnitude of E.

It was shown in the earlier paper that this method of treatment could be applied to a gas whose adsorption on a given surface was of two types, one involving a low heat of adsorption and a low activation energy, the other a high heat of adsorption and a high heat of activation. It was shown that this led to two theoretical adsorption isobars, that with the high heat of adsorption involving greater amounts of adsorbed gas at a given temperature and pressure. Dependent on the magnitude of the two activation energies it was shown that, at sufficiently low temperatures, the lower adsorption would be the only type occurring, at higher temperatures the higher adsorption, while, in an intermediate temperature range, dependent on the respective magnitudes of the two activation energies, a transition region of pseudo-equilibrium adsorption values would be

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[1] Taylor, THIS JOURNAL, 53, 578 (1931).

obtained, showing increasing amounts of gas adsorbed with increase in temperature, the velocity of adsorption at a given temperature being determined by the activation energy of the high temperature adsorption. An examination of data for hydrogen adsorption on various surfaces abundantly confirmed the general conclusions thus reached. There were, however, no data of a quantitative nature relative to the *velocity* of adsorption. It was primarily to ascertain if such could be secured that the present work on manganous oxide surfaces was performed. This surface was chosen because of its known efficiency in hydrogenation reactions, involving activated hydrogen, and also because of its known resistance to reduction by hydrogen in the temperature range to be studied, It was anticipated and actually found that the transition from one type of adsorption to another would occur in a temperature range above room temperature. This permits a more easily operable experimental technique than is possible with such surfaces as nickel where, as Benton and White have already shown,[2] the transition interval from one to the other type of adsorption occurs below −110°. Our choice was a fortunate one in that, on a manganous oxide surface and on a surface of manganous oxide promoted with chromic oxide, we have been able to segregate the two types of hydrogen adsorption and separately examine their heats of adsorption and activation energies of adsorption. We also have made excellent measurements of the velocity of activated adsorption and from them deduced the activation energy of the process as a function of the extent of surface covered.

Experimental Details

Apparatus.—The adsorptions were measured in an apparatus of the type frequently used[3] in our work with catalytic surfaces. The adsorbent was contained in a 25-mm. Pyrex tube attached through capillary tubing and suitable stopcocks to a gas buret graduated in 0.10 cc., a mercury manometer of 10 mm. bore, an evacuation system and a gas supply and purification train.

For evacuating the system when collection of the gas was not necessary, a two-stage mercury diffusion pump was used in series with a Hyvac oil pump. To recover the adsorbed gas on evacuation, use was made of an automatic Sprengel pump built according to the plans given by Dunoyer.[4] With this, the system could be exhausted to very low pressures in a relatively short time, the pump pulling steadily as fresh gas was released from the surface of the adsorbent. Even the last small stubbornly held portion of the adsorbate could be removed completely by holding the adsorbent at 450° overnight with the Sprengel pump operating.

The adsorbent was heated by a close-fitting cylindrical electric furnace whenever the contact material was to be freed of adsorbate. When isotherms and isothermal rates were being studied, much closer temperature control was required. At the lower temperatures this was obtained by immersing the tube in a Dewar flask filled with solid

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[2] Benton and White, THIS JOURNAL, 52, 2325 (1930).

[3] See, for example, Pease, *ibid.*, 45, 1197 (1923).

[4] Dunoyer-Smith, "Vacuum Practice," G. Bell and Sons, London, 1926.

carbon dioxide–ether, water–ice or pure water as the regulating media. At higher temperatures excellent isothermal baths could be obtained by refluxing pure materials at their boiling points. The boiler was a Pyrex "test-tube," 50 mm. in diameter, which was equipped with an asbestos jacket and a reflux tube sealed into its shoulder. It was closed at the top by a plug formed of asbestos tape. An electric heater, moulded to fit snugly, could be regulated to give steady ebullition which would fill the whole tube with saturated vapor, this vapor being completely condensed after moving a few centimeters up the reflux tube.

Materials.—Manganous oxide was prepared by ignition of manganous oxalate, made[5] by the interaction of concentrated solutions of potassium permanganate and oxalic acid in presence of acetic acid. On ignition above 300° the oxalate decomposes yielding the gray-green monoxide. In the air this material, when active, takes up oxygen, changing to a darker color. Sabatier[6] found that it was stable in the presence of hydrogen at a red heat, while Meyer[7] found no evidence of reduction by hydrogen below 1200°. The samples used were submitted to a final reduction in *situ* with hydrogen at 350°.

Manganous-chromic oxide was prepared by ignition of manganous ammonium chromate formed as a dark precipitate by mixing solutions of manganous nitrate and ammonium chromate, ammonia being then added until the supernatant solution gave a neutral reaction to litmus.[8] The filtered precipitate was washed with ammonium nitrate solution to prevent the formation of suspensoids, dried and then decomposed at about 400°. The product contains approximately two moles of MnO to one oi Cr_2O_3. Prior to use it was given a final reduction in *situ*, yielding a grayish-brown powder. When exposed to air it oxidized to a velvety black higher oxide of manganese.

Manganous pyrophosphate was prepared hy ignition of manganese ammonium phosphate at 650°.

Electrolytic hydrogen, carbon monoxide from formic acid, cylinder nitrogen and ethylene were subjected to careful purification and drying before use.

Procedure.—The adsorptions were in all cases measured by comparison of the quantities of adsorbable gas required to produce a given pressure at a stated temperature with those required for a non-adsorbed gas (nitrogen). The pressures and volumes recorded have all been reduced to standard conditions. It was found necessary to evacuate the surfaces prior to a measurement for many hours at 450° in order to ensure reproducibility of experimental results.

In the determination of adsorption isotherms measurements were made in some cases with ascending pressures and in other cases by removal of measured amounts of gas from the surface saturated with a known volume of gas at moderate pressures. The chosen procedure is indicated in the tabulated results by ascending or descending values of the pressure.

The velocities of adsorption were generally determined by introducing a known volume of gas, measuring the pressures produced by such gas over certain time intervals. The pressure at zero time was calculated from the data obtained under the given conditions with nitrogen.

Experimental Results

The data presented below are a summarized form of the detailed experimental results by one of us (A. T. W.) elsewhere.[9]

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[5] Kessler, *Z. anal.* Chem., **11**, 270 (1872).

[6] Sabatier, *Ann. chim. phys.*, [8] **20**, 289 (1910).

[7] Meyer, *Chem. Abstracts*, **22**, 936 (1928).

[8] Lazier, U. S. Patent 1,746,783, Feb. 11, 1930; *Chem. Abstracts*, **24**, 1649 (1930).

[9] Williamson, "Thesis," Princeton, 1931.

A. Manganous **Oxide.** I.—Mass of sample, 22.8 grams: no measurable quantity of hydrogen was adsorbed by this surface at 0°, even over a period of several hours. At 184° no observable adsorptions were recorded at 101 mm. and 296 mm. pressure after fifteen minutes' time of contact but at 393 and 615 mm. adsorptions of 0.8 and 1.0 cc., respectively, were recorded after the system had stood for two or three hours under the given conditions. It was evident that slow activated adsorption was making its appearance so that an experiment, using a large volume of hydrogen (V), was made, pressures being recorded at stated intervals. The data obtained together with similar data at 305° are presented in Table I.

TABLE I

VELOCITY OF ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE I AT 184 AND 305°

T, 184"; V, 358 cc.			T, 305°; V, 37.7 cc.		
Time, hours	P_{mm}	$V_{ads.}$, cc	Time, hours	$P_{mm.}$	$V_{ads.}$, cc.
0	595	0.0	0	760	0.0
5	559	2 2	<1	668	4.5
8	543	3.1	2	618	7.0
22	525	4 2	3	613	7 3
26	523	4 3	8	581	8.9
35	516	4.8	10	577	9.1
46	508	5 2	16	566	9.6
51	506	5.4	22	562	9.8

It is evident from these data that the rate of adsorption at 305° is much greater than at 184°. In addition, a higher pseudo-equilibrium adsorption is approached. The velocity of adsorption at 305° suggested the possibility of obtaining an adsorption isotherm by removal of successive measured amounts of gas, allowing between each a period of from two to three hours for the reestablishment of equilibrium. The data thus obtained are presented in Table II. It will be realized that the amounts adsorbed represent upper limits for the isotherm at each pressure owing to the operation of the high activation energy of desorption as discussed in the introduction. The data do show, however, a normal adsorption and also illustrate the reversibility of the process.

TABLE II

ADSORPTION ISOTHERM OF HYDROGEN ON MANGANOUS OXIDE I AT 305°

V, cc.	$V_{ads.}$	P	V, cc.	$V_{ads.}$	P
37.7	9.5	567	14.0	4.8	186
32.2	8.6	476	10.8	4.1	134
28.5	8.1	412	7.4	3.6	77
25.1	7.5	355	5.3	3.1	44
20.6	6.5	284	3.4	2.7	14
17.2	5.9	228	2.0	2.0	0

The last two cc., which were held with an equilibrium pressure of less than 1 mm., were recovered by evacuation at 400°. There was no evidence of any water formation. Further experiments with this preparation were precluded by the accidental introduction of mercury into the adsorbing system.

Manganous oxide II was prepared by ignition of a commercial preparation of c. P. manganous oxalate. The product was very inert, difficult to reduce to the lowest state of oxidation, showed no tendency to take up oxygen on exposure to air and adsorbed no measurable amount of hydrogen even after seven hours' contact at 184°.

Manganous oxide III was a sample, 34.1 g. in weight, prepared in the same manner as manganous oxide I. To determine more accurately the energy of activation of the slow adsorption, rates of adsorption were measured carefully at 184 and 218°. The hydrogen was introduced in such a quantity that the pressure range would be approximately the same for each temperature, thereby eliminating any corrections for the variation of rate with pressure and permitting the study of the variation in rate with temperature and extent of surface covered. The data obtained are presented in Table III.

TABLE III

VELOCITY OF ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE III AT 184 AND 218°

T, 184°; V, 37.0 cc.			T, 218; V, 36.4 cc.		
Time, hours	P_{mm}	$V_{\text{ads.}}$, cc.	Time, hours	$P_{\text{mm.}}$	$V_{\text{ads.}}$, cc.
0.0	633	0.0	0.0	659	0.0
1.0	613	1.2	.25	644	.8
2.0	607	1.5	.4	639	1.1
3.0	603	1.7	.9	631	1.5
12.3	585	2.7	1.4	627	1.8
16.3	581	3.0	3.0	614	2.5
19.8	577	3.2	4.5	605	3.0
27.0	570	3.6	6.5	596	3.4
38.0	563	4.0	8.5	588	6.9
			13.75	580	4.3

Comparison of the data at 184° with those in Table I shows that this preparation is not quite as active as manganous oxide I, so far as velocity and extent of adsorption are concerned. From a plot of these values it is possible to determine the time necessary to adsorb a given amount of gas on the surface at each temperature. The ratio of the required lengths of time is the inverse ratio of the average velocities of adsorption. By direct substitution of such ratios in the equation

$$\ln \frac{v_2}{v_1} = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

the following values for E, the activation energies of adsorption, were obtained.

These results show clearly that adsorption of hydrogen on manganous oxide at temperatures in the neighborhood of 200° requires a high activa-

TABLE IV

ACTIVATION ENERGIES OF ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE III

Adsorbed amount, cc.	Time required, hours 218°	184°	E, cal. per mole, adsorbed
First two	1.8	4.6	12,400
Third	2.7	11.7	19,400
Fourth	4.7	21.7	20,800

tion energy, which is a minimum for the first areas covered and rises to higher values for less active areas of the surface.

Adsorption is still marked at 444°. A single charge of hydrogen was left in the system at this temperature for seven hours, at the end of which time the rate of adsorption had become negligible. The adsorption amounted to 7.3 cc. at a pressure of 706 mm. On removing a sample of gas a new equilibrium at the end of twelve hours showed an adsorption of 6.8 cc. at a pressure of 495 mm.

Experiments at −78.5° showed no measurable adsorption of hydrogen even after five hours' contact time at a pressure of 330 mm.

The data obtained with this sample and manganous oxide I have been utilized to construct an adsorption isobar of hydrogen on manganous oxide in the temperatue range −78–444° at a pressure of 506 mm. The data are collected in Table V.

TABLE V

ADSORPTION ISOBAR OF HYDROGEN ON MANGANOUS OXIDE AT p = 506 MM.

Temperature, ° Abs.	194.5	273	457	578	717
$V_{ads.}$, cc./g.	0.000	0.000	0.024	0.039	0.020

Since the value at 578° Abs. is on manganous oxide I, the sample of greater activity (see page 2171), the table has only semi-quantitative significance. It serves well to indicate however the increase of pseudo-equilibrium adsorption with increase of temperature. A more quantitative exemplification will now be presented for the case of hydrogen adsorption on a manganous-chromic oxide surface.

B. Manganous-Chromic Oxide.—Weight of sample, 46.5 g.: with this material a striking experimental demonstration of slow adsorption increasing in velocity with rise of temperature has been performed. Hydrogen was introduced into the adsorption vessel at room temperature until a pressure of approximately 500 mm. was obtained. The vessel was then heated very gradually by the electric furnace and the accompanying pressure change was noted. Up to about 100° the gas pressure increased normally. Shortly after this temperature was passed the expansion ceased and, with the temperature still rising, a contraction took place. This contraction accelerated and, between 200 and 300°, the gas was adsorbed with great rapidity. A minimum pressure of 10 mm. was reached between 350 and 400°. Above 400° the pressure slowly increased again although to only a slight degree and at 430° it had built up to approximately 20 mm. This experiment constitutes startling evidence of activated adsorption. It also indicates the necessity of high temperature evacuation for complete removal of adsorbed gas. In preparing the surface for the experiments now to be presented, evacuation was effected at 450–470°.

An adsorption measurement at 184° revealed the tremendous adsorptive capacity of the sample. In all a volume of 179 cc. of hydrogen was admitted to produce a pseudo-equilibrium pressure of 209 mm. after five days of adsorption. The adsorption was very rapid in the first stages, subsequent quantities of hydrogen being taken up at progressively decreasing rates. Desorption of successive samples gave the following pseudo-equilibrium data which show the tenacity with which hydrogen is held.

TABLE VI

ADSORPTION ISOTHERM OF HYDROGEN ON MANGANOUS–CHROMIC OXIDE AT 184°

V, cc.	$V_{\text{ads.}}$, cc.	P_{mm}
173.9	166.3	209
173.6	166.3	121
169.6	166.2	57
166.1	165.6	8

On cooling the system to 0° and holding at that temperature for twenty hours, no desorption occurred, although, as will later be shown, only minor amounts of the gas can be adsorbed in reasonable time intervals at this lower temperature.

High Temperature Isotherms.—Adsorption isotherms at 305 and 444° were next obtained by saturating at a given pressure and then removing the gas adsorbed in measured amounts by means of the Sprengel pump. Suitable time intervals were allowed between each successive removal to permit the approximate establishment of equilibrium. The data are presented in Table VII.

TABLE VII

ADSORPTION ISOTHERMS OF HYDROGEN ON MANGANOUS–CHROMIC OXIDE AT 305 AND 444°

	T, 305°			T, 444°	
V, cc.	$V_{\text{ads.}}$, cc.	$P_{\text{mm.}}$	V, cc.	$V_{\text{ads.}}$, cc.	P_{mm}
184.7	171.6	269	107.8	100 9	165
182.3	171.1	230	101.3	98 1	77
176.8	1696	151	97.0	95.0	48
172.9	167.0	121	84.2	83.3	22
166.7	163.6	63	57.2	57.1	3
163.3	160.8	51			
159.0	156 9	44			

Velocity of Adsorption.—For measurement of the velocity of adsorption on the mixed oxide the temperatures chosen were 100 and 132°. The pressure range **was** again kept approximately the same in the two cases in order to limit the variables to temperature and surface. The data are presented in Table VIII.

TABLE VIII

VELOCITY OF ADSORPTION OF HYDROGEN ON MANGANOUS–CHROMIC OXIDE AT 100 AND 132°

T, 100°; *V*, 43.8 cc.			*T*, 132°; V, 41.4 cc.		
Time, min.	$P_{\text{mm.}}$	$V_{\text{ads.}}$, cc	Time, min.	P_{mm}	$V_{\text{ads.}}$, cc.
0	612	0.0	0	624	0.0
4	485	9.1	2.5	486	9.1
9	455	11 2	3.8	464	10.5
13	438	12.4	5.5	441	12.1
22.5	410	14.4	8	417	13.7
29	396	15.4	13	382	16.0
36	382	16.4	20	347	18.3
49.5	361	17.9	24.5	330	19.5
67	341	19.4	43	280	22.8
98	313	21.4	49	269	23.5
127	293	22.8	51	265	23.8
153	278	23.9	61	249	24.8
185.5	263	25.0	71	235	25.8

These velocity data yield, by the same type of calculation used in the case of manganous oxide III, the following results for the activation energies of adsorption on successive areas of the surface.

TABLE IX

ACTIVATION ENERGIES OF ADSORPTION OF HYDROGEN ON MANGANOUS–CHROMIC OXIDE

Adsorbed amount	Time required, min. 132°	100°	*E*. cal. per mole adsorbed
First 10 cc.	3.2	6.0	5,920
10th–15th	7.3	20.0	9,500
15th–20th	15.9	48.0	10,400
20th–25th	37.2	111.5	10,400

As with manganous oxide, the activation energy is lowest for the first portions of gas adsorbed, which signifies that the velocity of adsorption is most rapid on the most active areas of the surface. With increased covering of the surface, E rises to a value which is constant for a considerable region of covered surface. Undoubtedly, with additional areas covered, the value of *E* would rise still further. The absolute values of the numerical results for E differ widely in the two cases and the same is true for the quantities adsorbed. With the single oxide, the activation energy ranges over the first four cc. adsorbed from 12,000 to 20,000 calories per mole. With the mixed oxide surface the range is from 6000–10,000 for the first twenty-five cc. adsorbed. The effect of this divergence on the velocity of adsorption at, for example, 177° = 450°Abs., on the areas having E = 6000 and 12,000 cal., respectively, is best exhibited by reference to the relation

$$v_{\text{MnO-Cr}_2\text{O}_3} : v_{\text{MnO}} = e^{-6000/2 \times 450} : e^{-12000/2 \times 450} = e^{6000/900} = e^{6.6} = 750$$

where v is the velocity of adsorption and is proportional to the expression $e^{-E/RT}$. This enormous effect of the admixture of chromic oxide with manganous oxide on both the velocity and extent of adsorption is undoubtedly of fundamental importance in the phenomenon of promoter action in the field of heterogeneous catalysis.

Low Temperature Adsorption.—The magnitude of the activation energy on the manganous–chromic oxide, $E = 6000$, indicates that this type of adsorption will be very slow indeed at −78.5°, actually e^{-15} or 3×10^{-7} of that at 132°. It might therefore be possible to measure the molecular adsorption of hydrogen at such temperatures. An isotherm was, therefore, measured. An immediate rapid adsorption, complete in a few minutes, occurred. In addition there appeared a very slow adsorption which continued for many hours and which is probably adsorption of the activated type on areas of the surface on which the activation energy is even less than 6000 calories. The following Table X which records results obtained both with increasing and decreasing pressure indicates the existence of the secondary type by reason of the divergence between the two sets of data, ascending and descending. That even the activated adsorption involved low activation energies is evident from the fact that the residual 3.2 cc. of gas indicated in the table was almost completely recovered by Sprengel evacuation at 0°.

TABLE X

ADSORPTION ISOTHERM OF HYDROGEN ON MANGANOUS–CHROMIC OXIDE AT −78.5°

V, cc.	$V_{\text{ads.}}$, cc.	P	V, cc.	$V_{\text{ads.}}$, cc.	P
4.1	2.6	12	22.1	10.4	91
15.7	7.6	63	17.1	9.9	56
33.4	10.2	181	10.1	6.5	28
38.7	11.2	215	8.0	5.8	17
35.0	11.3	185	4.8	4.4	3
27.7	10.9	131	3.2	3.2	0

The change in adsorption with time at −78.5' and the rapid desorption of gas on heating to 0° is indicated in Table XI, which also shows that at 0° the desorption of gas is followed by its slow readsorption in the activated form.

TABLE XI

EFFECT OF TEMPERATURE CHANGE ON HYDROGEN ADSORPTION AT −78.5° AND 0°

$V = 35.4$ cc.

	−78.5"			0°	
Time, hours	$P_{\text{mm.}}$	$V_{\text{ads.}}$, cc.	Time, hours	$P_{\text{mm.}}$	$V_{\text{ads.}}$, cc.
0.0	276	0.0	1.0	Temperature raised to 0°	
.05	196	10.3	1.82	270	9.9
.26	184	11.9	5.3	256	11.3
.45	183	12.0	29.5	237	13.0
.82	182	12.1			

Heat of Low Temperature Adsorption.—On a clean surface of the mixed oxide, hydrogen was rapidly adsorbed at 0° to the extent of 7 cc. at a pressure of 165 mm. From the previous data at —78.5' we find that the same quantity of gas is adsorbed at a pressure of approximately 40 mm. Substituting these values in the Clapeyron–Clausius equation

$$\frac{d \ln P}{dt} = \frac{\lambda_{L.T.}}{RT^2}$$

we obtain as an approximate value for the heat of low temperature adsorption the value, $\lambda_{L.T.} = 1900$ calories per mole.

Heat of High Temperature Adsorption.—A similar calculation is possible for the high temperature data already presented in the isotherms at 305 and 444'. For 100 cc. of adsorbed gas the pressures at 578 and 717' Abs. are <5 mm. and 140 mm., respectively. Substitution of these data in the above equation gives $\lambda_{H.T.} \sim 20{,}000$ calories per mole. The ten-fold variation between the two magnitudes $\lambda_{L.T.}$ and $\lambda_{H.T.}$ is the best evidence of the fundamental distinction between the two types of adsorption.

The Adsorption Isobar.—The data in the several regions of temperature may be utilized to construct adsorption isobars. The data of Table XII present the values obtained at a pressure of 165 mm. **A** graph of these data is given in Fig. 1.

TABLE XII

ADSORPTION ISOBAR OF HYDROGEN ON MANGANOUS–CHROMIC OXIDE AT $P = 165$ mm

Temp , °Abs.	Amount adsorbed, cc.	Nature of adsorbed gas
194.5	10.6	Molecular
273	7.0	Molecular
273	14.0"	Molecular + activated
457	166[a]	Mainly activated
578	170	Mainly activated
717	101	Mainly activated

[a] These values represent only pseudo-equilibria.

The data and diagram give a clear picture of the temperature range where molecular, mixed and activated adsorptions occur. The transition from one form to another is shown to cover a range of several hundred degrees.

Adsorption of Carbon Monoxide.—With carbon monoxide, an orientation experiment similar to that performed initially with hydrogen on manganous–chromic oxide also showed that two types of adsorption occur. Adsorption at —78.5' took place almost instantaneously and produced **a** low equilibrium pressure in a few minutes. On heating from —78.5 to 100°, the adsorbed quantity decreased normally, a normal pressure increase also occurring. Above 100° activated adsorption appeared, as evidenced by the increase in adsorption and decrease in pressure with rise of temperature. At 225° the transition seemed to be complete and at

450° desorption of the activated form was occurring. We can, therefore, conclude that carbon monoxide shows adsorption phenomena paralleling, qualitatively, those of hydrogen on manganous-chromic oxide. A quantitative study is being undertaken.

Adsorption of Ethylene.—With ethylene vigorous adsorption occurred at —78.5'. On warming the catalyst as far as 300° nothing but steady desorption was observed. Above 300° there was a slight decrease in pressure. This may have been due, however, to incipient polymerization,

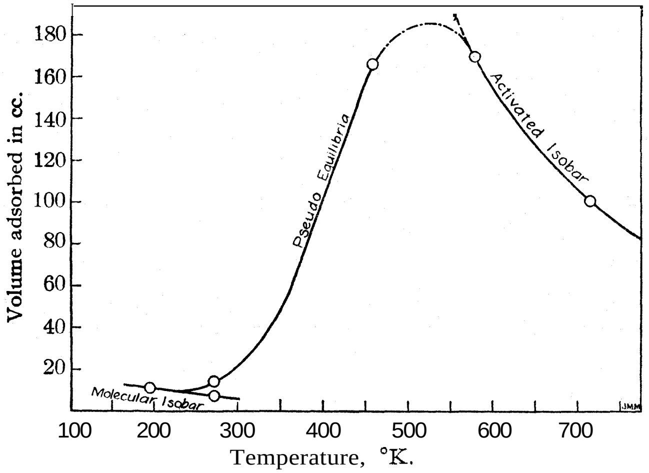

Fig. 1.—Adsorption isobar of hydrogen on manganous-chromic oxide at P = 165 mm.

C. Manganous Pyrophosphate.—Weight of sample, 34.7 g.: with this material a slow adsorption of hydrogen occurred at 305 and 444'. In magnitude and velocity it was far less than that obtained even with the single manganous oxide. The adsorption would appear to be activated since no hydrogen was adsorbed at 0°. The low magnitude and velocity of adsorption are consistent with the absence of dehydrogenation activity found for this material in other work to be reported elsewhere.

General Conclusions

The present investigations on manganous oxide and manganous-chromic oxide surfaces decisively demonstrate the adsorption of hydrogen on such surfaces in two different forms which are sharply differentiated. At low temperatures on manganous-chromic oxide the hydrogen is adsorbed rapidly with a negligible activation energy and with a heat of adsorption of approximately 1900 calories per mole. Adsorption of hydrogen in this form is readily reversible, for the gas can be completely recovered by evacuation at low temperatures. We describe such adsorption as "molecular" adsorption, The second type of adsorption predominates at higher temperatures. On manganous-chromic oxide surfaces it makes its appearance at 0° as a slow drift in pressure after the initial rapid adsorption of the molecular form. . The adsorption occurs with a definite velocity determined by the magnitude of an activation energy and the temperature. in its turn, the activation energy is a function of the surface area being covered. The first portions covered, with the mixed oxide, have a mean activation energy of 6000 calories; successive portions are associated with values rising gradually to higher magnitudes, for example, 10,400 calories. Over a range of several hundred degrees this activated adsorption apparently increases in magnitude with the temperature, a phenomenon to be ascribed to the influence of the activation energy on the velocity of adsorption.' Above 300° with manganous-chromic oxide the isobar begins to show a normal decrease with increase in temperature, and from isotherms in this temperature range heats of adsorption of the activated form of the order of 20,000 calories have been deduced. These high heats of adsorption coupled with the activation energy of adsorption adequately account for the observation that desorption of the activated adsorbate requires an evacuation lasting for several hours at temperatures above 450°.

With manganous oxide the results are similar in character but differ greatly in magnitude. There is no measurable adsorption of the molecular form at $-78.5°$. The activated form makes its appearance first in the neighborhood of 100°. The initial velocity of adsorption is some 750 times slower at 450° Abs. than on the mixed oxide since the initial activation energy is 12,000 calories, rising to 20,000 calories on successive areas covered. The quantities of adsorbed hydrogen on the single oxide are much smaller than those taken up by the mixed oxide at corresponding temperatures.

These experiments represent the first decisive measurements of thr velocity of gaseous adsorption at surfaces and have yielded the first unequivocal calculations of the activation energies of adsorption processes. They yield abundant experimental proof of the theory of activation energy of adsorption recently put forward by one of us (H. S. T.). They introduce into the problem of gaseous reaction velocities at surfaces the velocity of activated adsorption, a factor of fundamental importance, hitherto ignored, of especial significance in the so-called problem of promoter action and in the specificity of reactions at such surfaces.[10]

Since the phenomena observed with hydrogen are also shown, qualitatively at least, by carbon monoxide, it is evident that the type of investigation here initiated with hydrogen can be extended to other gases activated at surfaces. Such studies are in progress.

[10] See Taylor, *Chem. Reviews*, August, 1931.

Summary

1. The adsorptions and velocities of adsorption of hydrogen on manganous oxide and manganous-chromic oxide have been measured in the temperature range −78.5 to 444°.

2. Two forms of hydrogen adsorption have been demonstrated and differentiated, each with characteristic heats of adsorption and activation energies of adsorption on a given surface.

3. The activation energy of adsorption is a function of the composition of the surface and of the physical state of the surface; the velocity of adsorption is small on sintered surfaces and decreases rapidly with increased surface area covered.

4. Activated adsorption of the type here studied is not necessarily a rapid process but may, at certain temperatures, occur at rates so slow as to be immeasurable over periods even of years.

5. Similar observations have been made, qualitatively, with carbon monoxide. This type of investigation can, therefore, probably be generalized for various gases and surfaces.

PRINCETON, NEW JERSEY

NOTES

A Micro Hydrogen Electrode.—The electrode described in this paper was designed to be used where small amounts of liquid were available for the determination. The electrode was made from an ordinary platinum hypodermic needle. The tip was cut off and the needle was threaded for about 5 mm. on the outside. A small shield made of platinum was made to screw on the needle over the tip. A short length of copper wire was soldered to the side of the nub of the needle, leaving enough room at the end to attach a rubber tube for the hydrogen. The entire electrode and cap were insulated by covering with bakelite paint. The electrode was then platinized on the inside. The potassium chloride can be brought into the vessel by means of a capillary or a piece of cotton string soaked in the potassium chloride.

CONTRIBUTION FROM THE
DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
FELIX SAUNDERS

RECEIVED MARCH 28, 1931
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A Lampbank Rheostat.—A system of lamps in parallel makes a serviceable laboratory rheostat for use with magnetic stirrers, electric furnaces, motors, etc. The figure illustrates an easily and cheaply constructed lampbank that has proved to be very convenient. It avoids the use of the switches, sockets and wiring that the ordinary form of lamp board requires, occupies less area per lamp and its resistance can be more easily and rapidly altered.

On a narrow baseboard B whose length depends on the number of lamps it is desired to use are fastened two brass or copper "bus bars" A and C. The lower (C) is flat and serves as a contact for the lamp base terminals. The upper (A), which is round, is set out from the board and so forms a rack on which to hang the lamps. To the side terminal of each lamp is soldered a short hook made of narrow copper strip which hooks over C and so completes the circuit through the lamp. A light strip of wood D is set out about half the length of a lamp from the board and is pivoted at one end, the other being free to move. By raising and lowering the free end of D any required number of lamps may be instantly thrown in or out in a manner made obvious by the diagram. By means of pulleys and a cord attached to D the rheostat may be operated from a distance. The lamps may be adjusted easily to hang freely at right angles to the board by bending the hooks with a pair of pliers. For large resistance steps it has been found convenient to make up spools of nichrome wire equivalent to a given number of lamps that can be hooked over A and thrown in or out with the lamps by raising or lowering D.

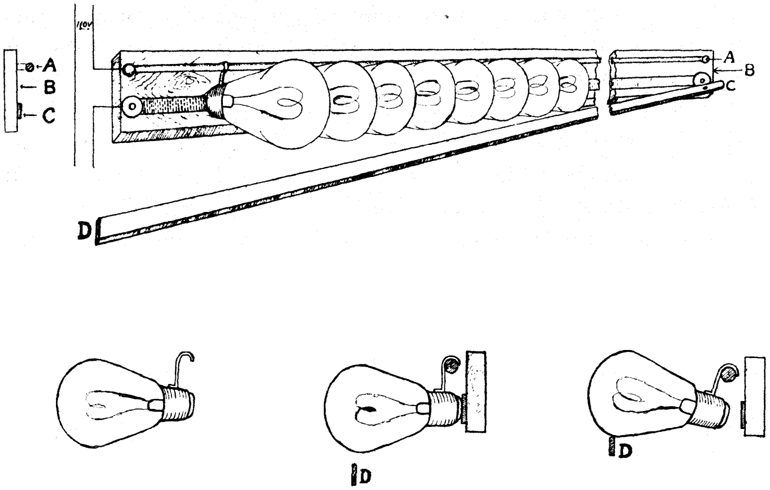

Fig. 1.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
DALHOUSIE UNIVERSITY
HALIFAX, CANADA

C. C. COFFIN

RECEIVED APRIL 23, 1931
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[CONTRIBUTION FROM THE QUEEN'S COLLEGE LABORATORY. OXFORD]

THE OXIDATION OF DITHIOPARACHLORAL

BY FREDERICK DANIEL CHATTAWAY AND EDWIN GEOFFREY KELLETT

RECEIVED SEPTEMBER 11, 1930 PUBLISHED JUNE 8, 1931

Dithioparachloral (2,4,6-tris-trichloromethyl-1,3,5-oxadithiane) (I) does not form a stable sulfone but easily breaks down under the influence of oxidizing agents.

When, however, the inhibiting influence of the trichloromethyl groups on the adjacent sulfur atoms is diminished by loss of hydrogen chloride, oxidation of one sulfur atom can occur with formation of a stable, partly unsaturated monosulfone.

Thus when 2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane (II) is submitted to the action of hydrogen peroxide at the ordinary temperature, it is oxidized to a monosulfone (2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide (III).

If dithioparachloral (I) is dissolved in acetic acid and kept at 60° for some hours, small quantities of hydrogen peroxide being added from time to time, it is partly destructively oxidized, but to some extent the same unsaturated sulfone (III) is formed, showing that loss of hydrogen chloride is necessary either as a preliminary to, or as a consequence of, oxidation of the sulfur atom.

The sulfone group in this compound (III) exerts upon the neighboring chlorine atoms an even more potent[1] negative activating influence than does a bivalent sulfur atom, an influence equivalent indeed to that produced by two adjacent bivalent sulfur atoms,' since under the influence of alcoholic potassium acetate or aqueous caustic soda the compound loses hydrogen chloride from the 2-position, yielding 6-trichloromethyl-2,4-bis-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide (IV).

When dithioparachloral is subjected to the more powerful oxidizing action of chromic acid in hot acetic acid solution, complete destructive oxidation of the molecule occurs to a predominant extent, but an unsaturated disulfone (2,6-bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide (VI)) is also produced in small amount. In the formation of this compound, the introduction of two sulfone groups not only necessitates the removal of chlorine as hydrogen chloride from both the 2- and 6-position but also its removal by hydrolysis of the trichloromethyl group in the 4-position (V), loss of carbon dioxide subsequently occurring.

The two hydrogen atoms in the 4-position in (VI) show a positive activation like the hydrogen in the 2-position in (111), but, naturally, in an even more marked degree. The compound (VI) dissolves in aqueous sodium carbonate, and is recovered unchanged on acidification; while on chlorina-

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[1] Chattaway and Kellett, J. *Chem. Soc.*, 2909 (1929).

tion the two hydrogen atoms are replaced by chlorine, yielding 2,6-bis-dichloromethylene - 4,4 - dichloro - 1,3,5, - oxadithiane - 3,3,5,5 - tetroxide (VII), which does not dissolve in aqueous alkalies.

These reactions of the disulfone (VI) serve to explain the curious behavior on chlorination of the monosulfone (III) which, in warm solution, produces the same compound (IV) as is obtained by the action of alcoholic potassium acetate or of aqueous caustic soda. In this reaction, the activated hydrogen atom in the 2-position must first be substituted by chlorine, forming (VIII). In the $=CClCCl_3$ group of this compound, the a-chlorine atom is positively, and the 8-atom negatively, activated, so that a molecule of chlorine splits off between these two positions, leaving the bis-unsaturated compound (IV).

On the same view, double bonds in positions adjacent to a sulfone group (as the 2- and 4-positions in (IV), and the 2- and 6-positions in (VI)) would not be expected to add on chlorine; and they are actually found not to do so.

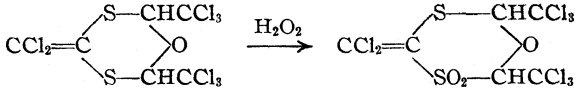
When the monosulfone (III) is treated with alcoholic caustic soda, the dichloromethylene group in the 4-position (which is subject to negative activation both by the sulfone group and the bivalent sulfur atom) is hydrolyzed; loss of hydrogen chloride also occurs from the 2- and 6-positions, yielding 2,6 - bis - dichloromethylene - 4 - carbethoxy - 1,3,5 - oxadithiane - 3,3 - dioxide (IX).

This compound, having a positively activated hydrogen atom in the 4-position, dissolves in aqueous caustic soda (not however, in sodium carbonate: it is therefore less acidic than the disulfone (VI)). On regulated chlorination, two atoms of chlorine are first added on—presumably to the double bond more remote from the sulfone group, giving 2-dichloromethylene - 6 - trichloromethyl - 6 - chloro - 4 - carbethoxy-1,3,5 - oxadithiane-3,3-dioxide (X), which is still soluble in aqueous alkali. On further chlorination, the acidic hydrogen atom is replaced by chlorine, giving 2 - dichloromethylene - 6 - trichloromethyl - 4,6 - dichloro - 4 - carbethoxy-1,3,5,-oxadithiane-3,3-dioxide (XI), which is not soluble in aqueous alkali.

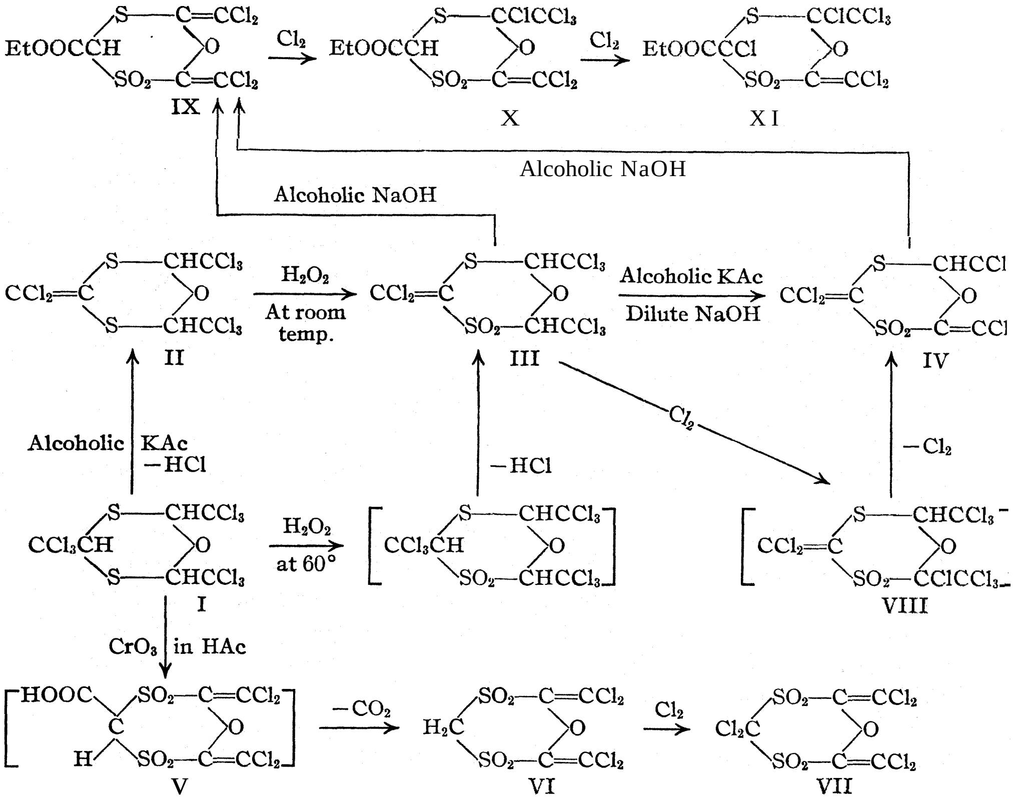
The reactions are represented in the scheme given.

Experimental

Oxidation of 2,6-Bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane to the Dioxide.—Eight grams of finely powdered β-2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane was suspended in 100 cc. of cold acetic acid and 10 cc. (excess) of 30% aqueous hydrogen peroxide added. The mixture was allowed to remain at the



II III

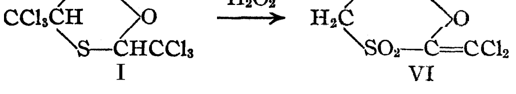


ordinary temperature for fourteen days, during which time the suspended solid passed into solution. The liquid was then diluted with water, and the 2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide, which separated as a colorless solid, crystallized from ligroin, in which it is somewhat sparingly soluble, and from which it separates in clusters of slender colorless prisms, m. p. 166–167°; yield, 7 g.

Anal. Calcd. for $C_6H_2O_3Cl_8S_2$: C, 15.3; Cl, 60.4; S, 13.6; mol. wt., 470. Found: C, 15.6; Cl, 60.8; S, 13.8; mol. wt., cryoscopic in benzene, 451.

This compound does not react with chlorine or bromine in the cold, nor is it reduced by tin in a boiling mixture of hydrochloric and acetic acids. After heating for thirty minutes at 100" with acetic anhydride and a little strong sulfuric acid, it crystallizes unchanged on cooling. It dissolves readily in cold strong sulfuric acid, and is recovered unchanged on pouring the solution over crushed ice.

Oxidation of Dithioparachloral to **2,6-Bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide.**—Five grams of **β-dithioparachloral** was dissolved in 60 cc. of acetic



acid at 100°; 10 g. of anhydrous chromic acid was added in small portions during one hour, after which heating was continued on the water-bath for another hour. Some carbon dioxide was evolved during this process, and sulfate ion could be detected in the solution, showing that disruptive oxidation had occurred to some extent.

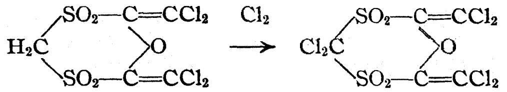
The reaction mixture was cooled and diluted with water, when the *tetroxide,* mixed with the dioxide (above) separated as a colorless solid. It was washed with aqueous sodium carbonate, which dissolves the tetroxide but not the dioxide; the filtrate was acidified with hydrochloric acid, and the tetroxide which again separated was crystallized from mixed chloroform and ligroin. It is only sparingly soluble in organic solvents, and separates as a felt of colorless silky needles, m. p. 185"; yield, 0.4–0.8 g.

Anal. Calcd. for $C_5H_2O_6Cl_4S_2$: Cl, 40.8; S, 18.4. Found: Cl, 40.5; S, 18.3.

The tetroxide may also be isolated by repeatedly recrystallizing the crude oxidation product from ligroin; showing that the bis-dichloromethylene structure arises in the actual oxidation process, and is not merely introduced by the use of the alkaline carbonate solvent in working up.

An identical product was similarly obtained from α-dithioparachloral.

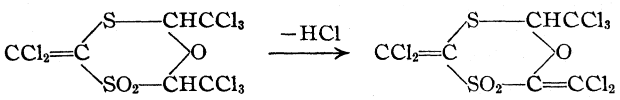
Chlorination of the **Tetroxide.**—Five grams of the tetroxide was dissolved in 4 cc. of warm acetic acid, and a rapid stream of chlorine passed through the solution for one hour. Hydrogen chloride was evolved during the chlorination. The solution was allowed to stand overnight, when 4,4-dichloro-2,6-bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide separated in large colorless rhombs, m. p. 143°. It is very readily soluble in acetic acid, and moderately easily soluble in alcohol, from which it is best recrystallized; it does not dissolve in cold aqueous caustic soda.



VI VII

Anal. Calcd. for $C_5O_5Cl_6S_2$: Cl, 51.1; S, 15.4. Found: Cl, 51.4; S, 15.5.

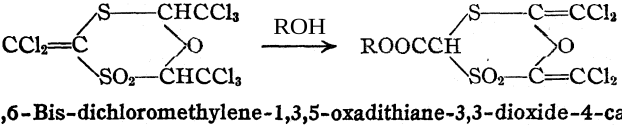
Preparation of **2,4-Bis-dichloromethylene-6-trichloromethyl-1,3,5-oxadithiane-3,3-dioxide.**—One gram of the dioxide (III) was suspended in 20 cc. of 10% aqueous caustic soda, and warmed gently for a few minutes at 40–50°. After cooling and acidifying with hydrochloric acid, the solid was separated and crystallized from petroleum, in which it is somewhat sparingly soluble, and from which it separates as *a* felt of colorless needles, m. p. 148°.



Anal. Calcd. for $C_6HO_3Cl_7S_2$: Cl, 57.3. Found: Cl, 57.6.

The same compound was obtained by heating the dioxide with alcoholic potassium acetate, and also by chlorinating it in warm acetic acid solution; hydrogen chloride is evolved during the chlorination.

Hydrolysis of the Dioxide.—To obtain a clean workable product in these hydrolyses, the procedure given below must be followed with some care. It is especially essential to work in dilute solution.



Ethyl 2,6-Bis-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate.—Eight grams of the dioxide was dissolved in 800 cc. of cold ethyl alcohol, and aqueous caustic soda (10%) added until the mixture was permanently alkaline. It was then bright yellow in color; 350 cc. of water, followed by 100 cc. of strong hydrochloric acid, was then added. The solution became practically colorless and on diluting with about 3 liters of water, the ester separated as a flocculent precipitate. It was crystallized from ligroin (500 cc.), from which it separates in plume-like clusters of colorless needles, m. p. 112.5°; yield, 4 g.

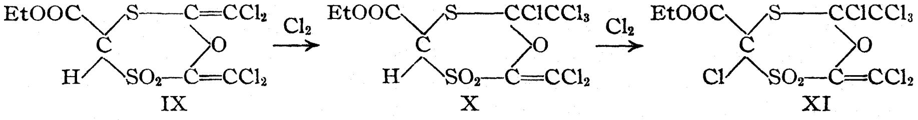
Anal. Calcd. for $C_8H_6O_5Cl_4S_2$: C, 24.9; H, 1.3; Cl, 36.6; S, 16.6. Found: C, 25.0; H, 1.9; Cl, 37.0; S, 16.8.

Methyl **2,6-Bis-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate.**—This ester was similarly prepared by using methyl alcohol instead of ethyl alcohol as the solvent. It crystallizes from ligroin, in which it is sparingly soluble, in colorless needles, m. p. 126°.

Anal. Calcd. for $C_7H_4O_5Cl_4S_2$: Cl, 38.2; S, 17.2. Found: Cl, 38.5; S, 17.2.

The ethyl and methyl esters are somewhat unstable and turn brown on long exposure to air. Attempts to prepare the free carboxylic acid from them were unsuccessful. On heating with acids or alkalies, they are decomposed and tarry products formed. Similarly, when the hydrolysis of the dioxide was carried out in aqueous acetone instead of an alcohol with a view to obtaining the free acid directly, only an uncrystallizable tarry product was obtained.

Chlorination of the Ethyl Ester



First Stage.—One gram of the ethyl ester (IX) was suspended in 5 cc. of cold acetic acid, and a slow stream of chlorine bubbled through for half an hour. During this time the solid went into solution, and on allowing the mixture to stand for two hours, ethyl 6-chloro-6-**trichloromethyl**-2-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate crystallized out. This was filtered off and recrystallized from ligroin, in which it is moderately easily soluble, and from which it separates in slender colorless prisms, m. p. 151–152°.

Anal. Calcd. for $C_8H_6O_5Cl_6S_2$: Cl, 46.6. Found: Cl, 47.0.

This compound dissolves in aqueous alkalies, but decomposes rather rapidly in alkaline solution, and consequently separates in an impure brownish state on acidification. It is somewhat unstable, and even when kept in a sealed tube decomposes in time into a brown tarry mass.

Second Stage.—Two grams of the ester (IX) was suspended in 20 cc. of acetic acid and chlorinated as above. After the chlorine addition product had crystallized out, chlorine was again passed through. Hydrogen chloride was slowly evolved, and the crystals again went into solution. When all had dissolved, the solution was very gradually diluted by addition of cold water, when ethyl **4,6-dichloro-6-trichloromethyl-2-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate** separated. It was recrystallized from alcohol, in which it is readily soluble, and from which it separates in colorless rhombic plates, m. p. 161.5°.

Anal. Calcd. for $C_8H_5O_5Cl_7S_2$: C, 19.4; H, 1.0; Cl, 50.2; S, 12.9; mol. wt. 493. Found: C, 19.8; H, 1.1; Cl, 50.5; S, 13.0; mol. wt., cryoscopic in benzene, 452.

This compound is insoluble in aqueous alkalies, and, unlike the compounds above, which contain the acidic hydrogen atom, it is perfectly stable at the ordinary temperature.

Summary

Dithioparachloral does not form stable sulfoxides or sulfones owing to the mutual influence of the chlorine and bivalent sulfur atoms. Oxidation only occurs when some of the chlorine is removed either by previous treatment or in the oxidation process itself.

On oxidation with hydrogen peroxide it yields 2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide, and with hot chromic acid 2,6-bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide.

The behavior of these oxidation products toward alkaline reagents and on chlorination illustrates both the activating influence of bivalent sulfur and the alternating effect originating from sulfone groups.

THE QUEEN'S COLLEGE LABORATORY
OXFORD, ENGLAND

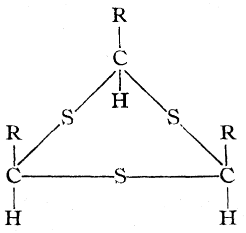
[CONTRIBUTION FROM THE QUEEN'S COLLEGE LABORATORY, OXFORD]

THE SUPPOSED ISOMER OF 1,3,5-TRITHIANE

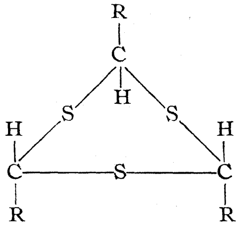
BY FREDERICK DANIEL CHATTAWAY AND EDWIN GEOFFREY KELLETT

RECEIVED SEPTEMBER 11, 1930 PUBLISHED JUNE 8, 1931

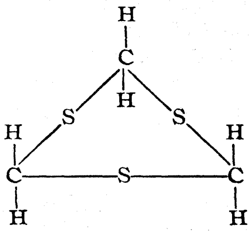
Accepting the view that the trithioaldehydes are 1,3,5-trithianes, strictly analogous in their isomerism to the paraldehydes, there can be no *cis-trans* isomerism of 1,3,5-trithiane itself.



Cis



Trans



1,3,5-Trithiane

Hinsberg,[1] however, has stated that this compound, which melts at 216°, is converted under the influence of hydriodic acid (which converts *a*- into *β*-trithioacetaldehyde) into an isomeric modification which melts with decomposition at 247°. It is reconverted into the "stable form" on crystallization from benzene.

Fromm and Schultis,[2] and Bell and Bennett,[3] have since reëxamined this phenomenon without arriving at any satisfactory conclusion.

Since, however, by the action of other reducing agents upon 1,3,5-trithiane, a product of the same or only slightly lower m. p. (247°) is ob-

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[1] Hinsberg, *J. prakt. Chem.*, *85*, 341 (1912).

[2] Fromm and Schultis, *Ber.*, *56*, 937 (1923).

[3] Bell and Bennett, *J. Chem. Soc.*, 19 (1929).

tained and this compound on mild oxidation yields again the original material of m. p. 216,° it seems probable that the supposed higher-melting isomer is actually an unstable reduction product (or mixture of products) of 1,3,5-trithiane, and that the latter compound exists as the theory demands in only a single modification.

Experimental

The Alleged Isomerism of 1,3,5-Trithiane.—When hydrogen sulfide is passed into a mixture of 1 volume of formalin with 2 volumes of strong hydrochloric acid, the colorless solid which separates (after washing with air-free water and drying in *vacuo*) melts at 247° (decomp.). After crystallization from any solvent, it melts at 216°; the same lowering of the melting point takes place on solution even at the ordinary temperature,' since if the compound of m. p. 247° is dissolved in cold benzene and precipitated out with ligroin, the product melts at 216°. The compound of m. p. 247° is also converted into ordinary pure 1,3,5-trithiane, m. p. 216°, on exposure to air for about twenty-four hours, or on heating for more than a short time on the steam-bath, or on shaking for a minute with cold dilute aqueous hydrogen peroxide. The high-melting product can be obtained from normal 1,3,5-trithiane, m. p. 216°, not only (as Hinsberg found) by the action of hydriodic acid, but also by the action of other reducing agents, *e.* g., stannous chloride, or metals and hydrochloric acid, reagents which do *not* effect steric inversion in the trithioacetaldehydes. The melting point is not perfectly constant, and may be as low as 243°, but there appears to be no reason to doubt that the same compound is present in each case.

If a weighed quantity of the freshly-prepared substance of m. p. 247° is shaken with a known amount of dilute aqueous hydrogen peroxide, filtered and washed, and the filtrate back-titrated against standard permanganate, an appreciable decrease in the amount of available oxygen present is observed; but no consistent analyses have been obtained by this method.

These observations appear to show that the compound, m. p. 247°, is of the nature of an unstable reduction product (or mixture of products) of 1,3,5-trithiane.

Summary

The compound of m. p. 247°, which Hinsberg supposed to be isomeric with 1,3,5-trithiane, has not the properties of an *isomer* of the latter compound but rather those of an unstable *reduction product.*

THE QUEEN'S COLLEGE LABORATORY
OXFORD, ENGLAND

[CONTRIBUTION NO. 37 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE EQUILIBRIUM $C_6H_6 + CO_2 \rightleftharpoons C_6H_5COOH$[1]

BY CORLISS R. KINNEY AND DAVID P. LANGLOIS

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The decomposition of organic acids into carbon dioxide has been studied extensively, as has the decomposition of malonic acid and derivatives into carbon dioxide and monobasic acids; but we are not aware of any attempt to determine whether the reaction is reversible and if so whether the reaction proceeds sufficiently far to be of practical value.[2] With these points in view several investigations have been started.

The reaction of benzene with carbon dioxide was chosen for the first study because of the adaptability of the substances involved. An approximate calculation of the free energy of the reaction

$$C_6H_6 + CO_2 \rightleftharpoons C_6H_6COOH$$

showed that the position of equilibrium would be far to the left, but that provided an equilibrium could be established, a small amount of benzoic acid would be produced.

The search for an appropriate catalyst was made by studying the rate of decomposition of benzoic acid in contact with various catalytic mixtures at various temperatures, assuming that an active catalyst for the reverse reaction would catalyze the forward reaction as well. The percentage decomposition at various time intervals and temperatures for some of the better catalysts are listed in the experimental part. The most effective were of the Zn–Cu–Cr oxide type used in methanol synthesis. Such catalysts produced considerable decomposition of benzoic acid at temperatures as low as 250°, the boiling point of the acid. This temperature is much lower than any recorded previously. The rate of decomposition at 300° is shown in the accompanying diagram. The shape of the curve indicates that after about five days of heating, an equilibrium was being approached.

The forward reaction was studied by heating benzene and carbon dioxide in glass bomb tubes containing the catalyst to pressures between 17 and 35 atmospheres. At 300° and about 35 atmospheres' pressure the crude yield of acid products amounted to 0.13% based on the weight of benzene

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[1] Presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] Two patents on the reaction of methane with carbon dioxide are of interest in this connection. Plauson and Vielle, Brit. Pat. 156,148 (1920); *Chem. Abstracts*, 15, 1726 (1921), and H. Dreyfus, Brit. Pat. 226,248 (1923); *Chem. Abstracts*, 19, 2057 (1925). Friedel and Crafts [*Ann. chim. phys.*, [6] *14*, 1441 (1887)] found that benzoic acid was produced in traces by the action of aluminum chloride on benzene and carbon dioxide. An attempt to use the method commercially was unsuccessful [Frydlender, *Revue des Produits Chimiques*, 21, 24 (1918)].

used. When the crude acid product was heated, benzoic acid sublimed, giving a yield of 0.08%.

Since benzoic acid has been obtained from benzene and carbon dioxide, and benzoic acid is decomposed by heat into those substance, it should be possible to establish an equilibrium. The determination of the position of equilibrium under various conditions has not been attempted, because, unfortunately, catalysts sufficiently active for a rapid attainment of equilibrium have not been found.

The search for more active catalysts is being continued, as well as the extension of the method to the formation of other acids.

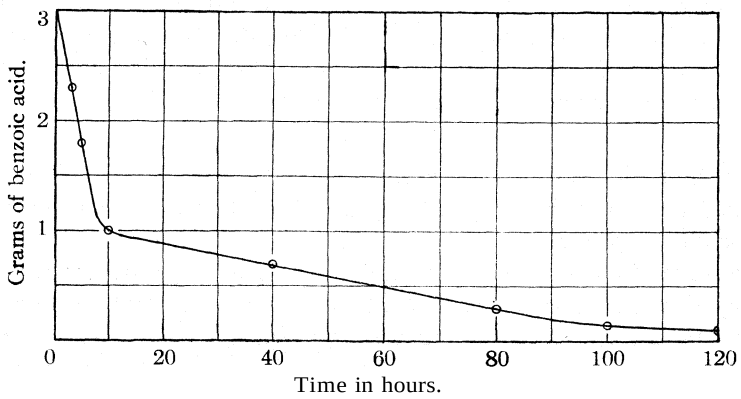

Fig. 1.—Rate of drcomposition of benzoic acid at 300° in contact with a Zn–Cu–Cr oxide catalyst.

Experimental Part

After a number of preliminary experiments, the two reactions were studied by heating pairs of bomb tubes, both of which contained a given catalyst, together with **3** g. of pure benzoic acid in the first tube, and 2 g. of pure benzene and 2.2 g. of carbon dioxide[3] (introduced as snow) in the second. The two tubes were then heated in a Carius furnace at as nearly a constant temperature as possible. This seldom varied more than three or four degrees in either direction. After heating, the tubes were opened and the contents digested for several minutes with boiling potassium hydroxide. The solution was cooled, filtered and extracted twice with ether. The potassium hydroxide was neutralized with dilute hydrochloric acid and if there was sufficient benzoic acid present to be precipitated, it was filtered out before extracting the remaining acid with two portions of ether. The ether was evaporated and the weight combined with that of the precipitated acid. In the experiments on the decomposition of benzoic

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[3] In several experiments 4 4 g. of carbon dioxide was introduced. The pressure in these tubes was calculated to be about **35** atmospheres at 300° and about **17** atmospheres in the tubes containing 2.2 g. of carbon dioxide.

acid an odor of phenol was often pronounced, although the amount actually produced was quite small. The more characteristic of the results obtained are listed in Table I.

TABLE I

CHARACTERISTIC RESULTS

Catalyst	Temp, °C.	Time of heating, hours	Amount of benzoic acid decomposed, %	Amount of benzoic acid produced
3 g. Zn–Cu–Cr oxides'''	355–360	10	27	Trace
3 g. Zn–Cu–Cr oxides[h]	245–250	10	27	Trace
	273–283	10	47	Trace
	280–290	10	47	Trace
3 g. Zn–Cu–Cr oxides'	300	3	13.3	
3 g. Zn–Cu–Cr oxides[c]	300	5	40	
3 g. Zn–Cu–Cr oxides[c]	300	10	67	Trace
3 g. Zn–Cu–Cr oxides"	300	40	77	Trace
3 g. Zn–Cu–Cr oxides[c]	300	80	90	Trace
3 g. Zn–Cu–Cr oxides[c]	300	100	95	Trace[3]
3 g. Zn–Cu–Cr oxides[c]	300	120	96.6	Trace
3 g. manganous oxide[d]	290–300	10	3	None
3 g. Zn–Cu–Cr, oxides[c] mixed with 1 g. of manganous oxide[d]	290–300	10	85	Trace
3 g. Zn–Cu–Cr, oxides' mixed with 1 g. of manganous oxide[e]	270	10	33	None[3]
3 g. Zn–Cu–Cr, oxides" mixed with 1 g. of ferric oxide[e]	290–300	10	70	Trace
3 g. Zn–Cu–Cr, oxides' mixed with 1 g. of nickel oxide"	290–300	10	60	Trace
3 g. Zn–Cu–Cr, oxide[c] mixed with 1 g. of cadmium oxide"	300	10	67	Trace[3]
3 g. of manganous oside[d] mixed with 1 g of ferric oxide'	270–280	10	23	None[3]

[a] Prepared by the method of Fenske and Frolich, *Ind. Eng. Chem.*, 21, 1052 (1929), except that the oxides were reduced by heating them with benzoic acid. [b] Same as [a] except that the oxides were reduced with benzoic acid in a stream of carbon dioxide. [c] Same as [a] except that the oxides were not reduced, but were heated in air until the mixture turned black. [d] Made by heating the carbonate in a stream of hydrogen. [e] Made by heating the nitrate in an open crucible until all of the nitrogen oxides were driven off.

In order to determine the yield of benzoic acid from benzene and carbon dioxide, six tubes, each containing 2 g. of benzene and 4.4 g. of carbon dioxide, were heated with catalyst (c) for ten hours at 300°. The pressure was calculated to be about 35 atmospheres. Upon opening the tubes, the acid produced in four of them was extracted with hot sodium hydroxide, the solution cooled, filtered, acidified, and extracted four times with ether. The ether was evaporated and the weight of the brown crystalline mass remaining was 0.0165 g. The ether extract from the last two tubes was extracted four times with dilute sodium carbonate, the sodium carbonate solution acidified and extracted four times with ether. Upon removing the ether, the residue was no purer than that obtained by extracting with dilute sodium hydroxide. There was no odor of phenol. The crude acid weighed 0.0080 g. and was sublimed onto a cold watch crystal. The weight was 0.0050 g. and the melting point 103–108°. Mixed with pure benzoic acid, the melting point was raised to 110–114°. A second sublimation did not raise the melting point.

Summary

Catalysts have been found which initiate the decomposition of benzoic acid into benzene and carbon dioxide at temperatures as low as 245–250°. The reaction was found to be slightly reversible, benzoic acid being produced by the reaction of benzene on carbon dioxide in small amounts.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

SOME SUBSTITUTED DI-(BETA-PHENYLETHYL)-AMINES AND BENZYL-BETA-PHENYLETHYLAMINES

BY JOHANNES S. BUCK

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A great deal of attention has been given to derivatives of β-phenylethylamine, particularly to their physiological action. This group contains compounds such as epinine, hordenine, tyramine, etc., and may also be considered as related to the hydrastinines (for example, Lodal), so that it is of great importance.

Much less work appears to have been done on secondary amines containing more than one benzene nucleus, of the type of di-(β-phenylethyl)-amine and benzyl-β-phenylethylamine, although a small number of these compounds is described in the literature and in some cases their pharmacological action has been examined. Di-(β-phenylethyl)-amine has been described by many workers; benzyl-b-phenylethylamine, *p*-methoxy-benzyl-β-phenylethylamine, *p*-hydroxybenzyl-β-phenylethylamine, *o*-hydroxybenzyl-β-phenylethylamine, and 3-methoxy-4-hydroxybenzyl-β-phenylethylamine, by Shepard and Ticknor;[1] o-veratrylhomopiperonylamine by Kaufmann and Miiller;[2] benzyl-*p*-hydroxy-β-phenylethylamine, piperonyl-*p*-hydroxy-β-phenylethylamine, veratryl-*p*-hydroxy-β-phenylethylamine, and *o*-hydroxybenzyl-*p*-hydroxy-β-phenylethylamine, by Hoffmann and La Roche;[3] and *p*,*p*′-diamino-di-(β-phenylethyl)-amine and *p*,*p*′-dihydroxy-di-(β-phenylethyl)-amine by von Braun and Blessing.[4] The last authors also prepared cyclohexyl-*p*-hydroxy-β-phenylethylamine and cyclohexyl-*p*-amino-β-phenylethylamine. No compound containing the physiologically important catechol group (adjacent hydroxyl groups, usually in the 3,4-positions) appears to have been described. It was with the idea of prepar-

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[1] Shepard and Ticknor, THIS JOURNAL, 38,381 (1916).

[2] Kaufmann and Miiller, *Ber.*, 51, 126 (1918).

[3] Hoffmann and La Roche, German Patent 259,874.

[4] Von Braun and Blessing, *Ber.*, 56, 2153 (1923).

ing such compounds that the present work was undertaken. A number of the desired amines (as salts) have been obtained and their pharmacological properties will be described in another place.

The usual method for preparing benzyl-β-phenylethylamines is to condense a phenylethylamine with an aldehyde to form the Schiff base and then to reduce this, usually with sodium amalgam or (in the author's experience by far the better way) by the Adams method. This route has also been used for di-(β-phenylethyl)-amine by Rupe and Hodel.[5] In the majority of compounds prepared by the present author, this method was adopted to obtain the ethers of the hydroxyamines, and the ethers were then demethylated. Another reaction was sometimes employed. This consisted of combining a primary amine with the requisite ω-halide, to give the secondary amine salt, and this was then demethylated as before. The direct combination of a 3,4-dihydroxyamine with an aldehyde to form the Schiff base was not investigated closely as the method held little promise. Which of the two methods is used is a matter of expediency, although naturally the Schiff base method offers fewer chances of secondary reactions. In the direct combination of an amine and a halide, the formation of tertiary and quaternary compounds was not observed under the conditions employed. In the case of homoveratrylhomoveratrylamine, however, considerable amounts of homoveratrylamine hydrochloride were produced, indicating either the liberation of free secondary amine or the decomposition of the chloride into dimethoxystyrene.

Experimental

Starting Materials

β-Phenylethylamine.—Some was obtained from Kahlbaum, but most of it was prepared by a Hofmann reaction on phenylpropionamide.

Homoveratrylamine.—This was prepared as described by Buck[6] by a Hofmann reaction on dimethoxyphenylpropionamide.

Homoanisylamine.—Anisaldehyde, heated with malonic acid and pyridine (Rupe method) gave *p*-methoxycinnamic acid in 79% yield. On reduction (sodium amalgam) p-methoxyphenylpropionic acid was obtained (86% yield). Heated in a stream of dry ammonia at 210° for two hours, this gave the amide (62% yield with one heating) which was then converted, by the theoretical amount of sodium hypochlorite, into the amine; yield, 56%; b. p. 132° (10 mm.).

β-Phenylethyl chloride was prepared by the method of Barger,[7] which proved to be satisfactory.

β-Phenylethyl bromide was obtained from the Eastman Kodak Co.

3,4-Dimethoxyphenylethyl Alcohol.—Homoveratrylamine, in dilute acetic acid solution, was converted into the alcohol by the addition of the theoretical amount of sodium nitrite. The product (90% yield) boiled at 180–193° (13 mm.). Redistilled,

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[5] Rupe and Hodel, *Helv. Chim. Acta*, 6,878 (1923).

[6] Buck, THIS JOURNAL, 52,4119 (1930).

[7] Barger, *J. Chem. Soc.*, 95,2193 (1909).

it forms a faint yellowish viscous oil, with only a slight odor; b. p. 166–168" (8 mm.); d_{20}^{20} 1.1426; n_{15} 1.5409.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.89; H, 7.74. Found: C, 65.94; H, 7.61

The **p-nitrobenzoate,** prepared by the Schotten-Baumann method, and recrystallized from alcohol, forms bright yellow, glittering, jagged plates, melting at 81° and readily soluble in the usual solvents to colorless solutions.

Anal. Calcd. for $C_{17}H_{17}O_6N$: C, 61.61; H, 5.18; N, 4.23. Found: C, 61.44; H, 5.66; N, 4.03.

The **urethan** was prepared by warming molecular amounts of the alcohol and phenyl isocyanate and washing the product with carbon bisulfide. Recrystallized from alcohol it forms white, pearly aggregates of thin plates, somewhat soluble in hot water and readily soluble in the usual solvents. It melts at 98–99".

Anal. Calcd. for $C_{17}H_{19}O_4N$: C, 67.74; H, 6.31; N, 4.65. Found: C, 67.62; H. 6.44; N, 4.47.

3,4-Dimethoxy-β-phenylethyl chloride could not be obtained in the pure state. The material used was obtained by treating the alcohol in carbon tetrachloride solution with the theoretical amount of phosphorus pentachloride and then removing all volatile matter under reduced pressure at 100°. A thick, reddish oil was obtained.

Schiff Bases.—In general these compounds were prepared by mixing the reactants in molecular proportions and then heating at 100° under reduced pressure until all water was evolved (usually thirty minutes). The yield is practically the theoretical. The compounds are well defined and are readily soluble in the usual solvents. They are best recrystallized by allowing their solutions in ether to evaporate spontaneously. They are tabulated below. Most of those previously known may be found in connection with the amines derived from them (see above). It is interesting to note that phenylacetaldehydes appear to give oily or ill-defined Schiff bases.[5,8]

TABLE I

SCHIFF BASES

Aldehyde	Amine	Appearance	M. p., "C.	Formula	Analyses Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Piperon-	H-piperonyl-	Tiny white prisms	114	$C_{17}H_{15}O_4N$	68.67	68.39	5.08	5.06	..	..
Anis-	H-anisyl-	White jagged prisms	74	$C_{17}H_{19}O_2N$	...	...	..	..	5.20	4.99
Veratric	β-phenylethyl-	Faint yellow pearly plates	60	$C_{17}H_{19}O_2N$	75.78	75.52	7.13	7.14	..	..
Piperon-	H-veratryl-	White glittering needles	101	$C_{18}H_{19}O_4N$	68.97	68.77	6.12	6.34	4.47	4.46
Anis-	H-veratryl-	Cream prisms	63	$C_{18}H_{21}O_3N$			..	..	4.68	4.77
Veratric	H-anisyl-	Cream stout prisms	69	$C_{18}H_{21}O_3N$	...	...	..	..	4.68	4.85
Veratric	H-veratryl-	White nodules	83	$C_{19}H_{13}O_4N$	69.27	69.55	6.99	7.15	..	..

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[8] Späth and Berger, *Ber.*, 63,2098 (1930).

Amines.—The Schiff bases are very readily reduced in acetic acid solution by platinum oxide and hydrogen, after the method of Adams. Excess acetic acid was removed under reduced pressure, the acetate dissolved in water and aqueous ammonia or sodium hydroxide solution added. The amine was then extracted with ether, the extract dried over potassium hydroxide and the ether removed. The amine was then recrystallized from alcohol–aqueous ammonia mixture or distilled under reduced pressure. The yield is practically the theoretical. Those amines not prepared *via* the Schiff base were obtained from the salts in an analogous manner.

In the second method of preparation, the halide and amine were mixed in molecular amounts and heated on the water-bath until the reaction was complete. Bromides react much more rapidly than the chlorides and the reaction mixture may not require heating. With the chlorides up to twenty hours' heating may be required. Usually the amine hydrobromide separates in the solid state, but the hydrochlorides remain oily. In all cases, ether is added to the reaction mixture and the salt filtered off and recrystallized.

The amines tend to form carbonates in air. Two salts were made from each amine, the hydrochloride, wherever possible, for pharmacological test, and another salt for analytical check. The amines and salts are tabulated.

Phenolic **Amines.**—β-Phenylethylamine derivatives are somewhat unstable to strong acids, but by carefully regulating the reaction it was found possible to obtain, in most cases, the demethylated (phenolic) derivatives in good yield. The demethylation, which goes extraordinarily easily, was carried out by means of hydriodic acid (52%, *d* 1.7), which must be colorless. The amine, mixed with ten times its weight of acid, was cautiously heated in a current of carbon dioxide until the evolution of methyl iodide had ceased. One-fifth of the acid was then distilled over and the rest removed under reduced pressure. The hydriodide usually remained as a crystalline mass.

The phenolic amine salts are generally well-defined, crystalline compounds, stable when quite pure. They possess, as might be expected, powerful reducing properties, reducing gold and silver salts in the cold. Those containing two adjacent hydroxyl groups give intense green colors with ferric chloride. Aqueous alkalies, when not present in excess, give white precipitates of the bases, at once soluble in excess to unstable yellowish solutions which rapidly oxidize.

In one case, 4-hydroxybenzyl-4'-hydroxy-β-phenylethylamine, no adjacent hydroxyl groups are present and only a faint violet color is obtained with ferric chloride. The powerful reducing properties are also absent and the base is stable.

TABLE II

DATA ON AMINES

Amine	Prepd. from	Cryst. solvent	Properties	B. p. or m. p., °C.	Formula	Analyses Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
Homoveratryl-β-phenylethyl-	Salt	......	Faint yellow oil	178" (0.48 mm.)	$C_{18}H_{23}O_2N$					4.91	4.57
Hydrochloride	2	Dil. HAc + HCl	White pearly crusts	183	$C_{18}H_{24}O_2NCl$	67.15	67.19	7.52	7.67		
Hydrobromide	2	Dil. HAc	Bulky cryst. powder	172	$C_{18}H_{24}O_2NBr$	58.99	59.37	6.61	6.79		
Homoveratrylhomoveratryl-	Salt	......	White crystals	*ca.* 240 (1.0 mm.) (m. p. 51°)	$C_{20}H_{27}O_4N$					4.06	4.33
Hydrochloride	2	Abs. alc.	Pearly cryst. masses	196	$C_{20}H_{28}O_4NCl$	62.83	62.54	7.37	7.48		
Hydriodide	Chloride	Water	Pearly plates	182 soft 175	$C_{20}H_{28}O_4NI$	50.72	50.58	5.97	6.13		
Veratrylhomoanisyl-	1	......	Pale yellow oil	197 (0.48 mm.)	$C_{18}H_{23}O_3N$					4.65	4.59
Hydrochloride	Amine	Dil. HCl	Pearly plates	223	$C_{18}H_{24}O_3NCl$	63.94	64.17	7.13	7.36		
Hydrobromide	Amine	Dil. HAc-HBr	Pearly plates	233	$C_{18}H_{24}O_3NBr$	56.52	56.83	6.33	6.62		
Anisylhomoanisyl-	1	Alc. + NH₄OH	Fluffy, whitish leaves	44	$C_{17}H_{21}O_2N$					5.16	5.31
Hydrochloride	Amine	Dil. HCl	Small rhombs	271	$C_{17}H_{22}O_2NCl$	66.31	66.46	7.21	7.54		
Hydrobromide	Amine	Dil. HBr	Glittering hexagons	254	$C_{17}H_{22}O_2NBr$	57.94	58.09	6.29	6.02		
Piperonylhomoveratryl-	1	......	White crystals	203[b] (0.44 mm.) (m. p. 34)	$C_{18}H_{21}O_4N$					4.44	4.32
Hydrochloride	Amine	Dil. HCl	Fluffy tiny needles	219	$C_{18}H_{22}O_4NCl$	61.43	61.50	6.31	6.65		
Hydrobromide	Amine	Water	Tiny nodules	204	$C_{18}H_{22}O_4NBr$	54.54	54.56	5.59	5.56		
Hydriodide	Amine	Dil. HAc	Faint yellow prisms	198	$C_{18}H_{22}O_4NI$	48.75	48.65	5.00	5.09		

TABLE II (*Concluded*)

Amine	Prepd. from[d]	Cryst. solvent	Properties	B. p. or m. p., °C.	Formula	Analyses Carbon, % Calcd.	Analyses Carbon, % Found	Analyses Hydrogen, % Calcd.	Analyses Hydrogen, % Found	Analyses Nitrogen, % Calcd.	Analyses Nitrogen, % Found
Anisylhomoveratryl-	1	Cold ether	Large yellowish crysts.	47	$C_{18}H_{23}O_3N$					4.65	4.79
Hydrochloride	Amine	Dil. HAc	Long prisms	234	$C_{18}H_{24}O_3NCl$	63.97	64.15	7.14	7.18		
Perchlorate	Amine	Dil. HAc	Small prisms	198	$C_{18}H_{24}O_7NCl$	53.78	53.79	6.02	5.79		
Veratryl-β-phenylethyl-	1	......	Pale yellow oil	182 (0.35 mm.)	$C_{17}H_{21}O_2N$					5.16	5.01
Perchlorate	Amine	Alc.–ether	Faint yellow tables	177	$C_{17}H_{22}O_6NCl$	54.89	54.77	5.97	6.15		
Hydriodide	Amine	Alc.–ether	Faint yellow nodules	170	$C_{17}H_{22}O_2NI$	51.11	51.06	5.56	5.78		
Benzylhomoveratryl-	1	......	Faint yellow oil	178 (0.75 mm.)	$C_{17}H_{21}O_2N$					5.16	5.08
Hydrochloride	Amine	Water	Pearly leaves	200	$C_{17}H_{22}O_2NCl$	66.32	65.99	7.22	7.35		
Picrate	Amine	HAc	Canary yellow needles	160	$C_{23}H_{24}O_9N_4$	55.17	54.85	4.84	4.54		
Piperonylhomopiperonyl-[9]	1	Cold ether	Faint yellow crystals	51	$C_{17}H_{17}O_4N$					4.68	4.97
Hydrochloride	Amine	Dil. HCl	Pearly leaves	243	$C_{17}H_{18}O_4NCl$	60.79	60.89	5.43	5.50		
Acid sulfate	Amine	Water	Granular cryst. powder	Indef.	$C_{17}H_{17}O_4N\cdot H_2SO_4$	51.37	51.54	4.83	4.95		
Veratrylhomoveratryl-	1	Aq. alc.	White glittering plates	79	$C_{19}H_{25}O_4N$	68.84	68.68	7.61	7.58		
Hydrobromide	Amine	Water	Chalky aggregates	187	$C_{19}H_{26}O_4NBr$	55.33	55.57	6.36	6.51		
Oxalate	Amine	Aq. alc.	Pearly plates	230	$C_{21}H_{27}O_8N$	59.83	59.43	6.46	6.42		
Di-(β-phenylethyl)-[e]	......	......	......	...	$C_{16}H_{19}N$	...	...	..	..	..	..
Hydrochloride	2	Dil. HCl	White needle-prisms	233[c]	$C_{16}H_{20}NCl$	73.38	73.08	7.71	7.39	5.36	5.71
Hydrobromide	2	Dil. HAc	Stout white prisms	193	$C_{16}H_{20}NBr$	62.78	62.55	6.58	6.86	4.58	4.69

[a] B. p. rises to 220°. [b] Possibly some change. [c] Literature gives 260, 265°. [d] Under the heading "Preparation" 1 signifies that the amine was prepared via the Schiff base, and 2 signifies that the compound was obtained from a phenylethyl chloride and an amine. [e] Previously obtained by various other methods. Beilstein, 4 Auf., Bd. XII, p. 1098; Rupe and Glenz, *Helv. Chim. Acta*, **5**, 940 (1922); Rupe and Hodel, *ibid.*, **6**, 865 (1923); v. Braun, Blessing and Zobel, *Ber.*, **56**, 1988 (1923).

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[9] *Cf.* Malan and Robinson, *J. Chem. Soc.*, 2653 (1927).

TABLE III

PHENOLIC AMINES

Phenolic amine salt	Parent amine and preparation	Cryst. solvent	Appearance	M. p., °C.	Formula	Analyses Carbon, % Calcd.	Analyses Carbon, % Found	Analyses Hydrogen, % Calcd.	Analyses Hydrogen, % Found
Benzyl-3,4-dihydroxy-β-phenylethylamine hydrochloride	Benzylhomoveratryl-, by AgCl on hydriodide	Dil. HCl, alc.–ether	Chalky, cryst. powder	87, solid, 120, remelts 180	$C_{15}H_{18}O_2NCl$	64.37	64.49	6.49	6.58
Picrate	Alc. picric acid and hydrochloride	Dil. HAc	Red-brown irreg. prisms	131	$C_{15}H_{17}O_2N\cdot 2C_6H_3O_7N_3$	46.28	46.26	3.36	3.87
Methylenedioxybenzyl-3,4-dihydroxy-β-phenylethylamine hydriodide[a]	Piperonylhomoveratryl-, demethylation	Dil. acetic	Buff, tiny nodules	237	$C_{16}H_{18}O_4NI$	46.26	46.34	4.37	4.52
Hydrochloride	By AgCl on hydriodide	Dil. HCl	Buff, cryst. powder	219	$C_{16}H_{18}O_4NCl$	59.33	59.41	5.61	5.77
4-Hydroxybenzyl-4′-hydroxy-β-phenylethylamine hydriodide	Anisylhomoanisyl-, demethylation	Dil. HI	Tiny prisms	192	$C_{15}H_{18}O_2NI$	48.51	48.43	4.89	5.16
Hydrochloride	By AgCl on hydriodide	Dil. HCl	Stout rect. prisms	234	$C_{15}H_{18}O_2NCl$	64.38	64.50	6.49	6.96
Base	Aq. ammonia on salts	Dil. alc.	White prisms	118 frothing	$C_{15}H_{17}O_2N$	N, 5.76	5.77		
4-Hydroxybenzyl-3′,4′-dihydroxy-β-phenylethylamine hy'chloride	Anisylhomoveratryl-, by AgCl on hydriodide	Dil. HCl	Tiny nodules	200–205	$C_{15}H_{18}O_3NCl$	60.89	61.06	6.17	6.33
Picrate	Aq. picric acid and hydrochloride	Dil. HAc	Red-brown nodules	97, solidifies, remelts *ca.* 140	$C_{15}H_{17}O_3N\cdot 2C_6H_3O_7N_3$	45.18	45.08	3.23	3.28

TABLE III (*Concluded*)

Phenolic amine salt	Parent amine and preparation	Cryst. solvent	Appearance	M. p., °C.	Formula	Analyses: Carbon, % Calcd.	Analyses: Carbon, % Found	Analyses: Hydrogen, % Calcd.	Analyses: Hydrogen, % Found
3,4-Dihydroxybenzyl-4′-hydroxy-β-phenylethylamine hydriodide	Veratrylhomoanisyl-, demethylation	Dil. HI	Faint yellow prisms	*ca.* 163 after softening	$C_{15}H_{18}O_3NI$	46.50	46.22	4.69	5.04
Hydrochloride	By AgCl on hydriodide	Dil. HCl	Tiny nodules	180	$C_{15}H_{18}O_3NCl$	60.89	61.06	6.14	6.33
3,4-Dihydroxybenzyl-3′,4′-dihydroxy-β-phenylethylamine hydrochloride	Veratrylhomoveratryl-, by AgCl on hydriodide	Dil. HCl	Flesh-colored tiny prisms	182	$C_{15}H_{18}O_4NCl \cdot H_2O$	H_2O, 5.46	5.44	Cl, 10.76	10.87
Anhydrous	Dried at 110°		White cryst. powder		$C_{15}H_{18}O_4NCl$	57.78	57.57 N, 4.50	5.78 4.80	5.80
Picrate	Aq. picric acid and hydrochloride	Water	Red-gold plates	173	$C_{15}H_{17}O_4N \cdot 2C_6H_3O_7N_3$	44.19	44.19	3.16	3.19
3,4,3′,4′-Tetrahydroxy-di-(β-phenylethyl)-amine hydriodide	Homoveratrylhomoveratryl-, demethylation	Alc.–ether	Powdery prisms	187	$C_{16}H_{20}O_4NI$	46.02	45.95	4.83	5.07
Hydrochloride	By AgCl on hydriodide	Alc.–ether	Chalky crusts	230	$C_{16}H_{20}O_4NCl \cdot 2.5H_2O$	51.80	51.66	6.79	6.68

[a] This demethylation was carried out by adding 3.3 moles of hydriodic acid (as 52% solution) to the amine, and keeping the mass just fused for five minutes. On adding alcohol the product crystallized.

In general, the solubility of all the salts is of the same order. They are readily soluble in warm water, warm alcohol and warm acetic acid, but are much less soluble in a dilute solution of the acid from which they were formed. A number of the salts have distinct colors when freshly recrystallized (usually a pink tint) due to water of crystallization. The color disappears on drying the salt at 110°.

Veratrylphenylethylamine and homoveratrylphenylethylamine failed to demethylate normally with hydriodic acid. The products formed are being examined.

The melting points above cited are corrected. Boiling points were taken on Anschütz thermometers. The author is indebted to Mr. Walter S. Ide for the majority of the micro analyses in this paper.

Summary

A series of 3,4-dihydroxybenzyl-β-phenylethylamines and 3,4-dihydroxy-di-(β-phenylethyl)-amines is described, together with the intermediate Schiff bases and secondary amines.

TUCKAHOE, NEW YORK

[CONTRIBUTION NO. 70 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

CATALYSIS IN ORGANIC CHEMISTRY. IV. DECOMPOSITIONS OF ESTERS AND ACIDS BY ANHYDROUS ZINC CHLORIDE

BY H. W. UNDERWOOD, JR., AND O. L. BARIL

RECEIVED DECEMBER 29, 1930 PUBLISHED JUNE 8, 1931

The types of decomposition of esters by anhydrous zinc chloride described in a previous paper[1] may be represented by the equations

$$RCOOC_nH_{2n+1} = RCOOH + C_nH_{2n} \qquad (I)$$
$$RCOOC_nH_{2n+1} = RH + CO_2 + C_nH_{2n} \qquad (II)$$
$$RCOOC_nH_{2n+1} = RC_nH_{2n+1} + CO_2 \qquad (III)$$

The transformation of ethyl benzoate into benzoic acid, benzene and ethylene and the conversion of methyl salicylate into o-cresol and carbon dioxide are typical decompositions. It has been noted that diethyl oxalate and succinate react with anhydrous zinc chloride, yielding ethyl chloride and zinc salts. The present paper gives an account of the behavior of twelve esters and seven acids.

Discussion of Experiments

Pure freshly distilled or crystallized esters or acids and 0.5 mole of anhydrous zinc chloride per mole of ester or acid were used. Unless otherwise stated, the decomposition products were isolated by the proced-

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[1] Underwood and Baril, THIS JOURNAL, 52,395 (1930).

ures described in a previous paper.[1] The results of our experiments with esters are given in Table I.

TABLE I

RESULTS WITH ESTERS

Carbon dioxide was evolved in all the decompositions except that of benzyl acetate. In the calculation of yields of products allowance was made for the ester recovered. The volatile unsaturated hydrocarbons were collected as dibromides. No evidence of decomposition was found in experiments with diethyl carbonate and ethyl *m*-nitrobenzoate.

				Products					
No.	Ester	Moles	Time of heating, hours	Hydrocarbon	%	Unchanged ester, %	Acids and other products	%	Type of decomp.
1	Ethyl chlorocarbonate	0.4	[a]	Ethylene	17.7	25.3	Ethyl chloride	25.7	II, III
							Hydrogen chloride		
2	*n*-Propyl chlorocarbonate	.2	[a]	Propylene	5.5		*n*-Propyl chloride	23.0	II, III
							Hydrogen chloride		
3	Diethyl carbonate	2	3			95.0			
4	Di-*n*-butyl carbonate	,125	2	Butene (1)	19.3	4.6	*n*-Butyl alcohol[b,c]	94.8	II
5	Isopropyl benzoate	25	2	Propylene	15.2		Benzoic acid[b]	68.8	I, II
				Benzene[b,d]	22.8		Isopropyl chloride[b,d]	22.0	
6	Di-*n*-butyl phthalate	.4	2	Butene (1)	18.0	5.4	Phthalic acid[b,e]	20.6	I, II
							Phthalic anhydride[b,e]	9.0	
							Benzoic acid[h]	5.5	
							Sec.-butyl alcohol[b,e]	44.1	
							n-Butyl chloride[e]	7.7	
7	Isoamyl salicylate[f]	.125	2	Isopropylethylene	7.2		Phenol[b]	72.9	II
				Dimer of isopropylethylene	3.6		High-boiling residue, 5 g.		
8	Methyl anthranilate	.1	1				*o*-Toluidine[b,g]	75.0	III
9	Ethyl anthranilate	.05	1.5				*o*-Ethylaniline[h]	66.0	III
10	Diethyl ester of methylmalonic acid[i]	.1	1	Ethylene	6.5	23.0	Ethyl propionate[b,i]	63.6	II
11	Benzyl acetate[7]	.2	2				Acetic acid[b,j]	96.0	I
12	Ethyl *m*-nitrobenzoate[k]	.125	3			91.0			

[a] The mixture of the ester and anhydrous zinc chloride evolved gases spontaneously until none of the liquid was left in the flask; a 50% aqueous solution of pyridine was used to absorb the hydrogen chloride. The decomposition of ethyl chlorocarbonate has been noted previously by Butlerow [Bull. *soc. chim.*, 586 (1863)] and Ulsch [Ann., **226**, 281 (1884)]. [b] The tests described by Mulliken ["Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, 1916, 1922, Vols. I, II and IV] were used for the identification of this compound. [c] The liquid secured by distillation of the reaction mixture was fractionated three times. [d] Evidently zinc chloride converts some of the benzoic acid formed by the decomposition of the ester into benzene and carbon dioxide. The presence of isopropyl chloride in the reaction products indicates that zinc chloride reacted with some of the isopropyl benzoate. [e] The phthalic anhydride sublimed in the neck of the flask and was removed before the reaction mixture was distilled. Phthalic and benzoic acids were separated by means of cold chloroform. Evidently anhydrous zinc chloride splits the ester into phthalic acid and butylene; the water formed in the transformation of some of the phthalic acid into the anhydride converts some of the butylene into *sec.*-butyl alcohol. The presence of n-butyl chloride in the products indicates that zinc chloride reacted with a small amount of di-*n*-butyl phthalate. [f] Apparently isoamyl salicylate does not undergo the previously noted type of decomposition[1] which converts methyl and ethyl salicylates into o-cresol and *o*-ethylphenol, respectively. [g] The reaction mixture was cooled and extracted with

two 100-cc. portions of ether; the solution thus formed was shaken with three 80-cc. portions of water to remove zinc chloride, dried overnight with 5 g. of anhydrous sodium sulfate and fractionated. [h] o-Toluidine and o-ethylaniline were identified by the preparation of acetyl derivatives. [i] It is interesting to note that the ethyl ester of an alkyl substituted acetic acid can be prepared in one step from the diethyl ester of an alkyl substituted malonic acid. [j] The residue in the reaction flask was dark colored and tarry; possibly this was formed from the fragments of the benzyl groups by the zinc chloride. [k] The reaction mixture was cooled and extracted with two 75-cc. portions of ether. The ether solution was shaken with six 30-cc. portions of water to remove zinc chloride and dried with 5 g. of anhydrous sodium sulfate. The solvent was subsequently removed by distillation on a water-bath. Evidently the presence of the nitro group in this ester makes it more stable than ethyl benzoate.

Formic, Acetic, Propionic and *n*-**Butyric** Acids.—No evidence of decomposition was found in experiments with these compounds.

Benzoic, Salicylic **and Cinnamic** Acids.—From one-fourth mole of benzoic acid which had been refluxed with anhydrous zinc chloride for half an hour we obtained five-hundredths mole (20%) of benzene[b] and carbon dioxide. A mixture containing one-fourth mole of salicylic acid was refluxed for one and one-half hours and distilled. Thirteen-hundredths mole (52%) of phenol[b] and carbon dioxide were obtained. One-fourth mole of cinnamic acid was refluxed with anhydrous zinc chloride for an hour. The products were five-hundredths mole (20%) of styrene, six-hundredths mole (48%) of distyrene, carbon dioxide and 6 g. of a dark brown material which had the properties of metastyrene. The styrene and distyrene were identified by the procedures cited in a previous paper.'

Anhydrous zinc chloride acts partly as a catalyst and partly as a reagent in some of the decompositions described in this paper.

The authors wish to express their thanks for a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences which partly defrayed the cost of this work.

Summary

This paper describes the decompositions of a series of esters and acids by anhydrous zinc chloride; the transformations observed involve the elimination of an aliphatic unsaturated hydrocarbon or carbon dioxide or both. Alkyl chlorides, apparently formed by the reaction of zinc chloride with the ester, are found in the products obtained from two of the compounds studied. Several aliphatic acids remain unchanged when heated with anhydrous zinc chloride.

CAMBRIDGE, MASSACHUSETTS

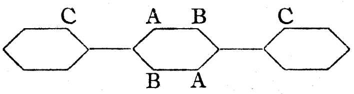
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OR ILLINOIS]

STEREOCHEMISTRY OF DIPHENYLBENZENES. THE CIS AND TRANS FORMS OF 2,5-DI-(3-BROMO-2,4,6-TRIMETHYLPHENYL)-1,3,4,6-TETRAHYDROXYBENZENES AND THE CORRESPONDING ACYLATES. XV[1]

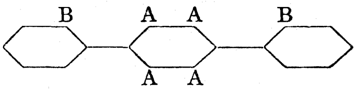
BY P. R. SHILDNECK[2] AND ROGER ADAMS

RECEIVED JANUARY 22, 1931 PUBLISHED JUNE 8, 1931

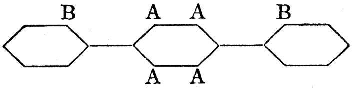
In previous papers the various possibilities for stereoisomerism in the diphenylbenzenes[1a,d] have been discussed and compounds have been synthesized which indicate the validity of the theoretical speculation. The compounds thus far studied have been of the general type (I) and have been found in meso and racemic modifications. Another very interesting type (II) is that in which all four groups on the central ring are the same and each of the two end rings is asymmetrically substituted. Assuming the same restricted rotation between the rings as in the diphenyl series, and therefore that the two end rings are not co-planar with the central ring, it would be impossible to obtain any compound the mirror image of which would not be identical with the object, so that optical isomerism is excluded. On the other hand there are two forms possible, represented by Formulas (III) and (IV). These correspond directly to *cis–trans* isomers of the usual type, and neither is resolvable. If each of the two end rings in such molecules were symmetrically substituted, however, the two isomers indicated would become identical.



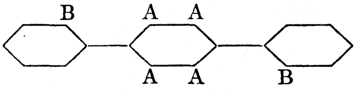
I



II



III



IV

In this communication are described the synthesis and properties of cis and *trans* modifications of compounds falling in this group. The 2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,5-dibromoquinones (V) and (VI) described in the last publication in this series are readily converted by means of dilute sodium hydroxide solution into the corresponding hydroxy-

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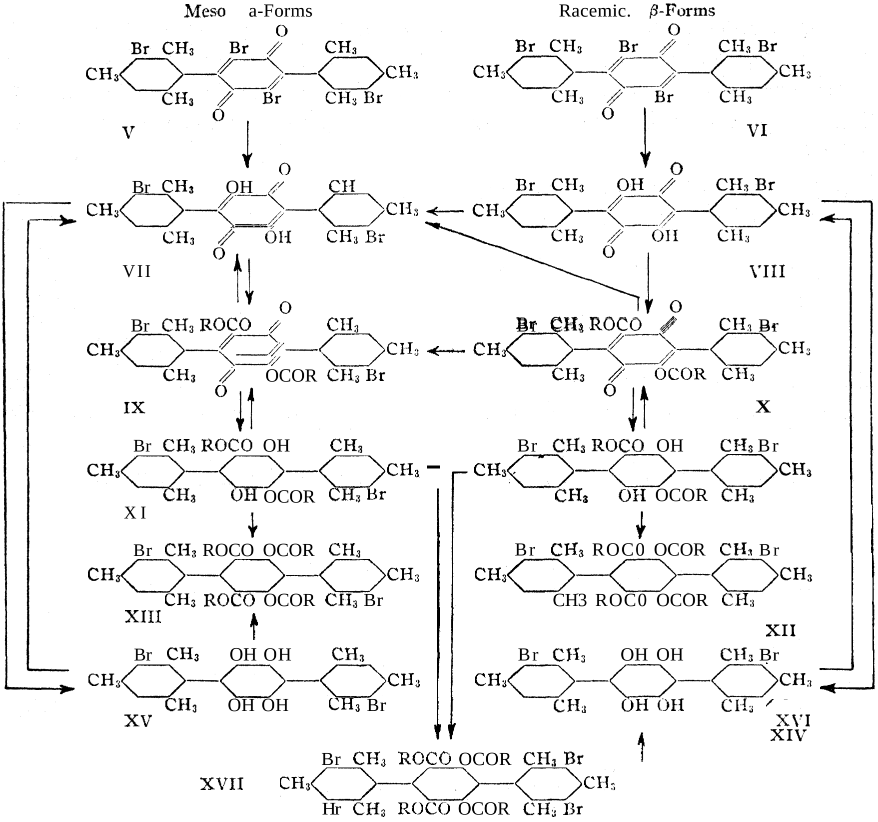
[1] For the last papers in this series see: (a) Browning and Adams, THIS JOURNAL, 52, 4098 (1930); (b) Steele and Adams, *ibid.*, 52, 4528 (1930); (c) Stoughton and Adams, *ibid.*, 52, 5263 (1930); (d) Shildneck and Adams, *ibid.*, 53, 343 (1931); (e) Bock and Adams, *ibid.*, 53, 374 (1931).

[2] This communication is a portion of a thesis submitted by P. R. Shildneck in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

quinones, (VII) and (VIII). These, in turn, may be acylated to the diacyloxyquinones (IX) and (X) or reduced to the tetrahydroxybenzenes (XV) and (XVI). Moreover, the diacyloxyquinones may be hydrolyzed to the corresponding hydroxyquinones or reduced to the diacyloxyhydroquinones (XI) and (XII), which may be hydrolyzed to the corresponding tetrahydroxy compounds or acylated to the tetraacyloxy derivatives (XIII and (XIV).



Each of the original dibromoquinones gives its own characteristic derivatives in the series of reactions just described. The tetrahydroxy compounds and the tetraacyloxy compounds, therefore, represent the cis and *trans* modifications (III) and (IV); the hydroxyquinones, the acyloxyquinones and the acyloxyhydroquinones represent stereoisomers corresponding to type (I).

To show that such isomerism will disappear upon making the two ends symmetrical, the two tetraacetoxy compounds (XIII) and (XIV), were brominated with liquid bromine and there was thus obtained a single 2,5-di-(3,5-dibromo-2,4,6-trimethylphenyl)-1,3,4,6-tetraacetoxybenzene (XVTI).

The derivatives from the less soluble dibromoquinone have been denoted as the α- and from the more soluble as the β-forms. Throughout the series with one exception a decided difference in solubility in the two forms is to be found.

Most of the compounds melt very high, generally in between 250 and 400°. The difference in the melting points of the *a*- and the β-forms of any of the substances varies usually from 10–25°. In the case of the diacetoxyquinones, however, the melting points are essentially identical and it was necessary to convert each of the compounds to the corresponding tetraacetoxy analog in order to show definitely that one was different from the other. The stereoisomeric dibutyroxyquinones, however, have a difference of 20" in the melting points. The use of mixed melting points in this work was more or less excluded since it was shown that in many instances it was impossible to get a lowering of the melting point from the mixture of a pair of isomers. In the case of the tetrabutyroxy compounds, however, which were comparatively low melting, five parts of the higher melting and 95 parts of the lower melting melted about 5° below the lower melting form. The identification of any individual compound was always made by conversion to the corresponding tetraacetoxy derivative, which was markedly different in melting point and solubility from its isomer. Owing to the high melting point of some of these compounds the Bloc Maquenne was employed for melting points above 350°.

In the examples of *cis–trans* isomerism known in other fields of organic chemistry the *trans* form is usually the higher melting of the two. **As** a consequence, the higher melting tetrahydroxy and tetraacyloxy compounds were assumed to be the *trans* modifications and the stereoisomeric forms the *cis* modifications. All of the a derivatives would, therefore, be *trans* modifications and all of the β derivatives *cis* modifications. Since, from the standpoint of optical isomerism, the *trans* modifications are meso forms, all of the compounds of the *a* series should be non-resolvable. The *cis* modifications or β forms on the other hand would be racemic derivatives and these should be capable of resolution. The decision as to whether the assumptions just made are correct or not will depend upon the results of resolution studies.

In most cases of *cis–trans* isomerism where one form is less stable than the other under action of heat or catalysts of the ordinary type, the *cis* is usually the unstable modification and is convertible into the *trans* form. It might be anticipated, therefore, that in these compounds certain of the *cis* derivatives might be converted into the *trans* modifications or from the standpoint of optical isomerism the racemic forms might be convertible into the meso forms, providing conditions could be found which would allow free rotation between the rings.

An attempt was made to convert each of the β derivatives into the corresponding α derivatives.[*] This was done by heating the β form, usually in mesitylene, sometimes in glacial acetic acid or in sodium hydroxide solution, for many hours at the boiling temperature. By this procedure it was found that the β-diacetoxyhydroquinone (XII), the β-tetrahydroxy (XVI), the β-tetraacetoxy (XIV) and the β-dibromoquinone (VI) "derivatives were apparently, perfectly stable under the conditions used and no conversion took place. On the other hand, the β-dihydroxyquinone (VIII), the β-diacetoxyquinone (X) and the β-dibutyroxyquinone (X), when treated in the manner described were readily converted into the corresponding α modifications. By holding the β-dibutyroxy compound 20° above its melting point for three hours, a product resulted which after two crystallizations gave pure a form. Moreover, upon hydrolyzing the β-diacetoxyquinone (X) in glacial acetic acid and hydrochloric acid, the a-dihydroxyquinone (VII) was obtained.

It is interesting to consider these experiments from the standpoint of x-ray data which have been discussed from time to time in the previous communications. In the case of the β-diphenylbenzene compounds which were not convertible to a forms and which, therefore, resisted tendency to any free rotation between the rings, there are, with the exception of the β-dibromoquinone, between each of the two end rings and the center ring either two methyl groups and two hydroxyl groups or two methyl groups and one hydroxyl and one acylated hydroxyl group. On the assumption that the acylated hydroxyl group does not have an appreciably greater interference value than the unacylated group, the tetrahydroxy (XVI) compound may be considered to be characteristic of the three stable β compounds. The x-ray data show that there is appreciable interference on either side of each pair of rings in the molecule as follows: $C—CH_3$, 1.73 Å. + C—OH, 1.54 Å. = 3.19 Å. Subtracting from this value 2.90 Å. (the distance between the 2,2′-carbon atoms in the two rings) there is obtained a difference of 0.37 Å. on each side. This is, apparently, sufficient to prevent any rotation under the conditions used. On the other hand, in the case of the corresponding quinones the following interferences would be in force. On one side of each pair of rings in the molecule where the methyl and the hydroxyl meet, there would be an interference of 0.37 Å. On the other side, however, there would be $C—CH_3$, 1.73 Å. + C=O, 1.15 Å. = 2.88 Å., which is –0.02 Å. when the distance between the 2,2′-carbon atoms is subtracted from the total value. It follows, therefore, that if the rings are held in a more or less fixed relative position to one another, free rotation could not take place because one or the other of the methyl groups would interfere with the hydroxyl group and convertibility of the β-form to the a-form would be prevented. On the other hand, if the molecule is heated so that the rings may be bent toward each other in one or another direction, it is possible to reach a position where there is only

0.175 Å. interference simultaneously on each of the two sides [(0.37 Å. − 0.02 Å.)/2 = 0.175 Å.]. It may, therefore, be either that an interference of 0.175 Å. can be overcome by a high temperature so as to allow free rotation, or that free rotation is possible on account of the quinone ring, about which comparatively little is known as far as its exact structure is concerned. It may be expected that a quinone nucleus is more mobile within itself than a benzene ring and, therefore, might readily be distorted somewhat by a decided temperature change. On the other hand, the stability of the β-dibromoquinone to rearrangement indicates that the size of the groups even in the quinones is an important factor. The interference in this compound ($C-CH_3$, C–Br and $C-CH_3$, C=O) when the rings are in a relative position most advantageous for free rotation is 0.39 Å., [(0.80 Å. − 0.02 Å.)/2 = 0.30 Å.], a value which has been shown in previous diphenyl compounds to be sufficient to prevent free rotation under ordinary methods of treatment. The 0.80 Å. represents the interference between the methyl and bromine groups ($C-CH_3$, 1.73 Å. + C–Br, 1.97 Å. = 3.70 Å. —2.90 Å. = 0.80 Å.) and the —0.02 Å. that between the methyl and carbonyl group as indicated above.

Experimental

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dihydroxyquinone (a-Form), **(VII).**—In a 5-liter, two-necked flask equipped with a mechanical stirrer and reflux condenser, were placed 35 g. of α-2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromoquinone, V, m. p. 295–296° (corr.), 2 liters of 95% ethyl alcohol and a solution of 300 g. of sodium hydroxide in 1200 cc. of water. The mixture was stirred and refluxed for eight hours. During this time the dibromoquinone dissolved, forming a deep red solution, and a portion of the dihydroxyquinone precipitated in small flakes as the scarlet sodium salt.

After filtration and drying, the sodium salt amounted to 20 g. The clear red filtrate was diluted with 2 liters of water, and acidified with concentrated hydrochloric acid. Upon heating nearly to boiling a flocculent, orange precipitate coagulated. The product was filtered on a Büchner funnel, washed free of chloride with hot water and sucked to a completely dry powder on the filter paper. The sodium salt obtained from the original reaction mixture was dissolved in hot water and acidified with 6 N hydrochloric acid and the hydroxy compound washed and dried as described. The yield amounted to 25.4 g. (7 g. from the filtrate and 18.4 g. from the filtered sodium salt) of the α-dihydroxyquinone or 90% of the theoretical. The dihydroxyquinone as obtained was essentially pure and was used directly for conversion into derivatives.

The a-dihydroxyquinone is practically insoluble in all the common organic solvents except nitrobenzene, from which it crystallizes in very minute yellow needles. It is sparingly soluble in ether, glacial acetic acid and mesitylene. One hundred cc. of boiling mesitylene dissolves about 0.05 g. The needles from mesitylene are larger than those obtained from nitrobenzene and are orange in color. Samples recrystallized to purification from either solvent decomposed on the Bloc Maquenne at 397–400° (obs.).

Anal. (Parr Bomb) Calcd. for $C_{24}H_{22}O_4Br_2$: Br, 29.93; C, 53.93; H, 4.16. Found: Br, 29.85; C, 53.42; H, 4.18.

Sodium Salt of the **α-Dihydroxyquinone, (VII).**—The sodium salt obtained from the hydrolysis of the a-dibromoquinone was purified by recrystallization from an alkaline water–alcohol mixture (2 g. of salt in 600 cc. of 50% alcohol and 5 g. of sodium hydroxide). The red flakes were washed with acetone and air dried. For analysis 0.5 g. was finely pulverized and dried under reduced pressure at 110°.

Anal. (Parr Bomb). Calcd. for $C_{24}H_{20}O_4Br_2Na_2$; Br, 27.65. Found: Br, 27.28.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-diacetoxyquinone (or-Form), **(IX).**—A mixture of 4 g. of the α-dihydroxyquinone VII was placed in a 300-cc. Erlenmeyer flask with 80 cc of acetic anhydride and brought to a boil under a reflux condenser. Through the condenser was added 80 cc. of pyridine, the solution again brought to a boil and held for one minute. The orange solution was then poured rapidly with stirring into 1 liter of 4 N hydrochloric acid. The yellow, crystalline product was filtered from the hot mixture and washed with 4 N hydrochloric acid, followed by cold water. The yield was quantitative, the weight of air-dried product amounting to 4.7 g. Two recrystallizations from 200 cc and 150 cc., respectively, of n-butyl alcohol yielded a product consisting of yellow plates melting constantly at 272–273° (corr). It is very soluble in mesitylene, somewhat less soluble in toluene, moderately soluble in glacial acetic acid and acetone and sparingly soluble in 95% ethyl alcohol.

Anal. (Parr Bomb). Calcd. for $C_{28}H_{26}O_6Br_2$: Br, 25.86,. Found: Br, 25.71.

Hydrolysis of **α-Diacetoxy** Compound, **(IX).**—The diacetoxy compound is hydrolyzed rapidly upon heating for twenty to thirty minutes in a mixture consisting of 80% of glacial acetic acid and 20% of 6 N hydrochloric acid (50 cc. of glacial acetic acid, 10 cc. of 6 N hydrochloric acid, 0.25 g. of diacetoxy quinone) to the insoluble **α-dihydroxy**-quinone (VII) melting at 397–400° on the Bloc Maquenne. **A** portion of the dihydroxyquinone so obtained (0 21 g.) was reacetylated to an acetyl derivative identical with the above in melting point, solubility and crystalline appearance.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-1,3,4,6-tetrahydroxybenzene (a-Form), **(XV).**—A mixture of 5 g. of the a-dihydroxyquinone (VII), 500 cc. of 95% ethyl alcohol and 10 g. of stannous chloride was refluxed for fifteen minutes. A greenish-yellow precipitate formed Addition of 10 cc. of 6 N hydrochloric acid dissolved the precipitate About 40 cc. more of the acid was then added. This was followed by ten minutes of refluxing, after which a clear, colorless solution had formed. Hot water was gradually added to the boiling solution until a faint turbidity appeared. The condenser was removed and alcohol removed by distillation until a considerable crop of white crystals appeared in the boiling mixture The mixture was cooled and filtered. The minute, crystalline flakes were washed several times with 6 N hydrochloric acid and finally with cold water. The white product so obtained was air dried in the dark, since light discolored it; yield, 4.8 g. Two recrystallizations from dilute alcohol containing hydrochloric acid and a trace of stannous chloride yielded small, white, shining flakes melting with decomposition at 360–362° (obs.) on the Bloc Maquenne.

It is readily soluble in alcohol, acetone and pyridine. The pyridine solution rapidly turns dark red in air

Anal (Parr Bomb). Calcd for $C_{24}H_{24}O_4Br_2$: Br, 29.82. Found: Br, 30.14.

Oxidation of the **α-Form** of the **Tetrahydroxy** Compound, **(XV).**—Addition of *p*-benzoquinone to an alcoholic solution of the a-tetrahydroxy compound caused an immediate precipitate of the orange, insoluble or-dihydroxyquinone melting with decomposition at 397–400° on the Bloc Maquenne.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-1,3,4,6-tetraacetoxybenzene (a-Form), **(XIII).**—A mixture of 4 g. of the a-tetrahydroxy compound (XV) and 50 cc. of acetic anhydride was placed in a 300-cc Erlenmeyer flask and brought to a boil under a reflux condenser. Then 50 cc of pyridine was added through the condenser and the solution was refluxed for one minute. The solution was then added with stirring to 750 cc. of 4 N hydrochloric acid. The white, crystalline product was filtered from the hot solution, washed twice with 4 N hydrochloric acid and then free of the acid with water. A quantitative yield, 5.2 g., of the air-dried tetraacetate was obtained. The crude product was recrystallized first from a mixture of 50 cc. of acetic anhydride and 50 cc. of pyridine and then from 50 cc. of acetic anhydride. Finally one crystallization from n-butyl alcohol gave a pure product consisting of long. white needles, melting constantly at 294–295° (corr.)

Anal. (Parr Bomb). Calcd. for $C_{32}H_{32}O_8Br_2$: Br, 22.76. Found: Br, 22.93.

2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-1,3,4,6-tetraacetoxybenzene, (XVII). In a 20-cm. test-tube was placed 1 5 g of the crude a-tetraacetoxy compound (XIII) and 3 cc. of dry, liquid bromine was added with stirring in 1-cc. portion. The contents were thoroughly stirred and allowed to stand for thirty minutes at room temperature. Hydrogen bromide was freely evolved. The excess bromine was removed by suction and the light yellow solid material remaining was removed and triturated with a saturated solution of sodium bisulfite It was then filtered, washed with hot water and air dried. The yield of crude product amounted to 1.8 g. It was recrystallized twice from a mixture of 45 cc. of acetic anhydride and 5 cc. of pyridine and a third time from 70 cc. of acetic anhydride alone. There was obtained 1 g. of short white needles melting constantly at 347–348° (corr.).

Anal (Parr Bomb) Calcd. for $C_{32}H_{30}O_8Br_4$: Br, 37.09. Found: Br, 36.76.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-diacetoxyhydroquinone (a-Form), (XI).—A mixture of 3 g. of the α-diacetoxyquinone (IX), 200 cc. of 95% ethyl alcohol and 5 g. of stannous chloride was refluxed for fifteen minutes. Then 25 cc. of 6 N hydrochloric acid was added to discharge the pale yellow color and hot water immediately and gradually added to precipitate the product as white, short, slender needles. The mixture was quickly cooled under the tap and filtered. The mat of needles was washed with 4 N hydrochloric acid and then with hot water. The yield was 2.9 g. Two recrystallizations from 75 cc. and 60 cc. of carbon tetrachloride, respectively, gave a white product consisting of short, slender needles, melting constantly at 251–252° (corr.). The compound is readily soluble in acetone, ethyl alcohol and pyridine. The pyridine solution remains colorless in air, in contrast to the pyridine solution of the tetrahydroxy derivative, which quickly turns deep red when exposed to the air.

Anal. (Parr Bomb). Calcd. for $C_{28}H_{28}O_6Br_2$: Br, 25 78. Found: Br, 25.61

Hydrolysis of **a-Diacetoxyhydroquinone,** (XI).—A mixture of 0.1 g. of the α-diacetoxyhydroquinone (XI), 30 cc. of glacial acetic acid and 5 cc. of 6 N hydrochloric acid was refluxed for fifteen minutes. The product was precipitated by adding water. The crude product thus obtained showed no signs of melting or charring at 325" (obc.) in a paraffin-bath and yielded an acetyl derivative with acetic anhydride and pyridine which, when recrystallized from n-butyl alcohol, was identical with the a-tetraacetate (XIII) in melting point, solubility and crystalline appearance.

Acetylation of a-Diacetoxyhydroquinone, (XI).—The a-diacetoxyhydroquinone (XI) yielded an acetyl derivative with acetic anhydride and pyridine identical in melting point, solubility and crystalline appearance with the a-tetraacetoxy compound (XIII) obtained by acetylation of the a-tetrahydroxy compound (XV).

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dihydroxyquinone (β-Form), (VIII).—In a 5-liter, round-bottomed flask equipped with a mechanical stirrer were placed 30 g. of β-2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromoquinone (VI), m. p. 284–285" (corr.), 2 liters of 95% ethyl alcohol and a cold solution of 300 g. of sodium hydroxide in 1500 cc. of water. The mixture was stirred at room temperature for forty-eight hours. As with the a-bromoquinone, the β-bromoquinone slowly dissolved, forming a deep red solution from which part of the β-dihydroxyquinone crystallized in flakes as the deep red sodium salt. Only 7 g. of the sodium salt was thus obtained. The filtrate from this was diluted with 4 liters of water, allowed to stand for twenty-four hours, decanted and filtered from a small amount of insoluble material and acidified with concentrated hydrochloric acid. The orange, flocculent precipitate was sucked dry on a Biichner funnel. The sodium salt was converted to the dihydroxy compound as described under the alpha compound. The yield of free β-dihydroxyquinone amounted to 22 g. (91%). This material was used for preparing derivatives. It was purified by crystallization from benzene or toluene and formed minute yellow needles melting with decomposition at 387–390" on the Bloc Maquenne.

Anal. (Parr Bomb). Calcd. for $C_{24}H_{22}O_4Br_2$: Br, 29.93; C, 53.93; H, 4.16. Found: Br, 30.03; C, 53.48; H, 4.20.

The difference in solubility in acetone of the a- and 8-forms of the dihydroxyquinone is quite marked: 0.05 g. of the 8-form dissolved in 10 cc. of hot acetone to a clear, orange-colored solution; 0.05 g. of the a-form would not form a clear solution in 150 cc. of boiling acetone. Likewise the β-form was found to be more soluble in benzene and toluene, in both of which solvents the a-form is practically insoluble. The 8-form is also slightly soluble in glacial acetic acid and mesitylene but when attempts were made to crystallize from those solvents a partial conversion of the β-form into the a-form was found to take place.

Sodium Salt of the **β-Dihydroxyquinone, (VIII).**—The sodium salt of the β-dihydroxyquinone (VIII) was recrystallized from 3% sodium hydroxide solution (4 g. of salt in 150 cc. of alkaline solution). For analysis 0.5 g. was finely pulverized and dried at 110° under reduced pressure.

Anal. (Parr Bomb). Calcd. for $C_{24}H_{20}O_4Br_2Na_2$: Br, 27.65. Found: Br, 27.32.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-diacetoxyquinone (8-Form), **(X).—The** β-dihydroxyquinone (VIII) was acetylated with acetic anhydride and pyridine under the same conditions as the a-form. Purification from 70% acetone gave light yellow prisms melting constantly at 272–273° (corr.).

Anal..(Parr Bomb). Calcd. for $C_{28}H_{26}O_6Br_2$: Br, 25.86. Found: Br, 25.70.

It is to be noticed that the β-diacetoxyquinone melts at the same point as the α-form. However, there can be no doubt about the existence of two forms, since the solubility of the β-form in acetone is four times as great as the a-form and in 95% ethyl alcohol three to four times greater. Moreover, conversion into various derivatives showed the β-form to be different.

Hydrolysis of **β-Diacetoxyquinone, (X).**—Upon refluxing 0.25 g. of the β-diacetoxyquinone X for one hour with a mixture of 50 cc. of glacial acetic acid and 10 cc. of 3 N hydrochloric acid, the a-dihydroxyquinone (VII) separated as an orange, crystalline precipitate in the boiling solution and separated completely on cooling (0.22 g.). The product was insoluble in acetone. To identify further the a-dihydroxyquinone prepared in this way, it was reduced and acetylated in the manner used previously for this compound and yielded, after purification from n-butyl alcohol, long white needles (0.22 g.) which melted at 294–295° (corr.) and proved to be identical with the a-tetraacetoxy compound (XIII).

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-1,3,4,6-tetrahydroxybenzene (β-Form), (XVI).—The β-dihydroxyquinone (VIII) was reduced to the tetrahydroxy derivative in the same manner as the a-form. The β-tetrahydroxy compound crystallized from dilute alcohol in white, shining plates melting constantly at 355–357° (obs.) on the Bloc Maquenne.

Anal. (Parr Bomb). Calcd. for $C_{24}H_{24}O_4Br_2$: Br, 29.82. Found: Br, 29.62.

It is readily soluble in acetone, ethyl alcohol and pyridine. As with the a-form, the pyridine solution of the β-form rapidly turns red in air. The β-form is more soluble in dilute alcohol, dilute acetone and glacial acetic acid than the a-form.

Oxidation of the β-Tetrahydroxy Compound, (XVI).—Addition of *p*-benzoquinone to an alcoholic solution of the β-tetrahydroxy compound (XVI) immediately caused a precipitate of the orange, insoluble β-dihydroxyquinone (VIII). That it was the β-dihydroxyquinone rather than the a-form was determined by the fact that the product had the proper melting point and solubility.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-1,3,4,6-tetraacetoxybenzene (β-Form), (XIV).—The β-tetrahydroxy compound (XVI) was acetylated with pyridine and acetic anhydride, following the procedure employed for the a-form. After two recrystallizations from n-butyl alcohol, a product consisting of long, white needles was obtained, melting constantly at 269–270° (corr.) without decomposition.

Anal. (Parr Bomb). Calcd. for $C_{32}H_{32}O_8Br_2$: Br, 22.76. Found: Br, 22.61.

Of all the derivatives of the two series the tetraacetates differ most widely with respect to melting point and solubility; 0.05 g. of the β-form dissolves in 2 cc. of boiling n-butyl alcohol, whereas 0.05 g. of the a-form requires 10–12 cc. of boiling n-butyl alcohol. There exists a similar difference in solubility in glacial acetic acid and acetic anhydride.

Bromination of the β-Tetraacetoxy Compound, (XIV).—The β-tetraacetoxy compound (XIV) was brominated in the same way as the a-form. The product was identical with that obtained from the a-form with respect to melting point, solubility, crystalline appearance and bromine content.

Anal. (Parr Bomb). Calcd. for $C_{32}H_{30}O_8Br_4$: Br, 37.09. Found: Br. 36.86.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-diacetoxyhydroquinone (@–Form), **(XII).**—The β-diacetoxyquinone (X) was reduced and the product purified according to the procedure used for the a-form. After two recrystallizations from carbon tetrachloride, a product consisting of short, fine, white needles was obtained melting constantly at 240–241° (corr.).

Anal. (Parr Bomb). Calcd. for $C_{28}H_{28}O_6Br_2$: Br, 25.78. Found: Br, 25.65.

The two forms have approximately the same solubility in carbon tetrachloride, ethyl alcohol and glacial acetic acid, but the β-form is more soluble in acetone. The pyridine solution of the diacetoxyhydroquinone remains colorless in air in contrast to the tetrahydroxy compound which turns red.

Hydrolysis of the β-Diacetoxyhydroquinone, (XII).—A mixture of 0.1 g. of the β-diacetoxyhydroquinone (XII) with 30 cc. of glacial acetic acid and 5 cc. of 6 N hydrochloric acid was refluxed for thiiy minutes. The product was precipitated with water. In the crude state it showed no sign of melting at 325° in an oil-bath. It was acetylated with pyridine and acetic anhydride and the crude product recrystallized from n-butyl alcohol. It melted constantly at 269–270° (corr.), the pure β-tetraacetoxy compound.

Acetylation of β-Diacetoxyhydroquinone, (XII).—Acetylation of 2 g. of the β-diacetoxyhydroquinone (XII) with pyridine and acetic anhydride according to the procedure employed for acetylation of the a-tetrahydroxy compound (XV) yielded an acetyl derivative identical in melting point, solubility and crystalline appearance with the β-tetraacetate.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibutyroxyquinone (a–Form), **(IX).**—A solution of 1.5 g. of the a-dihydroxyquinone (VII) in 20 cc. of pyridine and 10 cc. of n-butyric anhydride was boiled for one minute and immediately thrown into 250 cc. of 6 N hydrochloric acid. The mixture was shaken until all of the butyric anhydride was decomposed and the light yellow product solidified. The crude yield amounted to 2.0 g.

It was recrystallized twice from 95% ethyl alcohol, using 80 cc. the first time and 65 cc. the second. One and one-half grams of yellow plates melting constantly at 167° (corr.) was obtained.

Anal. (Parr Bomb). Calcd. for $C_{32}H_{34}O_6Br_2$: Br, 23.72. Found: Br, 23.92.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibutyroxyquinone (β-Form), (X).—The β-dibutyroxy form was made in exactly the same way as the a-form. It was crystallized twice from 95% ethyl alcohol. From 1.4 g. of β-dihydroxyquinone (VIII) 1.1 g. of large yellow needles of the β-dibutyroxyquinone melting constantly at 147° (corr.) was obtained. The 8-form is more soluble in ethyl alcohol, methyl alcohol and acetone than the α-form.

Anal. (Parr Bomb). Calcd. for $C_{32}H_{34}O_6Br_2$: Br, 23.72. Found: Br, 23.80.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-1,3,4,6-tetrabutyroxybenzene (a-Form), **(XIII).**—A mixture of 1.5 g. of the a-dihydroxyquinone (VII), 150 cc. of 95% ethyl alcohol, and 3.0 g. of stannous chloride was refluxed for fifteen minutes. Fifteen cc. of 6 *N* hydrochloric acid was added and refluxing continued until a colorless solution had formed. The a-tetrahydroxy compound was precipitated by adding hot water. It was filtered and treated with a mixture of 10 cc. of n-butyric anhydride and 20 cc. of pyridine. The 2.0 g. of crude product was isolated in the same way as the dibutyroxyquinones and crystallized three times from methyl alcohol, using 15 cc., 12 cc. and 9 cc., respectively. One gram of white prisms melting constantly at 124° (corr.) was obtained.

Anal. (Parr Bomb). Calcd. for $C_{40}H_{48}O_8Br_2$: Br, 19.58. Found: Br, 19.57.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-1,3,4,6-tetrabutyroxybenzene (β-Form), (XIV).—Two and one-half grams of the β-dihydroxyquinone (VIII) was reduced and converted to the tetrabutyrate following the method used for the a-form. The crude product was colored dark blue, but three crystallizations from methyl alcohol, using 15 cc., 10 cc. and 5 cc. respectively, yielded 1.3 g. of pure white prisms melting constantly at 103° (corr.). The p-form is more soluble in methyl alcohol than the a-form. A mixture of 95 parts of this β-form and 5 parts of the corresponding a-form melted 98–99.5".

Anal. (Parr Bomb). Calcd. for $C_{40}H_{48}O_8Br_2$: Br, 19.58. Found: Br, 19.64.

Conversion of the **β-Dihydroxyquinone** (VIII) to the a–Form in Boiling Mesitylene or in Boiling Glacial Acetic Acid.—A solution of 0.25 g. of the β-dihydroxyquinone (VIII) in 150 cc. of mesitylene was refluxed for ten hours. Then 125 cc. of mesitylene was distilled off. The distilling flask was cooled and the product filtered; 0.24 g. of fine orange needles was recovered. It was reduced with 95% ethyl alcohol, **6** *N* hydrochloric acid and stannous chloride. The white product thus obtained was acetylated with **5** cc. of acetic anhydride and 5 cc. of pyridine. The crude tetraacetate weighed 0.27 g. It was crystallized from 60 cc. of n-butyl alcohol, from which was obtained 0.23 g. of white needles melting constantly at 294–295" (corr.). This product had all the properties of the a-tetraacetate (XIII).

A solution of 0.25 g. of the β-dihydroxyquinone (VIII) in 250 cc. of glacial acetic acid was refluxed for ten hours. Initially all of the material was in solution. At the end of five hours a precipitate of short, fine, yellow needles appeared. By distillation 225 cc. of solvent was removed and the remaining mixture cooled and filtered; 0.24 g. of material was recovered. It was reduced and acetylated as usual The 0.25 g. of crude tetraacetate was crystallized from 60 cc. of n-butyl alcohol. There was obtained 0.21 g. of white needles of the a-tetraacetate melting at 294–295" (corr.) (XIII).

Conversion of the **β-Diacetoxyquinone (X)** to the a–Form in Boiling **Mesitylene.**—A solution of 0.25 g. of the β-diacetoxyquinone (X) in 50 cc. of mesitylene was refluxed for ten hours. Then 40 cc. of mesitylene was removed by distillation; the remainder was steam-distilled out The solid, yellow residue was reduced with ethyl alcohol, hydrochloric acid and stannous chloride The white diacetoxyhydroquinone was precipitated by adding water. The product was acetylated with pyridine and acetic anhydride and the tetraacetatc isolated as usual by pouring into excess 4 *N* hydrochloric acid. The yield of crude product amounted to 0 22 g This, when crystallized from 50 cc. of n-butyl alcohol, gave 0 18 g. of material melting at 292–294° (corr) Another crystallization gave the correct melting point of 294–295° for the or-tetraacetate (XIII)

Conversion of the β-Dibutyroxyquinone (X) to the **α-Form** in Boiling Mesitylene or by Heating.—A solution of 0.2 g. of the β-dibutyroxyquinone (X) in 50 cc. of mesitylene was refluxed for ten hours. By distillation 40 cc of mesitylene was removed and the remainder was steam-distilled out. There was thus obtained 0 17 g. of product which was crystallized from 8 cc. of methyl alcohol; 0.13 g. of yellow plates melting at 165–167° was obtained which was obviously the α-dibutyroxy form (IX)

One-tenth gram of the β-dibutyroxyquinone (X) was placed in a 2-inch test-tube and heated at 175–180° (corr.) for three hours. The tube was carefully broken and the contents crystallized twice from 95% ethyl alcohol There was obtained 0 04 g. of small yellow plates melting at 166–167° (corr.), the or-form (IX).

Attempted Conversion of **β-Forms** to or-Forms.—The β-diacetoxyhydroquinone (XII), the β tetrahydroxy (XVI) compound and the β-tetraacetoxy (XIV) compound could not be converted to the or-forms after ten hours in boiling mesitylene. Neither could the β-dihydroxyquinone in boiling 3 N sodium hydroxide solution be converted to the a-form. The procedures followed were those employed in the above conversions.

The conversion of the p-dibromoquinone (VI) was attempted in two ways. A solution of 0.50 g. of the β-dibromoquinone in 100 cc. of boiling glacial acetic acid was refluxed for ten hours. Upon cooling 0.25 g of orange prisms separated. The remainder in solution was precipitated by adding water to the mother liquor; total material recovered, 0.49 g. This was reduced with pyridine and stannous chloride. The white reduction product was crystallized from a mixture of 10 cc. of acetone and 2 cc. of water containing ten drops of 6 *N* hydrochloric acid and a trace (10 mg.) of stannous chloride. Upon standing, long, slender, white needles formed. The first crop amounted to 0.15 g. and melted at 294–295" (corr.), the pure β-dibromohydroquinone.

A solution of 1.5 g. of the p-dibromoquinone in 150 cc. of mesitylene was refluxed for ten hours. The orange tint of the solution deepened somewhat. The mesitylene was steam distilled out and the orange solid remaining, which could not be crystallized satisfactorily from toluene, was dissolved in 750 cc. of boiling 95% ethyl alcohol to which 0.5 g. of benzoquinone was added. The orange-colored solution was filtered and concentrated to 200 cc., during which time an orange, crystalline precipitate appeared. After cooling, this was filtered and washed with cold methyl alcohol (0.50 *g.).* In the same bath with the pure p-dibromoquinone the orange material isolated above melted with decomposition at 282–283° (corr.); the pure p-form at 284–285° (corr.). The product was reduced with pyridine and stannous chloride. The white hydroquinone was crystallized from a mixture of 10 cc. of acetone and 2 cc. of water containing ten drops of 6 N hydrochloric acid and 5 mg. of stannous chloride. The first crop of long, slender, white needles amounted to 0.13 g. and melted at 294–295° (corr.), the pure β-dibromohydroquinone.

Summary

1. By treatment of the two diastereoisomeric 2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinones (V + VI) with aqueous sodium hydroxide there were obtained two stereoisomeric 2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dihydroxyquinones (VII + VIII).

2. Each of these two latter compounds formed an individual series of derivatives—namely, the diacetoxyquinone, the dibutyroxyquinone, the diacetoxyhydroquinone, the tetrahydroxy compound, the tetraacetoxy and tetrabutyroxy compounds.

3. The two series were designated as *a* and β. The *a* denotation was given to the series of higher melting and less soluble compounds, the β was given to the series of lower melting and more soluble compounds. On the assumption that the higher melting tetrahydroxy and tetraacylated derivatives are the *trans* modifications, it follows that throughout the two series, the *trans* or α forms are meso, the *cis* or β forms. are racemic.

4. The α and β tetrahydroxy, tetraacetoxy and tetrabutyroxy derivatives represent pairs of *cis* and *trans* isomers. No individual in any pair is capable of resolution. On the other hand, the α and β hydroxyquinones, acetoxyquinones, butyroxyquinones and the acylated hydroquinones represent pairs of *cis* and *trans* forms, in each pair of which one is a meso and the other a racemic modification.

5. The β-dihydroxyquinone, the β-diacetoxyquinone and the β-dibutyroxyquinone can be converted to the corresponding α forms by heating in a high boiling solvent. The β-diacetoxyquinone on hydrolysis gives the α-dihydroxyquinone.

6. The a and β tetraacetoxy compounds, on bromination, give the same compound, 2,5-di-(3,5-dibromo-2,4,6-trimethylphenyl)-1,3,4,6-tetraacetoxybenzene.

URBANA, ILLINOIS

[CONTRIBUTION NO. 73 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

DESOXYCODEINE STUDIES. I. THE DESOXYCODEINES[1]

BY LYNDON F. SMALL AND FRANK L. COHEN

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The name desoxycodeine has been used to designate the compound $C_{18}H_{21}O_2N$, containing one less oxygen atom than codeine. It was first described and investigated by Knorr and Waentig,[2,3] who prepared it by refluxing a-chlorocodide (11), bromocodide, β-chlorocodide[4] or pseudo-

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[1] This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

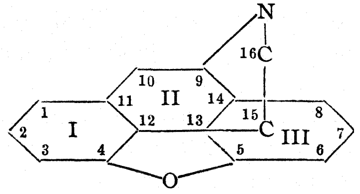
[2] Knorr and Waentig, *Ber.*, 40, 3860 (1907).

[3] A base having the same formula was mentioned by Wright [*Proc.* Roy. *Soc.* (London), 19,371 (1870); J. *Chem. Soc.*, 24,404 (1871)] as being formed when codeine is heated with hydrobromic acid; Wright's desoxycodeine has never been further investigated.

[4] Knorr and Hörlein, *Ber.*, 40,4883 (1907).

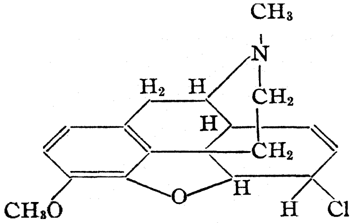
chlorocodide[2,5] with zinc dust in absolute alcohol; the fact that the isomeric chlorocodides all yield the same desoxycodeine in this reduction has been taken as evidence that the fundamental carbon–nitrogen skeleton in all of them is the same.

Desoxycodeine is a phenolic base (Formula III) which must be formed from the halogenocodides by addition of one molecule of hydrogen and loss of hydrogen halide or the equivalent of this process.[6]



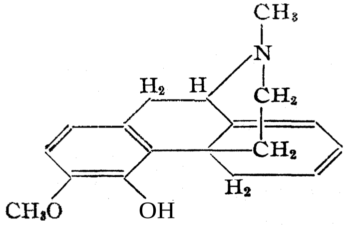
I

Numbering System[7]



II

α-Chlorocodide



III

Desoxycodeine-A[8]

a-Chlorocodide is derived from codeine through replacement of the alcoholic hydroxyl by chlorine, and is distinguished by the activity of this halogen atom. It may be hydrolyzed out by boiling with water[9] or with dilute acetic acid[4,10] to yield the isomers of codeine, or replaced with iodine[11] or the dimethylamino group[12] by suitable treatment with potassium iodide or dimethylamine, respectively. An experiment seemed warranted, therefore, to determine whether a-chlorocodide would react with methylmagnesium halide to yield, at least in part, a homolog of desoxycodeine,

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[5] Knorr and Horlein, *Ber.*, 40, 3341 (1907).

[6] Cf. Freund, *J. prakt. Chem.*, 101, 8 (1921).

[7] The linkage of C-15 to C-13, in accordance with the Gulland and Robinson [*Mem. Proc. Manchester Lit. Phil. Soc.*, 69, 79 (1925)] conception of the morphine structural formula is here adopted for the sake of uniformity with contemporary publications in the field of morphine chemistry.

[8] The position of the double bonds in ring III is arbitrary.

[9] Matthiessen and Wright, *Ann. Suppl.*, 7, 364 (1870); Gohlich, *Arch. Pharm.*, 231, 235 (1893).

[10] Knorr and Horlein, *Ber.*, 39, 4409 (1906); Pschorr and Rollet, *Ann.*, 373, 1 (1910); Schryver and Lees, *J. Chem. Soc.*, 79, 563 (1901).

[11] Knorr and Hartmann, *Ber.*, 45, 1350 (1912).

[12] Von Braun and Kindler, *ibid.*, 49, 2655 (1916).

in which the alcoholic hydroxyl of codeine would be replaced by a methyl group in the sense of the equation

$$C_{18}H_{20}O_2NCl + RMgX \longrightarrow C_{18}H_{20}O_2NR + MgXCl$$

a-Chlorocodide in absolute ethereal solution does, in fact, react vigorously with methylmagnesium iodide, with copious evolution of gas and separation of a powdery white solid. Decomposition of this solid in the usual way yields instead of the expected homodesoxycodeine, the known desoxycodeine in approximately 60% of the theoretical amount. The remaining 40% of the material consists of a clear basic oil which does not crystallize nor give crystalline salts.

When ethylmagnesium iodide is used, the same product, desoxycodeine, is obtained in somewhat better yields; it is evident from this that the organomagnesium halide functions in this reaction chiefly to remove the elements of hydrochloric acid, and to open reductively the 4,5-ether bridge of a-chlorocodide. Small amounts of iodocodide could frequently be isolated among the reaction products; further investigation has shown that iodocodide reacts with alkylmagnesium halide in the same way as *a*-chlorocodide to give desoxycodeine. It therefore seems probable to us that iodocodide, in which the halogen is very loosely bound, forms an intermediate in this reaction. As would be expected, in a reaction where methylmagnesium halide acts in a reducing capacity, considerable amounts of ethylene are present in the gases evolved in the reaction. β-Chlorocodide, an isomer of a-chlorocodide which is believed to differ from it only in the spatial arrangement of H- and Cl- on the asymmetric carbon atom in Position 6, does not react with alkylmagnesium halide. It is well known that the halogen in β-chlorocodide is far less active than that in α-chlorocodide;[13] it was further found in the present investigation that in contrast to the a-form, β-chlorocodide does not react with potassium iodide in boiling alcohol to give an iodocodide.

The iodocodide obtained as a by-product in the reaction of alkylmagnesium iodide with a-chlorocodide consisted of fine white needles, or clumps of thick white monoclinic prisms. The known iodocodide (from a-chlorocodide with potassium iodide)[11] is described as light orange needles, and it therefore seemed probable that our white iodocodide represented a stereoisomeric β-form, in analogy with α- and β-chlorocodide. This is, however, apparently not the case; careful comparison of physical and chemical properties of the bases and their salts indicates that they are identical. The orange color of the Knorr compound is due to traces of colored decomposition products formed through the use of higher boiling solvents.

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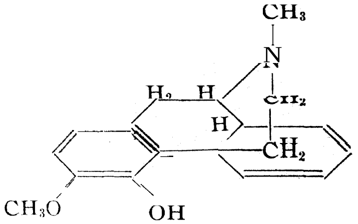
[13] Knorr and Horlein, *Ber.*, 41, 974 (1908) (hydrolysis); Knorr and Horlein, *ibid.*, 40, 4887 (1907) (rrduction): Mannich and Löwenheim, *Arrh. Pharm* , 258, 295 (1920) (reduction)

The desoxycodeine obtained from the Grignard reaction was identified by direct comparison with a sample prepared by refluxing α-chlorocodide with zinc dust in alcohol. With sodium and alcohol it reduced to the so-called α-tetrahydrodesoxycodeine,[14] which was also identified by direct comparison. By hydrogen and platinum, it was converted to @-tetrahydrodesoxycodeine (VI). The reduction products from desoxycodeine as well as those derived from the two new desoxycodeines described in this paper will be discussed in the following communication.

The Knorr desoxycodeine, as depicted in Formula III, represents one of the two possible phenolic desoxycodeines, the second of which may be conceived as having the conjugated double linkages in the hydroaromatic ring arranged in the alternative Positions, 5,6 and 7,8 (Formula IV). We propose for the present to name the Knorr compound of m. p. 126° desoxycodeine-A, the phenolic isomer, desoxycodeine-B,[15] and the non-phenolic desoxycodeine of the same empirical formula, to be described below, desoxycodeine-C.



IV

Desoxycodeine-B

Desoxycodeine-B, m. p. 119°, is formed when a-chlorocodide dissolved in 20% sulfuric acid is reduced electrolytically. Freund[16] first carried out this experiment, which he believed led to the formation of a dihydrodesoxycodeine, $C_{18}H_{23}O_2N + \frac{1}{2}H_2O$ of m. p. 117–119°, which is obviously the same as the compound which we describe. He claimed that the same substance resulted from the electrolytic reduction of @-chlorocodide(a statement which we have verified), of chlorodihydrocodide, and of desoxycodeine-A. Freund's evidence for considering his base of m. p. 117–119° as a dihydrodesoxycodeine was as follows. (1) Analyses: only those made on the 117° base prepared from α- and β-chlorocodides need be considered. These are in fair agreement with the value calculated for a dihydrodesoxycodeine containing one-half molecule of water. The bases prepared by electrolytic reduction of desoxycodeine-A and of chlorodi-

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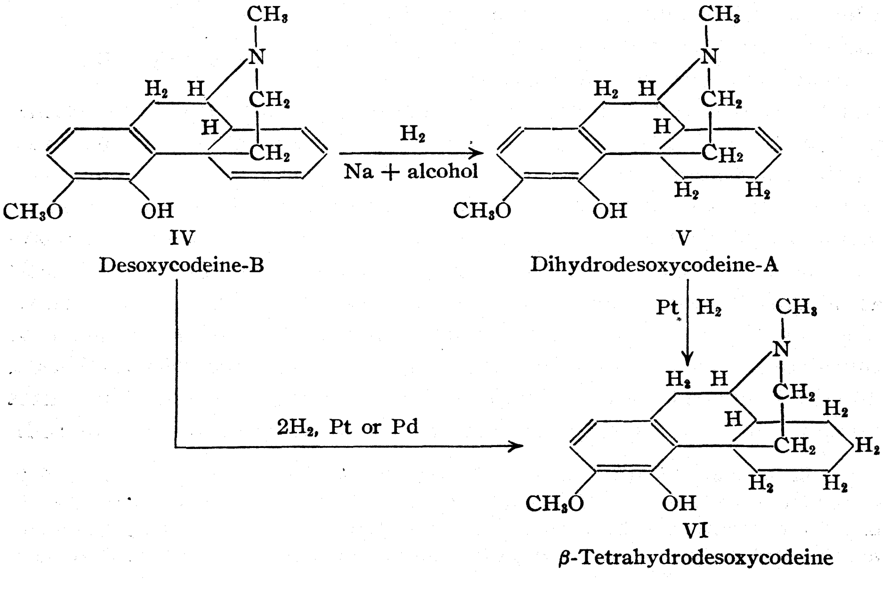
[14] Knorr and Waentig[2] reduced desoxycodeine with sodium in boiling alcohol to what they believed to be a dihydrodesoxycodeine, $C_{18}H_{23}O_2N$, which could also be obtained directly from a-chlorocodide through reduction with the same agents. This was disputed by Freund, who claimed that the reduction product was formed by addition of four atoms of hydrogen to desoxycodeine, and named it α-tetrahydrodesoxycodeine, to distinguish it from the tetrahydrodesoxycodeine which he obtained by reduction of desoxycodeine with palladium and hydrogen, and which was named β-tetrahydrodesoxycodeine.

[15] There is no evidence to show which of the Formulas III and IV should be assigned to desoxycodeine-A and which to desoxycodeine-B.

[16] Freund, J *prakt Chem*, **101,** 23 (1921).

hydrocodide which were thought to be identical with the 117° base are actually two different dihydrodesoxycodeines, of m. p. 134 and 111°, respectively, as will be shown in the next paper. (2) Catalytic reduction: this was carried out on but 0.4 g. of material, the source of which is not given. We can explain the absorption of but one molecule of hydrogen as noted by Freund only by the assumption that the sample taken for reduction was prepared from desoxycodeine-A or chlorodihydrocodide.

Since analytical proof of the presence of two hydrogen atoms more or less in a compound of molecular weight 292 is open to some question, we wish to stress the fact that our statement to the effect that the 119° base from electrolytic reduction of *a*- or *β*-chlorocodide is actually a desoxycodeine rests on reduction experiments. Desoxycodeine-B takes up two molecules of hydrogen on reduction by the catalytic method, using Adams' platinum oxide catalyst or palladium on barium sulfate, to give a quantitative yield of *β*-tetrahydrodesoxycodeine. When reduction of desoxycodeine-B is effected with sodium and alcohol, a dihydrodesoxycodeine (m. p. 134–136°) is formed, which may be further reduced by the catalytic method, with absorption of but one molecule of hydrogen to *β*-tetrahydrodesoxycodeine (VI).



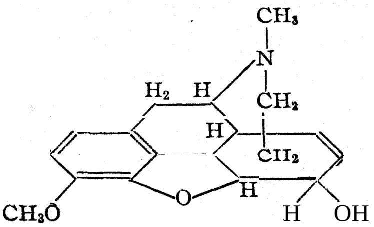
IV
Desoxycodeine-B

V
Dihydrodesoxycodeine-A

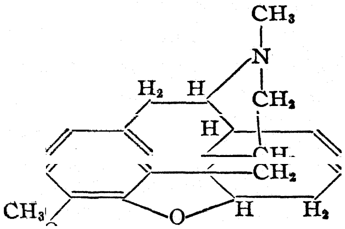
VI
β-Tetrahydrodesoxycodeine

The results of reduction, therefore, show beyond question that the phenolic base of m. p. 119° which Freund thought to be a dihydrodesoxycodeine is unsaturated to a degree corresponding to the presence of two double linkages, and is isomeric with desoxycodeine-A. It seems quite certain that the isomerism of these two phenolic desoxycodeines is due only to a difference in the arrangement of the unsaturated linkages in the hydroaromatic ring; on addition of two or four hydrogen atoms, the isomerism disappears.

The name desoxycodeine, which was introduced by Knorr, was somewhat unfortunately chosen. While the phenolic bases III and IV described above have the empirical formula $C_{18}H_{21}O_2N$ of codeine minus one oxygen, they correspond structurally to codeine less HOH, plus 2H. The name desoxycodeine should logically be applied to a compound derived from codeine (VII) through replacement of the alcoholic hydroxyl group by hydrogen (VIII) without scission of the 4,5-ether linkage.[17]



VII
Codeine



VIII
Hypothetical true desoxycodeine

We have been successful in preparing a compound of this nature, in whose structure, if the Gulland–Robinson formula (VII) for codeine be accepted, the only uncertain point is the position which the double linkage occupies in the hydroaromatic ring III. On the grounds given below, we consider it probable that the double bond lies between C-6 and C-7 (IX).

Desoxycodeine-C (IX) is prepared by treatment of chlorodihydrocodide in absolute methyl alcoholic solution with sodium methylate for twenty-four hours at 140°. Knoll and Co.,[18] heating chlorodihydrocodide with sodium methylate in methyl alcohol at 140° for forty-eight hours,[19] obtained a product of m. p. 111° which was called dihydrodesoxycodeine, and which is apparently identical with our desoxycodeine-C (whose melting point we have not been able to bring above 106°). The method of preparation of the two compounds is the same; the shorter period of heating was adopted by us because it resulted in better yields. The hydrochloride of desoxycodeine-C melts at the point given by Knoll and Co. for their dihydrodesoxycodeine hydrochloride (114°); the methiodide, on the other hand, we find to melt at 236–240°, in comparison with Knoll's 135–136°; we are forced to believe that this discrepancy in melting point of the methiodide arises from a misprint in Knoll and Co.'s patent. It is difficult

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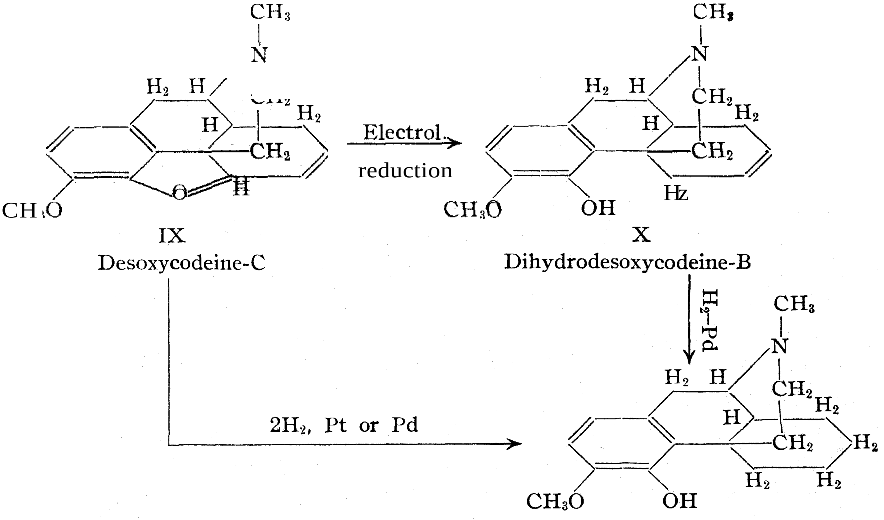
[17] Cf. Freund, *J. prakt. Chem.*, *101*, 7 (1921).

[18] Knoll and Co., German Patent 414,598 (1922); *Friedländer*, 15, 1518; *Jahresb. Chem. Tech.*, *71*, 123 (1925).

[19] Mannich and Löwenheim [*Arch. Pharm.*, 258, *295* (1920)] state that chlorodihydrocodide with sodium methylate at 120° forms no sodium chloride.

to explain, in any case, the formation of a dihydrodesoxycodeine, $C_{18}H_{23}O_2N$, as claimed by Knoll from chlorodihydrocodide, $C_{18}H_{22}O_2NCl$, through the agency of sodium methylate, since such a transformation involves reduction, *i. e.*, loss of HCl and addition of 2H, or direct replacement of Cl by H. The chemical behavior and analyses of desoxycodeine-C and its derivatives, on the other hand, show it to have been formed by loss of hydrochloric acid from chlorodihydrocodide.

Desoxycodeine-C (m. p. 105–106°) is not phenolic in nature. It is insoluble in alkali, and does not yield a methyl ether or acetyl derivative. In the presence of a palladium or platinum catalyst, it takes up two molecules of hydrogen, yielding β-tetrahydrodesoxycodeine (VI). By the electrolytic method, on the other hand, desoxycodeine-C is reduced to a new phenolic dihydrodesoxycodeine (X) of m. p. 128°, containing two more hydrogen atoms than desoxycodeine-C. This phenolic dihydrodesoxycodeine, on catalytic hydrogenation (palladium–barium sulfate catalyst), takes up one molecule of hydrogen to give β-tetrahydrodesoxycodeine. This may be represented by the following formulas, in which, however, we wish to make no claim concerning the exact location of the unsaturation in the hydroaromatic ring of desoxycodeine-C and its dihydro derivative.

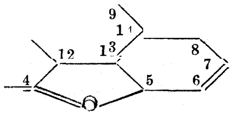


IX
Desoxycodeine-C

X
Dihydrodesoxycodeine-B

VI
β-Tetrahydrodesoxycodeine

The structure which we assign to desoxycodeine-C is based primarily upon its relationship to β-tetrahydrodesoxycodeine, and is put forward tentatively on the assumption that the latter substance actually possesses the generally accepted Formula VI. The fact that desoxycodeine-C cannot be reduced catalytically with saturation of the double bond only, to give a non-phenolic dihydrodesoxycodeine, recalls the similar behavior of other compounds in the codeine series. While codeine and isocodeine, and the methylmorphimethines, ci-, β-, γ- and 6-, can be reduced by simple saturation of the double linkages present, yielding non-phenolic hydrogenation products, pseudocodeine and allopseudocodeine, as well as ε- and ζ-methylmorphimethines take up two more hydrogen atoms than the corresponding isomeric substances mentioned above, to give phenolic hydrogenated derivatives. As Schöpf[20] has pointed out, the behavior of the grouping —O—CH—CH=CH—, generally accepted as being present in pseudo-, allopseudo-codeine, and ε- and ζ-methylmorphimethines, is to a certain degree comparable with that of a conjugated system of double linkages —CH=CH—CH=CH—, and the fact that hydrogenation of the substances mentioned takes place always with opening of the ether ring may be explained through the assumption that a 1,4-addition of hydrogen (at —O— and C-7) first takes place, followed by a saturation of the double linkage 5,6 in the intermediately formed compound. It is therefore not unreasonable to assume that in desoxycodeine-C the arrangement in the hydroaromatic ring corresponds to that shown in XI.



XI

There are at present three isomeric desoxycodeines known, two of which, desoxycodeine-A and desoxycodeine-B, are phenolic in nature. As will be shown in the next paper, the evidence which primarily led to the belief in an isomerism in the morphine series due to spatial differences in the hydrogen atom on C-14 is invalid. If this questionable configurational isomerism be disregarded, there are possible four non-phenolic desoxycodeines (isomerism due to differences in position of the double bond), only one of which is now known, and two phenolic desoxycodeines, as described above.

Experimental

a-Chlorocodide. —The a-chlorocodide used in these experiments was prepared by modifying the method of Freund,[16] in that the codeine and phosphorus pentachloride were allowed to react for only two hours instead of twenty-four hours as given by Freund. This resulted in an increased yield and less formation of amorphous by-products. Starting with crude codeine, the yield averaged 84–86% of the theoretical, while from pure codeine a 94% yield was obtained. The use of thionyl chloride'' proved to be less advantageous. Since no crystalline salts of α-chlorocodide have been previously described, we include the preparation of two of these.

α-Chlorocodide Acid Sulfate.—This salt was prepared by dissolving a-chlorocodide in the calculated amount of 20% sulfuric acid, whereupon the sparingly soluble acid sulfate separated as a white crystalline mass. It was purified from water; it softens at 135–140°, and melts with decomposition at 192–193°.

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[20] Schöpf, *Ann.*, 452,237 (1927); 483, 157 (1930).

[21] Wieland and Kappelmaier, *ibid.*, 382, 337 (1911).

Anal. Calcd. for $C_{18}H_{20}O_2NCl{\cdot}H_2SO_4 + 2H_2O$: H_2SO_4, 21.70. Found: H_2SO_4, 21.83.

The substance was dried to constant weight at 135–140°.

Anal. Calcd. for $C_{18}H_{20}O_2NCl{\cdot}H_2SO_4 + 2H_2O$: H_2O, 7.97. Found: H_2O, 7.55.

Anal. Calcd. for $C_{18}H_{20}O_2NCl{\cdot}H_2SO_4$: H_2SO_4, 23.02. Found: H_2SO_4, 23.61.

The hydrated salt in aqueous solution shows $[\alpha]_D^{20}$ +101.1°: $c = 2.720$, $l = 1$, a = +2.75°.

a-Chlorocodide Acid Tartrate.—This salt was prepared by dissolving the base in a dilute aqueous solution of the calculated amount of d-tartaric acid, evaporating to dryness in vacuum, and recrystallizing from water. It is very soluble in hot water; at 18° 100 cc. of water dissolves 1.36 g. of the salt. In aqueous solution, $[\alpha]_D^{27\ 5}$ −219.3": c = 1.856, $l = 1$, a = −4.07".

Anal. Calcd. for $C_{18}H_{20}O_2NCl{\cdot}C_4H_4O_6$: Cl, 7.62. Found: Cl, 7.61.

β-Chlorocodide.—This substance was prepared by a method similar to that of Pschorr[22] and Speyer,[23] by sealing a-chlorocodide (5 g.) in thin-walled test-tubes and heating for twenty-five minutes after complete melting in a bath of boiling bromoform or bromobenzene. The test-tube was cut while the contents were still soft, and 96% alcohol added, whereupon the brownish mass crystallized; yield after one recrystallization from alcohol, 75% of the theoretical. No salts of β-chlorocodide have been described previously.

β-Chlorocodide Hydrochloride.[24]—On addition of the calculated amount of 3 N hydrochloric acid to the base the hydrochloride crystallized from the clear solution almost immediately, and was filtered off and washed with cold water. It was recrystallized from water or from a mixture of alcohol and acetone. The purified salt sinters slightly at 162°, and melts at 168–171° (decomp.); it is slightly levorotatory, $[\alpha]_D^{30}$ −3.85": c = 2.335, $l = 1$, a = −0.09".

Anal. Calcd. for $C_{18}H_{20}O_2NCl{\cdot}HCl$: Cl, 20.03. Found: Cl, 19.99, 20.02.

β-Chlorocodide Acid Tartrate.—Prepared by dissolving β-chlorocodide in a dilute aqueous solution of the calculated amount of d-tartaric acid, evaporating to dryness in vacuum, and recrystallizing the glass-like product from a small amount of water. It is very soluble in cold water; in aqueous solution, $[\alpha]_D^{20}$ +8.3°; $c = 1.683$, 1 = 1, a = +0.14°.

Anal. Calcd. for $C_{18}H_{20}O_2NCl{\cdot}C_4H_4O_6$: Cl, 7.62. Found: Cl, 7.67.

Iodocodide.—(1) Orange form: this was prepared according to the directions of Knorr and Hartmann[25] and varied in color from yellow to red. It sintered strongly at 153–155°, formed a black solid at 159–162°, and melted with decomp. at about 200°: red crystals, $[\alpha]_D^{25}$ +134.1° in chloroform: $c = 3.72$, $l = 1$, a = +4.99°; yellow crystals, $[\alpha]_D^{26.5}$ +126.8° in chloroform: $c = 2.30$, 1 = 1, a = +2.92°. (2) White form: this was obtained when the yellow or red crystals were dissolved in boiling ligroin (90–110°) or ethyl acetate, filtered, and cooled quickly. White crystals were also obtained when a-chlorocodide (15 g.) with finely powdered potassium iodide (9 g.) was refluxed for ten hours in 150 cc. of methyl alcohol, yield 12.7 g., m. p. 159–160° after one recrystallization from methyl alcohol. The same substance was obtained as a by-product from the reaction of a-chlorocodide with methyl- or ethylmagnesium iodide. It is soluble in chloroform or benzene, slightly soluble in ethyl acetate, methyl alcohol, ethyl alcohol or

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[22] Pschorr and Rollet, *Ann.*, **373**, 6 (1910).

[23] Speyer and Rosenfeld, Ber., **58**, 1115 (1925).

[24] We are indebted to Mr. L. Eilers for the preparation and analysis of this salt.

[25] Knorr and Hartmann, Ber., **45**, 1352 (1912).

ligroin, almost insoluble in ether; $[\alpha]^{22.5}_{\mathrm{D}}$ +136.5° (chloroform): c = 2.62, l = 2, a = +7.15°.

Anal. Calcd. for $C_{18}H_{20}O_2NI$: C, 52.80; H, 4.93; I, 31.02. Found: C, 53.10; H, 5.04; I, 31.17.

When the white iodocodide was boiled in ethyl alcohol for a few minutes, the solution gradually turned yellow and the yellow or reddish crystals described by Knorr separated on cooling. After boiling in alcohol for three days, iodocodide could no longer be isolated.

Iodocodide Hydrochloride.—Five grams of pure iodocodide was treated with 10 cc. of cold 3 N hydrochloric acid. The gummy mass which first formed crystallized after a few minutes, and was recrystallized from methanol; yield 4.8 g.; after repeated crystallizations it melted at 190–191°. In water, $[\alpha]^{23}_{\mathrm{D}}$ +126.9°, +127.0°: c = 1.43, 0.693, l = 2, 1, α = +3.63°, +0.88'. It is soluble in water at 26° to the extent of 2.6 g. in 100 cc.

Anal. Subs., 0.1623 g. Calcd. for $C_{18}H_{20}O_2NI \cdot HCl + 2H_2O$: silver halide, 0.1275 g. Found: silver halide, 0.1257 g.

The salt lost weight corresponding to 2.5 H_2O (water could be observed) on heating to the point where decomposition started.

Iodocodide **Methiodide.**—Iodocodide in benzene solution was heated with an excess of methyl iodide in a sealed tube at 100° for three hours. The product was washed with ether and recrystallized from hot water, in which it is only very slightly soluble; m. p. 187–188°, yellow needles.

Anal. Calcd. for $C_{19}H_{23}O_2NI_2$: I, 46.06 Found: I, 46.22.

Iodocodide and **Methylmagnesium** Iodide: Desoxycodeine-A,—To a suspension of one gram of powdered iodocodide (white) in 50 cc. of dry ether was added 25 cc. of molar ethereal methylmagnesium iodide solution. After the mixture had refluxed for twelve hours, the excess of Grignard reagent and the powdery white addition compound were decomposed with a slight excess of 10% acetic acid, and concd. ammonia added dropwise with shaking until the solution was strongly alkaline. The ether layer was dried with sodium sulfate and distilled, leaving a yellow oil which soon crystallized. The addition of a small amount of cold methanol served to dissolve the desoxycodeine (0.4 g.) away from unreacted iodocodide (0.3 g.).

Iodocodide (white or orange) reacted with zinc dust in boiling absolute alcohol as does a-chlorocodide, to give desoxycodeine. In view of the unstable nature of iodocodide, the low yield of desoxycodeine (about 30%) is not remarkable.

Hydrolysis of Iodocodide: **Pseudocodeine.**—Eight grams of the white iodocodide was suspended in 40 cc. of hot water and 4 cc. of glacial acetic acid added. The clear yellow solution was refluxed for four hours, cooled, and treated with an excess of 15% potassium hydroxide. The resinous precipitate was extracted out with ether and the ethereal solution dried with potassium carbonate and distilled, yielding an oily solid. This was dissolved in the minimum amount of absolute alcohol and treated with alcoholic hydrochloric acid to acid reaction. After standing for twelve hours at 0°, the solution yielded 4.5 g. of crystalline pseudocodeine hydrochloride. About 2 g. of oily solid was obtained by treating the mother liquors with alkali, but the separation of isocodeine and allopseudocodeine from this was unsuccessful.

Iodocodide and Silver Chloride: **α-Chlorocodide.**—A small amount of white (or yellow) iodocodide was dissolved in 75% alcohol and shaken with freshly precipitated silver chloride. After a few minutes a change in color of the silver salt could be noted, and in three hours it had become quite yellow. The liquid on evaporation yielded α-chlorocodide, of m. p. 145–147°, which showed no depression with a-chlorocodide, but depressed the melting point of β-chlorocodide to about 120".

Desoxycodeine-A (Desoxycodeine).—The base prepared according to the directions of Knorr and Waentig, and Freund, by refluxing a-chlorocodide with zinc dust in absolute alcohol, showed the m. p. 121–122" even after the most careful purification by recrystallization from 50% methyl alcohol to constant rotation as well as over the hydrochloride or hydriodide; $[\alpha]^{22}_{\mathrm{D}}$ +118.1° $c = 3.32$ (96% alcohol), $l = 1$, or = +3.92° (Knorr, m. p. about 126° with previous sintering; $[\alpha]^{15}_{\mathrm{D}}$ +119°, +121°).

Preparation Using Methylmagnesium Iodide.—Eight grams of α-chlorocodide in 400 cc. of dry ether was treated with 75 cc. of molar methylmagnesium iodide solution. A precipitate formed immediately, the ether boiled, and considerable amounts of a gas which was largely unsaturated toward bromine were given off. The mixture was refluxed for six hours, the ether decanted from the heavy white precipitate and the latter brought into complete solution with 10% acetic acid. To the acid solution was added 100 cc. of ether, and an excess of ammonia sufficient to dissolve the magnesium hydroxide precipitate. The ammoniacal layer was extracted with a second 100 cc. of ether, and the combined dried ether distilled. The red oily residue crystallized on the addition of a little ether and was recrystallized from ether and then from 50% methanol. The product (5.5 g.) melted at 122°, $[\alpha]^{24}_{\mathrm{D}}$ +115 1°: c = 196 (96% alcohol), $l = 2$, α = +4.51°. The same product was obtained when ethylmagnesium iodide was used: 3 g. of a-chlorocodide yielded 2 g. of crude desoxycodeine and about 0.1 g. of white iodocodide. The iodocodide was separated from the desoxycodeine through its comparative insolubility in ether.

Desoxycodeine-A, prepared through the reaction of alkylmagnesium halide on a-chlorocodide, gave a hydrochloride of m p 265–270° and a hydriodide of m p. 255–260", identical with those obtained from Knorr's desoxycodeine Our product was further identified through its reduction products: with sodium and alcohol it reduced to the so-called a-tetrahydrodesoxycodeine, with hydrogen and platinum it took up two molecules of hydrogen to give a quantitative yield of β-tetrahydrodesoxycodeine of m. p. 143–145".

The reduction of desoxycodeine-A with sodium and alcohol as well as by the electrolytic method will be further described in the following paper.

Desoxycodeine-B.—Ten grams of pure or-chlorocodide was dissolved in 200 cc. of 20% sulfuric acid (separation of the sparingly soluble crystalline acid sulfate often caused difficulty at this point) and electrolyzed, using a current of 8 amperes and a prepared lead cathode of 60 sq. cm. area, in a cell which was kept at about 10 to 20°. Usually five to six hours was required for the reduction, which was complete when a small test portion dissolved to a clear solution in excess alkali. The acid solution from the reduction was filtered and treated with ammonia until barely alkaline to litmus. The base which precipitated was redissolved in the minimum amount of dilute hydrochloric acid, and the solution cooled to 0°; 200 cc of ether was added, and then 3 N ammonia dropwise with vigorous shaking. The clear yellow ether solution was dried with sodium sulfate and distilled, yielding 9.0 g of crude desoxycodeine-B of m. p. 110–115°. Two crystallizations from dilute alcohol gave a product melting at 118–119°, $[\alpha]^{24}_{\mathrm{D}}$ +42.4°. By exhaustive crystallization from dilute alcohol the melting point changed only slightly (119–120°), but the rotatory power rose to $[\alpha]^{22}_{\mathrm{D}}$ +71.3°: $c = 3.617$, $l = 1$, or = +2.58°.

Anal. Calcd for $C_{18}H_{21}O_2N + {}^1/_2H_2O$: C, 73.93, H, 7.58 Found C, 73 85; H, 7.84.

A dihydrodesoxycodeine $C_{18}H_{23}O_2N + {}^1/_2H_2O$ which Freund claimed this base to be would require *C*, 73.43; H, 8.21.

Desoxycodeine-B hydrochloride is formed when a saturated solution of the base in absolute alcohol is treated with alcoholic hydrochloric acid. The white crystals obtained darken rapidly on standing, and even after recrystallization from absolute alcohol are still unstable.

Desoxycodeine-B hydriodide results from treatment of a dilute acetic acid solution of the base with excess of aqueous potassium iodide. The oil which first separates crystallizes on standing, and may be purified by recrystallization from water, from which it separates as light yellowish-brown needles of m. p. 245°; $[\alpha]^{22}_{D}$ +38.3°: c = 1.698, l = 1, α = +0.65°.

Anal. Calcd. for $C_{18}H_{21}O_2N{\cdot}HI$: I, 30.87. Found: I, 30.92.

Desoxycodeine-B Methyl Ether Methiodide.—The methiodide of the desoxycodeine-B does not crystallize. The methyl ether methiodide, prepared in the usual way and recrystallized from dilute alcohol, melted at 242–243°. Freund gives the m. p. 245°.

Reduction of Desoxycodeine-B.—Nine and one-half grams of the base was dissolved in dilute hydrochloric acid to neutral solution, made up to 100 cc. with water, and hydrogenated in the presence of *2.5 g.* of palladium–barium sulfate; 1570 cc. *(2* moles) of hydrogen was absorbed in three hours (when platinum oxide was used the reduction ran to completion in twenty to thirty minutes). The filtered solution was made alkaline with ammonia and extracted with ether. The product, recrystallized from acetone, consisted of 9.5 g. of white crystals of m. p. 139–143°, which melted at 144–145° after further purification from acetone and were identical in every respect with β-tetrahydrodesoxycodeine; $[\alpha]^{20}_{D}$ −33.3": c = 1.499 (alcohol), l = 1, α −0.50°. The reduction of desoxycodeine-B with sodium and alcohol to a dihydrodesoxycodeine (the so-called α-tetrahydrodesoxycodeine) will be described in the following paper.

Desoxycodeine-C.—A solution of 9 g. of sodium in 400 cc. of methanol was prepared in a' steel autoclave, 5.0 g. of crystalline chlorodihydrocodide (m. p. 171–173°) added, and the mixture heated at 140° for twenty-four hours. After cooling, the clear deep red methanol solution was diluted with an equal volume of water, and the methyl alcohol removed with a bubble tube in vacuum at 40°. The alkali-insoluble desoxycodeine-C separated crystalline as the alcohol was removed, and was filtered out and purified by repeated crystallization from ethyl acetate. The yield of crude crystalline product was 4.2 g., of purified substance melting at 105–106°, 3.0 g.; in 95% alcohol. $[\alpha]^{20}_{D}$ −199.4°, −197.4': c = 1.745, 1.008; l = 1, 1; a = −3.48°, −1.99°.

Anal. Calcd. for $C_{18}H_{21}O_2N$: C, 76.28; H, 7.47. Found: C, 76.24; H, 7.65.

The formula of a dihydrodesoxycodeine, $C_{18}H_{23}O_2N$, as claimed by Knoll and Co., requires C, 75.74; H, 8.12.

It is extremely soluble in methyl or ethyl alcohol, ether, chloroform or benzene, moderately soluble in ethyl acetate, insoluble in alkali.

Desoxycodeine-C Hydrochloride.—A solution of the base in the minimum amount of 3 *N* hydrochloric acid was evaporated to dryness in vacuum and the white crystalline solid thus obtained was purified by recrystallizing from alcohol. It crystallizes with one molecule of water and melts at 114°; in aqueous solution $[\alpha]^{20.5}_{D}$ −132.7': c = 1.771, l = 1, a = −2.35°.

Anal. 0 1609 g. at 130" in vacuum lost 0.0088 g. Calcd. for $C_{18}H_{21}O_2N{\cdot}HCl + H_2O$: H_2O, 5.38 Found: H_2O, 5.50.

Anal. (dried substance) Calcd. for $C_{18}H_{22}O_2NCl$: Cl, 11.10. Found: Cl, 11.23.

Desoxycodeine-C Hydriodide.—The base was dissolved in dilute acetic acid and treated with an excess of potassium iodide solution. An oil separated, which crystallized on standing, and was purified by recrystallization from hot water. It consisted of fine light yellow prisms, sintering at 135–140°, melting at 160–165°, and containing one molecule of hydrate water; in 95% alcohol, $[\alpha]^{19}_{D}$ −131.6°: c = 1.401, l = 1, a = −1.84".

Anal. Calcd. for $C_{18}H_{21}O_2N{\cdot}HI + H_2O$: H_2O, 4.19. Found: H_2O, 4.18. Calcd. for $C_{81}H_{22}O_2NI$: I, 30.88. Found: I, 30.96.

Desoxycodeine-C Methiodide.—A solution of the base in methyl alcohol was boiled for ten minutes with an excess of methyl iodide. After removal of methyl iodide by distillation, water was added; the oily methiodide which separated was obtained crystalline by dissolving in hot water and cooling very slowly. The crude product melted at 210–211°; after crystallization to constant melting point from methyl alcohol it melted at 236–240°.

Anal. Calcd. for $C_{19}H_{24}O_2NI$: I, 29.86. Found: I, 30.22.

Reduction of **Desoxycodeine-C.**—One gram of desoxycodeine-C in 30 cc. of methyl alcohol with 0.1 g. of Adams' platinum oxide catalyst took up 180 cc. of hydrogen in twenty minutes. The calculated absorption for 2 moles of hydrogen is 176 cc. The mixture was filtered from the platinum and evaporated to dryness in vacuum, giving a quantitative yield of crystalline β-tetrahydrodesoxycodeine, which after one crystallization from acetone melted at 143–144°, showed no depression in m. p. with β-tetrahydrodesoxycodeine, and yielded a hydriodide of m. p. 251°, a methiodide of m. p. 263–265° identical with those from β-tetrahydrodesoxycodeine. The reduction product likewise showed the rotation of β-tetrahydrodesoxycodeine: $[\alpha]^{20}_{D}$ $-30.8°$, $c = 1.980$ (alcohol), $l = 2$, a $= -1.22°$. The reduction of desoxycodeine-C with the Willstatter platinum black catalyst, or in hydrochloric acid solution with a palladium-barium sulfate catalyst gave identical results. Desoxycodeine-C is recovered unchanged from treatment with sodium and alcohol, or zinc and acetic acid. The electrolytic reduction of desoxycodeine-C yields a dihydrodesoxycodeine of m. p. 128–131° which will be described in the following paper.

Summary

1. A study of the desoxycodeines and of their conversion to the dihydrodesoxycodeines and to β-tetrahydrodesoxycodeine has been made.

2. Desoxycodeine-A is shown to be the chief product of the reaction between a-chlorocodide and methyl- or ethylmagnesium iodide. Iodocodide, which is obtained as a by-product of the reaction, may play a part in the reaction mechanism.

3. The compound resulting from electrolytic reduction of α- or β-chlorocodide, which was formerly thought to be a dihydrodesoxycodeine, is shown to be a second, phenolic desoxycodeine. It can be reduced directly to β-tetrahydrodesoxycodeine, or indirectly, through an intermediate dihydrodesoxycodeine, to the same tetrahydrodesoxycodeine.

4. The action of sodium methylate on chlorodihydrocodide does not give a dihydrodesoxycodeine as claimed in the literature, but the nonphenolic desoxycodeine-C which reduces to a phenolic dihydrodesoxycodeine or to β-tetrahydrodesoxycodeine.

5. New crystalline salts of α-chlorocodide and of β-chlorocodide are described.

UNIVERSITY, VIRGINIA

[CONTRIBUTION NO. 74 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

DESOXYCODEINE STUDIES. II. THE DIHYDRODESOXYCODEINES[1]

BY LYNDON F. SMALL AND FRANK L. COHEN

RECEIVED FEBRUARY 9, 1931 PUBLISHED JUNE 8, 1931

In the preceding paper[2] the preparation of three isomeric desoxycodeines, $C_{18}H_{21}O_2N$, was described. The present communication deals with the dihydrodesoxycodeines obtained by partial reduction of the desoxycodeines, as well as with certain dihydrodesoxycodeines whose relationship to the desoxycodeines is not certain. Any systematic nomenclature of the dihydrodesoxycodeines as derivatives of the desoxycodeines is complicated by the fact that two of the latter reduce to give the same dihydro derivative, whereas the third, non-phenolic desoxycodeine yields on reduction a phenolic product which must be regarded as a dihydro derivative of the phenolic desoxycodeines. Until evidence is available through which the structure of the individual dihydrodesoxycodeines can be demonstrated, we will designate them by Roman letters, which are arbitrary and imply no genetic relationship to the desoxycodeines already described by the same device.

If the possibility of isomerism in this series due to differences in the spatial arrangement of the hydrogen atom on C-14 be disregarded, there *are* theoretically possible[3] two phenolic desoxycodeines of the type shown in Formula II, both of which have been described (desoxycodeine-A and desoxycodeine-B), and four non-phenolic desoxycodeines of the type of Formula III, whose isomerism will be due to differences in position of the double linkage in Ring III. Only one of the non-phenolic desoxycodeines is known, desoxycodeine-C.

By addition of two hydrogen atoms to either of the phenolic desoxycodeines of type II, there are possible four isomeric phenolic dihydrodesoxycodeines (Formula IV), all of which still contain one double bond, which may be imagined as occupying any one of the four possible positions in the hydroaromatic ring, and all of which must reduce to the same tetrahydrodesoxycodeine, provided addition of hydrogen at C-14 takes place always in but

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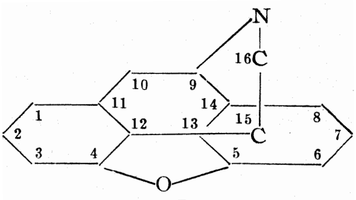
[1] This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

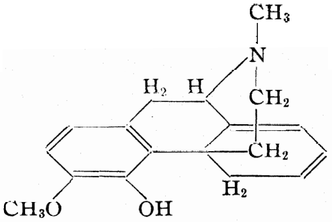
[2] Small and Cohen, THIS JOURNAL, 53, **2214 (1931).**

[3] No evidence exists in morphine chemistry which would make necessary the hypothesis of stereoisomerism at any other point, as at the asymmetric carbon atoms 5 or **9.** The recent work of Schopf and Pfeifer [**Ann.,** 483, 157 (1930)] on closure of the ether ring at C-5 includes theoretical speculations to the effect that but one configuration at C-5 is sterically possible (*loc. cit.,* page **164).** An arrangement of double linkages other than in conjugation in Ring III scarcely comes into consideration.



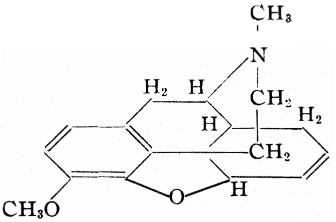
I

Numbering system



II

Desoxycodeine, phenolic

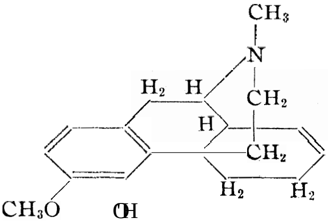


III

Desoxycodeine, non-phenolic

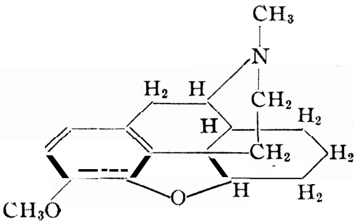
one way sterically. The four phenolic dihydrodesoxycodeines described below are, by addition of two hydrogen atoms, all converted to the same substance, β-tetrahydrodesoxycodeine (VI).

By addition of two hydrogen atoms to the double linkage of any of the hypothetical desoxycodeines of type III, only one non-phenolic dihydrodesoxycodeine (V) will be formed, again postulating addition of hydrogen in but one way at C-14 in the case where the double linkage lies between C-8



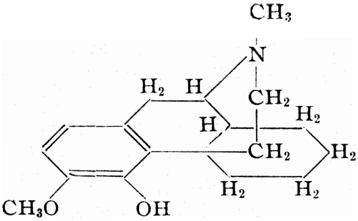
IV

Dihydrodesoxycodeine, phenolic



V

Dihydrodesoxycodeine, non-phenolic



VI

β-Tetrahydrodesoxycodeine

and C-14. By further addition of hydrogen, conducted under such conditions that the 4,5-ether linkage is opened, the same phenolic tetrahydrodesoxycodeine (VI) as resulted from complete reduction of the hydroaromatic ring in type II must be formed.

Desoxycodeine-A (m. p. 126°, Formula II, or the alternative formula with double bond at C-5 and C-7), which was first prepared by Knorr and Waentig in 1907,[4] reduces with sodium and alcohol to give a product of m. p. 134–136° (Knorr, melting point about 132°),[4,5] which these investigators believed to be a dihydrodesoxycodeine, and which may be more conveniently prepared by direct reduction of a-chlorocodide with sodium and alcohol.[4] Fourteen years later Freund, Melber and Schlesinger[6] conducted an investigation on dihydro- and tetrahydrodesoxycodeines which must be briefly summarized here. The relevant experiments will be numbered and referred to in the discussion by these numbers.

§1. Chlorodihydrocodide, derived from dihydrocodeine by substitution of the alcoholic hydroxyl by chlorine, was reduced by the electrolytic method of Tafel, and yielded a pale brown crystalline solid, m. p. 117–119°, which analyzed approximately for a dihydrodesoxycodeine, $C_{18}H_{23}O_2N + {}^1/_2\ H_2O$.

$2. a-Chlorocodide, reduced electrolytically, gave a compound of m. p. 117–119°, which was claimed to be identical with the dihydrodesoxycodeine of $1.

$3. β-Chlorocodide, reduced electrolytically, gave a product of m p. 126–130°, which showed the m. p. 117–119" when mixed with the product from $2 and was therefore considered to be identical with it.

$4. Desoxycodeine (m p. 126°), on electrolytic reduction, gave a product of m. p. 117–119° which was said to be identical with the product from §1.

$5. Desoxycodeine (m. p. 126°), in the form of the hydrochloride, hydrogenated in the presence of palladium, took up two molecules of hydrogen to give a product $C_{18}H_{25}O_2N + {}^1/_2\ H_2O$, which was named β-tetrahydrodesoxycodeine.

$6. The supposed dihydrodesoxycodeine of m. p. 117–119°, source not given, on hydrogenation in the presence of palladium took up one molecule of hydrogen to give a substance which crystallized in leaflets or rods, sintered at 130° and melted at 132°, of which the authors write, "Die Base scheint danach identisch zu sein mit der von Knorr und Waentig aus Desoxykodein durch Reduktion mit Natrium und Alkohol hergestellten und von denselben als Desoxydihydrokodein bezeichneten Base." ("The base appears according to this to be identical with the base prepared by Knorr and Waentig from desoxycodeine by reduction with sodium and alcohol, and designated by them as desoxydihydrocodeine.") Nowhere in Freund's paper is a direct comparison of this substance, which he calls a-tetrahydrodesoxycodeine, with the desoxydihydrocodeine of Knorr mentioned, nor are analytical data on it given.

$7. a-Chlorocodide, hydrogenated in the presence of colloidal palladium, yielded an amorphous alkali-insoluble base which did not crystallize nor give crystalline salts. It analyzed very poorly for dihydrodesoxycodeine $+ {}^1/_2\ H_2O$, and was named α-dihydrodesoxycodeine.

$8. The amorphous so-called a-dihydrodesoxycodeine of $7, on further reduction

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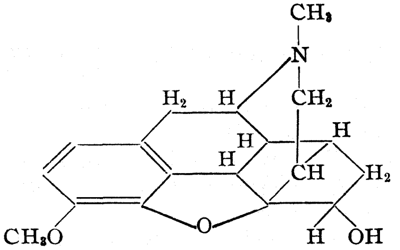
[4] Knorr and Waentig, ***Ber.***, 40, 3860 (1907).

[5] Cahn, *J.* ***Chem.*** *Soc.*, 2572 (1926), found it to sinter at 125° and melt at 134–135°.

[6] Freund. Melber and Schlesinger, *J prakt.* Chem., 101, 1 (1981).

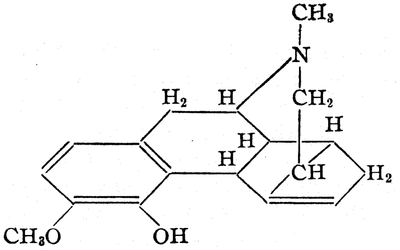
by the electrolytic method, gave a crystalline product of m. p. 131–132°, whose hydrochloride melted at 155°, and methyl ether methiodide melted at 247°. The substance of m. p. 131–132° was considered to be identical with that mentioned under §6, and with Knorr and Waentig's desoxydihydrocodeine.

On the basis of the experimental evidence outlined above, Freund believed that the Knorr and Waentig desoxydihydrocodeine was actually formed by addition of four atoms of hydrogen to desoxycodeine, was *therefore a tetrahydrodesoxycodeine, and isomeric with the β-tetrahydrodesoxycodeine* obtained in \$5. The possibility of the appearance of stereoisomeric tetrahydrodesoxycodeines which might owe their existence to differences in the spatial arrangement of hydrogen at C-14 was not recognized by Freund, nor by Gulland and Robinson[7] in their first publication in this field. Freund[6] used the supposed isomerism of α- and β-tetrahydrodesoxycodeines as a support for the bridge bond formula (VII) for codeine which had already been developed in connection with phenyldihydrothebaine,[8] and represented the formation of the isomers as below, where in Formula VIII reduction was thought to take place in the one case with saturation of Δ^5, and opening of the linkage C-15, C-8 to give IX, in the other case A^S was saturated, but linkage C-15, 6-5 was opened and X resulted.



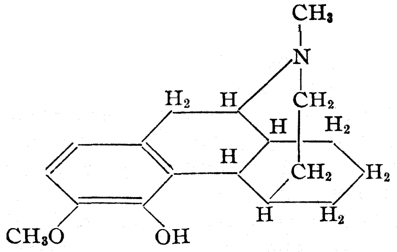
VII

Codeine (Freund 1916)



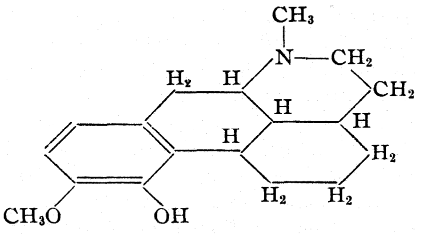
VIII

Desoxycodeine (Freund 1921)[9]



IX

α-Tetrahydrodesoxycodeine



X

β-Tetrahydrodesoxycodeine

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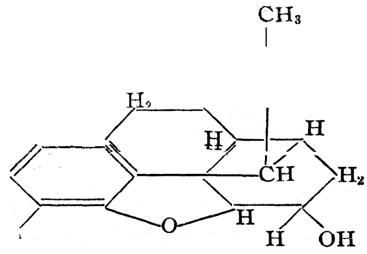
[7] Gulland and Robinson, *J.* Chem. *Soc.*, 123, 980 (1923).

[8] Freund and Speyer, *Ber.*, 49, 1287 (1916).

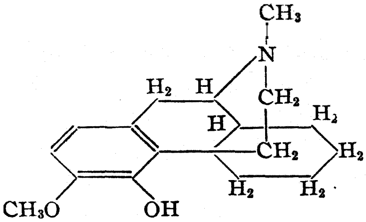
[9] Through a typographical error the double linkage between C-5 and C-6 was omitted in Freund's representation of desoxycodeine in Plate I (to page 9), J. *prakt. Chem.*. 101, 9 (1921).

Gulland and Robinson[10] adopted a similar hypothesis to account for the two tetrahydrodesoxycodeines; in this case C-15 was linked to C-13 and C-8 in codeine (XI), and the change from desoxycodeine to the two tetrahydrodesoxycodeines was explained by rupture of the bond C-15, C-13 or C-15, C-8, respectively. In a later publication by the same authors[11] the possibility of accounting for the isomerism through a stereochemical relationship, analogous to the decahydronaphthalene type of isomerism was recognized, with the implication that a- and β-tetrahydrodesoxycodeines should be represented as in XII and XIII a suggestion which was generally accepted by workers in the field of morphine chemistry.[12]

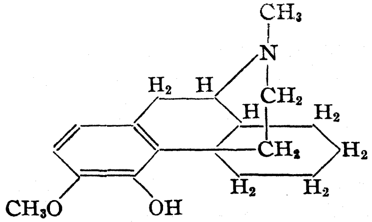


XI

Codeine
(Gulland–Robinson1923)



XII



XIII

In 1926, Cahn[5] conducted an investigation, the purpose of which was to show that the important isomerism of α- and β-tetrahydrodesoxycodeines actually existed. He prepared the supposed a-tetrahydrodesoxycodeine in a hitherto unattained state of purity, showed that it differed from β-tetrahydrodesoxycodeine, *but* failed to demonstrate that it was isomeric *with this* substance.

We find that the so-called a-tetrahydrodesoxycodeine of Freund is not a tetrahydro derivative of desoxycodeine, but is actually a *dihydro*desoxycodeine, as originally claimed by Knorr and Waentig. Hereby is eliminated a troublesome isomerism which has been difficult to explain on the basis of any of the existing structural formulas for morphine.

With the disappearance of the supposed isomerism of the tetrahydrodesoxycodeines, certain other difficultly explicable cases of isomerism in the morphine series, which have been more or less generally considered to be of the tetrahydrodesoxycodeine type, lose an important support. This is

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[10] Gulland and Robinson. J. *Chem. Soc.*, 123, 983 (1923).

[11] Gulland and Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **69, 79** (1925).

[12] *Cf.* Schöpf, *Ann.*, *458*, 164 (1927).

especially true in the case of the isomers of dihydrothebainone, and the suggestion that the relationships in this series may be of the type represented by the tetrahydrodesoxycodeines[13] must be reconsidered.

Dihydrodesoxycodeine-A.—The so-called a-tetrahydrodesoxycodeine, which we will hereafter designate as dihydrodesoxycodeine-A, is formed in good yields by reduction of a-chlorocodide or of desoxycodeine-A with sodium and alcohol, as described by Knorr and Waentig.[4] Following the procedure of Cahn,[5] we purified it exhaustively through the hydrochloride, obtaining constants for this salt nearly identical with those given by this investigator for his purest substance. The free base was precipitated by addition of dilute ammonia to a dilute solution of the hydrochloride, as beautiful snow white crystals, which appeared under the microscope as chains or clumps of diamond-shaped plates. It was recrystallized to constant rotation from dilute methyl alcohol; further purification from acetone did not change the melting point or rotatory power. This base, which sintered at 120–125° and melted at 134–136°, and analyzed for a dihydrodesoxycodeine, $C_{18}H_{23}O_2N + {}^1/_2\,H_2O$, on reduction with hydrogen in the presence of a platinum catalyst *was found to absorb one molecule of hydrogen, to give a quantitative yield of β-tetrahydrodesoxycodeine.* Dihydrodesoxycodeine-A in the form of its hydrochloride of m. p. 158–160° may likewise be hydrogenated, using palladium, to give quantitatively β-tetrahydrodesoxycodeine. This end-product was identified by analysis, rotation, melting point and the melting points of its derivatives, and by its conversion to the crystalline anhydrous β-tetrahydrodesoxycodeine of sharp melting point 123–124' which will be described in our next paper. Since there is but one tetrahydrodesoxycodeine the use of the Greek letter becomes unnecessary, and we will hereafter refer to the β-tetrahydrodesoxycodeine discovered by Freund as tetrahydrodesoxycodeine.

Dihydrodesoxycodeine-A is also obtained in practically quantitative yield when desoxycodeine-B (m. p. 119°),[2] hitherto believed to be a dihydrodesoxycodeine, is reduced with sodium and alcohol. The reduction product was identified not only by melting point and rotation, but by melting point and rotation of the hydrochloride, analysis of the latter, and its further reduction to tetrahydrodesoxycodeine.

It is sufficiently demonstrated in the foregoing paragraphs that the so-called α-tetrahydrodesoxycodeine is non-existent. There remains only an examination of the evidence upon which its supposed existence rested. The confusion of dihydrodesoxycodeine-A with a tetrahydrodesoxycodeine arose primarily from the mistaken conception that the electrolytic re-

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[13] *See,* for example, Gulland and Robinson, *J. Chem. Soc.,* **123,** 984, 1000 (1923); Schöpf and co-workers, *Ann.,* 452, 239, 240 (1927); 458, 155, 159, 164 (1927); Wieland and Kotake, *ibid.,* **444,** 80 (1925). The speculations of Schöpf, *Ann.,* 458, note 2, page 164 (1927), regarding the relationships between the tetrahydrodesoxycodeines and dihydrothebainone naturally become invalid.

duction products from a- and β-chlorocodides (§2 and 3), chlorodihydrocodide (§1) and desoxycodeine-A (§4) were identical, and from an insufficient examination of the end-product of catalytic reduction obtained in §6. Freund (§6) hydrogenated a "dihydrodesoxycodeine, m. p. 117–119°" to a base which was stated to melt at 130–132°. From the fact that one molecule of hydrogen was absorbed he concluded that the product was a tetrahydrodesoxycodeine, which on the basis of its melting point and the shape of its crystals he believed identical with the Knorr and Waentig desoxydihydrocodeine; he claimed that the latter was actually a tetrahydrodesoxycodeine and therefore isomeric with the (β-) tetrahydrodesoxycodeine obtained in §5.

It is certain that Freund obtained in this hydrogenation (β) tetrahydrodesoxycodeine (cf. diagram, page 2238) which when pure melts at 144–145°, but as obtained crude from catalytic reduction of all desoxy- and dihydrodesoxycodeines generally shows a melting point of about 130–133°.[14]

From the electrolytic reduction of a- and β-chlorocodides (§2 and 3), chlorodihydrocodide (§1) and desoxycodeine 126° (§4) Freund obtained bases which all showed the melting point 117–119°, gave no depression in melting point when mixed, and which he regarded as identical. In a repetition of these reductions we find: (a) that a- or β-chlorocodide, on electrolytic reduction, yield a base of m. p. 119°, which is however a desoxycodeine[2] (desoxycodeine-B, which reduces catalytically to tetrahydrodesoxycodeine by addition of two H_2); (b) that chlorodihydrocodide reduces electrolytically to give a dihydrodesoxycodeine, m. p. 111° (which in the crude state shows a melting point of 114–117°); (c) that desoxycodeine-A (126') reduces electrolytically with great difficulty to give dihydrodesoxycodeine-A (m. p. 134–136") in small amounts.

As a result of our experiments it seems very probable that the Freund "dihydrodesoxycodeine 117–119°" which was supposed to have reduced to "a-tetrahydrodesoxycodeine" actually was dihydrodesoxycodeine-C (m. p. 111°) in an impure state, which takes up one molecule of hydrogen to give a quantitative yield of "β-"tetrahydrodesoxycodeine.

Freund claimed further (§8) that an amorphous product which he called "a-dihydrodesoxycodeine" (§7) on electrolytic reduction, gave our dihydrodesoxycodeine-A. We have examined "a-dihydrodesoxycodeine" and find it to consist of a mixture of at least two hydrogenated desoxy-

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[14] No mention is made in Freund's paper of a direct comparison of his 130–132° product with the Knorr–Waentig base. We have found that crude tetrahydrodesoxycodeine, m. p. *ca.* 130–133°, does not depress the melting point (134–136°) of pure dihydrodesoxycodeine-A, and that a mixture of pure tetrahydrodesoxycodeine (m. p. 144–145°) with dihydrodesoxycodeine-A melts at an intermediate temperature (138–140'). This lack of melting point depression in the desoxycodeine series is further discussed under dihydrodesoxycodeine-B.

codeines,[15] one of which reduces electrolytically to give tetrahydrodesoxycodeine (m. p. 144–145°). We are at a loss to explain the hydrochloride of m. p. 155" and methyl ether methiodide of m. p. 247° ($8) which Freund mentions.

We have been able to find in the literature only one other investigation where "α-tetrahydrodesoxycodeine" was claimed as the end-product of reduction. In 1923 Speyer and Krauss,[16] by catalytic reduction of what was then thought to be allopseudochlorocodide but was later[17] shown to be the well-known β-chlorocodide, noted an absorption of three molecules of hydrogen and the formation of the so-called α-tetrahydrodesoxycodeine (which was identified only by the melting point of the methyl ether methiodide). The identical reduction was carried out three years earlier by Mannich and Lowenheim,[18] who found as the products two alkali-insoluble substances, which were named dehydroxydihydrocodeine and dehydroxytetrahydrocodeine. Neither substance resembled "α-tetrahydrodesoxycodeine." We have carried out the hydrogenation of β-chlorocodide with palladium[19] and can confirm the experimental results of Mannich. The absorption of hydrogen amounts to about 2.5 moles, and the only isolable products are a dihydrodesoxycodeine (Mannich's dehydroxydihydrocodeine) to be described below, and the tetrahydrodesoxycodeine of m, p. 144–145° (Mannich's dehydroxytetrahydrocodeine).[20]

The desoxytetrahydropseudocodeine hydrochloride obtained by Speyer and Krauss[21] through reduction of tetrahydropseudochlorocodide and stated to be identical with "α-tetrahydrodesoxycodeine" hydrochloride is too inadequately described to permit of critical discussion. It is obviously impossible that a reduction product of tetrahydropseudochlorocodide can be identical with dihydrodesoxycodeine-A.

There is no convincing evidence in the literature to show that dihydrodesoxycodeine-A has ever been obtained as the final product of catalytic reduction.

Dihydrodesoxycodeine-B.—Dihydrodesoxycodeine-B m. p. 128°, results from the electrolytic reduction of desoxycodeine-C (m. p. 106°, nonphenolic) which was described in the preceding paper. It is a phenolic base, formed by addition of two hydrogen atoms at the 4,5-ether bridge

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[15] The separation of the constituents of the so-called α-dihydrodesoxycodeine will be described in our next paper.

[16] Speyer and Krauss, Ann., 432,233 (1923).

[17] Speyer and Rosenfeld, Ber., 58, 1113 (1925).

[18] Mannich and Löwenheim, *Arch. Pharm.*, 258, 295 (1920).

[19] The reduction of β-chlorocodide with a platinum catalyst will be described in our next paper.

[20] *Cf.* Ochiai, *J. Pharm. Soc. Japan, No. 568,* 91 (June, 1929); Kondo and Ochiai, *Ber.*, 63, 646 (1930).

[21] Speyer and Krauss, Ann., 432,259 (1923).

which must be present in the non-phenolic desoxycodeine-C. Dihydrodesoxycodeine-B differs from dihydrodesoxycodeine-A in its melting point. in its rotation and that of its hydrochloride, and in the melting point of its methiodide. The isomers give no depression in melting point when mixed; we have encountered this phenomenon frequently in this series, as has also Cahn.[22] Dihydrodesoxycodeine-B reduces catalytically, with the absorption of one molecule of hydrogen, to give a quantitative yield of tetrahydrodesoxycodeine.

Dihydrodesoxycodeine-C.—Dihydrodesoxycodeine-C (m. p. 111°) is a phenolic base which is formed when chlorodihydrocodide (XIV) is reduced by the electrolytic method. The crude product from the reduction melts at about 114–117°, a fact which we believe led Freund to confuse it with the base of m. p. 119° from the reduction of a-chlorocodide (see §1 and 6), desoxycodeine-B. Dihydrodesoxycodeine-C differs from desoxycodeine-B not only in melting point and in composition as determined by analysis, but in having a negative rotation, in forming a stable hydrochloride, in the rotation of its hydriodide and in forming a crystalline methiodide. In contrast to desoxycodeine-B, which absorbs two molecules of hydrogen, this base takes up but one molecule of hydrogen, giving tetrahydrodesoxycodeine.

Dihydrodesoxycodeine-D.—The only non-phenolic dihydrodesoxycodeine as yet prepared was first described by Mannich[18] under the name dehydroxydihydrocodeine. He recognized it as a dihydrodesoxycodeine, isomeric with those which had just been reported by Freund in a preliminary communication,[23] but did not demonstrate that it could be further reduced. The base, which we will designate as dihydrodesoxycodeine-D,[24] may be prepared according to the directions of Mannich, by reduction of β-chlorocodide with a palladium catalyst[25] and is most advantageously separated from the other products of the reduction through its beautifully crystallized acid tartrate. The preparation of dihydrodesoxycodeine-D from a-chlorocodide or by methylation of dihydrodesoxymorphine will be described in further papers from this Laboratory.

Dihydrodesoxycodeine-D (XV) must be derived from our desoxycodeine-C (III) by addition of two hydrogens to the one remaining double linkage in the hydroaromatic ring, although for reasons which are probably connected with the position of the double linkage relative to the ether ring[2] this conversion has not yet been experimentally realized.

All attempts to prepare dihydrodesoxycodeine-D by addition of two hydrogen atoms to the double bond in III resulted in unchanged material

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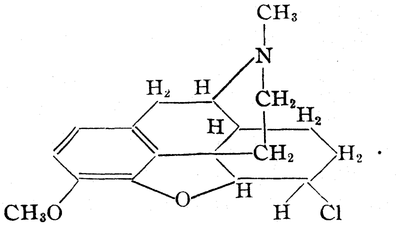
[22] Cahn, J. *Chem. Soc.*, 2567, 2568, 2572 (1926).

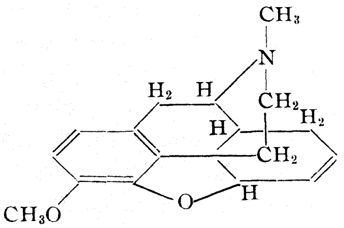
[23] Freund, *Ber. deut. pharm. Ges.*, 29, 110 (1919).

[24] The name employed by Mannich does not correspond to the empirical or structural formula of the compound.

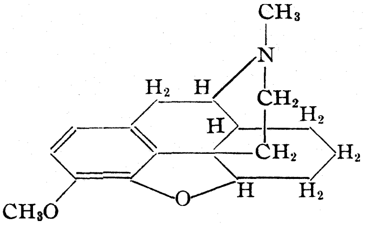
[25] When platinum is used the reduction takes a different course.



XIV
Chlorodihydrocodide



III
Desoxycodeine-C

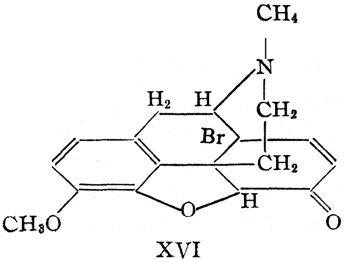


XV
Dihydrodesoxycodeine-D

or in addition of four hydrogens, with reductive scission of the 4,5-ether bridge to give the end-product, tetrahydrodesoxycodeine.

The nature of dihydrodesoxycodeine-D as a dihydrodesoxycodeine is shown by its analyses, and by its further reduction. On treatment with sodium in methyl alcohol, as well as by electrolytic reduction in sulfuric acid, it adds two hydrogen atoms, presumably opening the ether linkage, to give a nearly quantitative yield of tetrahydrodesoxycodeine (VI). This reduction could not be accomplished by the use of catalytic hydrogen.

A fifth dihydrodesoxycodeine, of m. p. 139–140°, which we will designate as **dihydrodesoxycodeine-E**, whose discovery is due to Speyer,[26] has been described. We have verified its preparation by electrolytic reduction of bromocodeinone (XVI), and the fact that it hydrogenates with addition of one molecule of hydrogen to yield tetrahydrodesoxycodeine, as described by Speyer, but wish to leave the further investigation of this base to its discoverer. It must be formed from bromocodeinone (XVI) by reductive elimination of bromine, reduction of the carbonyl to a methylene group and reductive scission of the ether ring.



XVI
Bromocodeinone

The relationships of the various known desoxycodeines and dihydrodesoxycodeines are expressed in the diagram below, which is accompanied by a table showing in condensed form the properties of these compounds. It

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[26] Speyer and Sarre, Ber., 57, 1404 (1924).

is a striking fact that all of the phenolic desoxycodeines and their hydrogenation products crystallize with one-half molecule of water; the two known non-phenolic members, desoxycodeine-C and dihydrodesoxycodeine-D, crystallize anhydrous.

As a result of the experiments described in this and the preceding paper, we believe that there is no evidence in the desoxycodeine series which warrants the assumption of an isomerism due to steric relationships on C-14 of the morphine structural skeleton, and we question seriously the validity of such an assumption in other series where the reality of otherwise unexplainable isomerism is less firmly established than it seemed to be in the case of the supposedly isomeric tetrahydrodesoxycodeines prior to the publication of the present account.

TABULAR SUMMARY

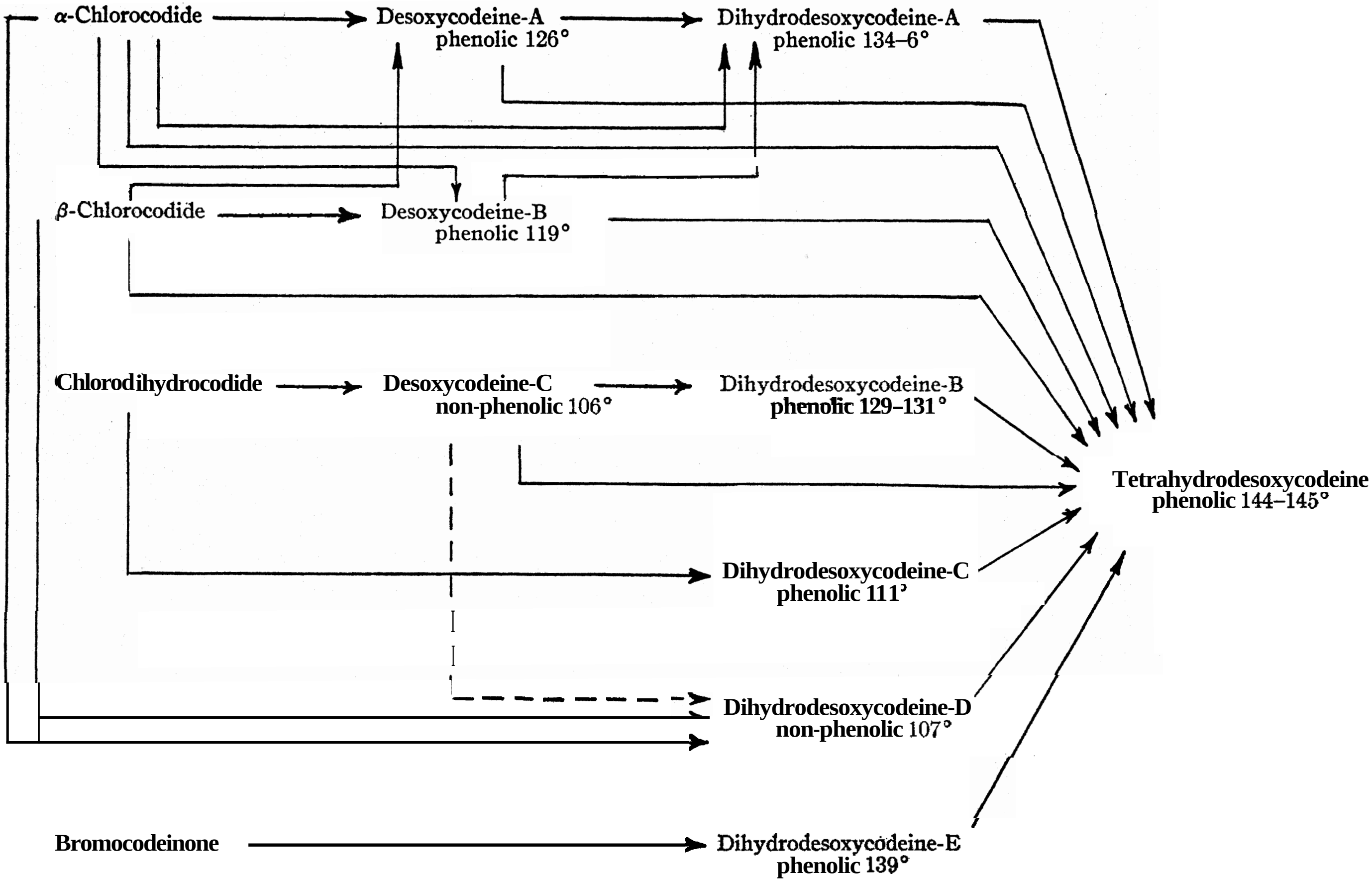
No.	Base	M. p., °C.	$(\alpha)_D$	Hydrochloride M. p. °C.	Hydrochloride $(\alpha)_D$
1	Desoxycodeine-A	ca. 122	+118 1°	ca.270	+ 87°
2	Desoxycodeine-B	119	+ 71.3"	Unstable	......
3	Desoxycodeine-C	106	–197 4°	114	–132.7°
4	Dihydrodesoxycodeine-A	134–136	– 27 1°	158–160	– 41.4'
5	Dihydrodesoxycodeine-B	128–131	–106.9°	154–156	– 76.4°
6	Dihydrodesoxycodeine-C	109–111	– 61 6°	241–242	– 3.fi°
7	Dihydrodesoxycodeine-D	107	– 82 5°	123–125"	– 39.6°[a]
8	Dihydrodesoxycodeine-E	139	+ 58.1°	.....	......
9	Tetrahydrodesoxycodeine	145	– 32.1"	262	......

No.	Hydriodide M. p., °C.	Hydriodide $(\alpha)_D$	Methiodide M. p., °C.	Methiodide $(\alpha)_D$	
1	265	......	.....	.....	Phenolic
2	245	+ 38.3"	Oil	.....	Phenolic
3	160–165	–131.6"	236–240	.....	Non-phenolic
4	242	......	250–251	– 7.5"	Phenolic
5	255–256	– 79.3"	ca. 175	.....	Phenolic
6	242–243	+ 52°	245–246	+ 15.4°	Phenolic
7	250–251	......	256	.....	Non-phenolic
8	.....	......	199	.....	Phenolic
9	241	......	263	.....	Phenolic

[a] Acid tartrate.

Experimental

Dihydrodesoxycodeine-A.—No detailed description of the preparation of the so-called a-tetrahydrodesoxycodeine is given in the literature. We prepared the base as follows: (1) from a-chlorocodide. Ten grams of pure α-chlorocodide was dissolved in 300 ec. of 95% alcohol, and to the boiling solution was added 50 to 60 g. of sodium in pieces of about 0.5 g. During the reduction the addition of three 100-cc. portions of alcohol was necessary. When all sodium was in solution, the mixture was diluted with 400 cc. of water, and concd. hydrochloric acid (about 220 cc.) added until the solution was just acid to Congo red. Most of the alcohol was removed by distillation in vacuum at 30–40°; a large amount of sodium chloride separated in this process, and the hydrochloride of dihydrodesoxycodeine-A, which is only sparingly soluble in saturated sodium chloride solution, precipitated as a yellow oil. The solution was poured off, layered over


α-Chlorocodide
Desoxycodeine-A phenolic 126°
Dihydrodesoxycodeine-A phenolic 134–6°
β-Chlorocodide
Desoxycodeine-B phenolic 119°
Chlorodihydrocodide
Desoxycodeine-C non-phenolic 106°
Dihydrodesoxycodeine-B phenolic 129–131°
Tetrahydrodesoxycodeine phenolic 144–145°
Dihydrodesoxycodeine-C phenolic 111°
Dihydrodesoxycodeine-D non-phenolic 107°
Bromocodeinone
Dihydrodesoxycodeine-E phenolic 139°

with ether, excess of ammonia added and the precipitate extracted. The oily hydrochloride was dissolved in water, treated in the same way, and the ether extracts combined. The ether was shaken out with two 15-cc. portions of normal hydrochloric acid, and then with successive small portions of 0.1 N hydrochloric acid until the acid layer gave no precipitate with Mayer's reagent The hydrochloric acid extract was evaporated to dryness in a vacuum desiccator, leaving a brittle glassy mass, which crystallized immediately on rubbing with absolute alcohol: 8 g. of crude hydrochloride was obtained, of m. p. 148–150°. After five recrystallizations from absolute alcohol this showed the m. p. 158–160° (gas evolution), and gave the value $[\alpha]^{22}_{\mathrm{D}}$ —41.4°: c = 5.289 (water), l = 1 a = —2.19". (Cahn found m. p. 158–159°, $[\alpha]^{17}_{\mathrm{D}}$ —40°.)

Eight and one-half grams of the purified hydrochloride was dissolved in 45 cc. of water, and treated dropwise with normal ammonia. The free base separated in the form of sparkling white flakes, which appeared under the microscope as chains and clumps of diamond-shaped plates. The base was recrystallized four times from dilute methyl alcohol and twice more from acetone. The last three fractions were identical in melting point and rotation. Due to the ease with which the base loses its hydrate water, the melting point is unsharp, as was observed by Cahn. Our purest product sintered and took on a wet appearance at 120–125°, and melted with slight gas evolution at 134–136°; $[\alpha]^{22}_{\mathrm{D}}$ —27.1°, —26.7°: c = 2.472, 2.472 (abs. alcohol), 1 = 2, 1; a = —1.34°, —0.66" (Cahn, m. p. 134–135"; Knorr, $[\alpha]^{15}_{\mathrm{D}}$ —24°).

Anal. Calcd. for $C_{18}H_{23}O_2N + {}^1/_2\, H_2O$: C, 73.43; H, 8.21. Found: C, 73.73, 73.79, 73.67; H, 8.24, 8.31, 8.16.

Attempts to determine the hydrate water failed because of the ease with which the base distils. At 70° in vacuum it slowly sinters together and melts to a colorless liquid, losing its hydrate water but also distilling to a slight extent. The anhydrous glassy solid crystallizes from dry petroleum ether in white granular crystals of unsharp m. p. 76–82"; on exposure to the air, the crystals change in form, and the melting point rises rapidly (after twenty minutes, m. p. 117–118°) until after several hours only the leaflets showing the normal melting point of the hydrated base are present. The base distils readily at 160–170° (1 mm.) as a colorless liquid, solidifying to a glass.

Anal. Calcd. for $C_{18}H_{23}O_2N$: C, 75.74; H, 8.12. Found: C, 75.84; H, 8.22.

(2) Dihydrodesoxycodeine-A from reduction of desoxycodeine-A: 5.5 g. of desoxycodeine-A of m. p. 122–124° was dissolved in 200 cc. of boiling alcohol and reduced with 30 g. of sodium, with addition of 200 cc. more of alcohol as necessary; the product was isolated and purified as in the case of the α-chlorocodide reduction above; 6.1 g. (86% of the calculated yield) of crude dihydrodesoxycodeine-A hydrochloride (m. p. 148–150°) was obtained, which melted with decomposition at 158" after three crystallizations from absolute alcohol.

Anal. Calcd. for $C_{18}H_{23}O_2N \cdot HCl + C_2H_5OH$: C, 65 28; H, 8.22. Found: C 65.10; H, 8.05.

The base precipitated from this hydrochloride and purified from dilute methyl alcohol and acetone sintered at 123–127° and melted at 133–135°; it did not depress the melting point of the product obtained by reduction of a-chlorocodide above. It gave $[\alpha]^{22}_{\mathrm{D}}$ —24.4': c = 4.068 (alcohol), l = 2, a = —1.99'.

(3) Dihydrodesoxycodeine-A from reduction of desoxycodeine-B (m. p. 119–120°): 5 g. of carefully purified desoxycodeine-B[27] was reduced in alcoholic solution with five

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[27] The first time this experiment was carried out using slightly impure desoxycodeine-B, a reduction product of m. p. 126–128" having $[\alpha]_{\mathrm{D}}$ 0° was obtained which was regarded as a new dihydrodesoxycodeine. In the light of our theoretical conclusions, the existence of a fifth phenolic dihydrodesoxycodeine seemed very improbable, and

times its weight of sodium; 4 3 g. of a base of m. p. 120–126° was obtained, which was purified through the hydrochloride until the melting point of the latter was constant at 158–159°. This hydrochloride showed $[\alpha]^{21}_{\mathrm{D}}$ -39.9": c = 2.003 (water), l = 1, a = -0 80° The base precipitated from an aqueous solution of the salt by ammonia melted at 128–129°, $[\alpha]^{21}_{\mathrm{D}}$ -22.6": c = 2.834 (alcohol), l = 2, a = -1.28". These values approach closely our constants for the purest samples of dihydrodesoxycodeine-A and its hydrochloride. Mixed melting points showed no depression.

Anal. Calcd. for $C_{18}H_{23}O_2N{\cdot}HCl + C_2H_5OH$: C, 65.28; H, 8 22, Cl, 9 64. Found: C, 65.34; H, 8.09; Cl, 9.57.

(4) Dihydrodesoxycodeine-A from electrolytic reduction of desoxycodeine-A (compare § 4, page 2229): 5.5 g. of desoxycodeine-A (m. p. 121–122°, $[\alpha]^{22}_{\mathrm{D}}$ $+115.9$°) in 200 cc. of 20% sulfuric acid was reduced electrolytically for nine hours, using a prepared electrode of 60 sq. cm. and a current of 8 amp. The product, worked up as described in our other electrolytic reductions, was obviously a mixture; conversion to the hydrochloride and three crystallizations from absolute alcohol gave a salt of m. p. 155–157°, $[\alpha]^{19}_{\mathrm{D}}$ $+34.6$°, which yielded a base of m. p. 124–128°, $[\alpha]^{19}_{\mathrm{D}}$ $+41.3$°. By laborious fractional crystallization of the hydrochloride it could be shown that the dextrorotation was due to the presence of a large amount of unchanged desoxycodeine-A (3.3 g., m. p 121–122°, $[\alpha]^{21}_{\mathrm{D}}$ $+110$°). The levorotatory fractions finally yielded a base of m p. 126–129°, $[\alpha]^{22}_{\mathrm{D}}$ -18": c = 1.984 (alcohol), l = 2, a = -0 71°, whose hydrochloride melted at 155–157°, $[\alpha]^{20}_{\mathrm{D}}$ -38.5': c = 1.011 (water), 1 = 2, a = -0.78".

Anal. Calcd. for $C_{18}H_{23}O_2N{\cdot}HCl + C_2H_5OH$: *C*, 65.28; H, 8.22. Found: C, 65.36; H, 8.03.

On the basis of the rotations given above (mixed melting points have no significance) we are convinced that this product is identical with dihydrodesoxycodeine-A, but do not consider the point conclusively proved.

Catalytic Reduction of **Dihydrodesoxycodeine-A.—Three** grams of pure dihydrodesoxycodeine-A (the so-called a-tetrahydrodesoxycodeine), prepared by sodium and alcohol reduction of a-chlorocodide, was dissolved in 30 cc. of methanol and shaken under hydrogen in the presence of 0.10 *g.* of platinum oxide. The absorption proceeded rapidly, and in eighteen minutes 265 cc. of hydrogen was taken up (calculated for one mole of hydrogen, 257 cc.). The reduction proceeded very slowly for one hour longer, with an absorption of 35 cc. more, and then stopped completely. The reduction mixture was filtered, brought to the boiling point, and water added slowly; 2.85 g. of crystalline material separated; after one crystallization from acetone it softened at 135°, melted at 143–146°, and evolved gas at 151°. It did not depress the melting point of (β-)tetrahydrodesoxycodeine. The product was further identified by its rotation, $[\alpha]^{19}_{\mathrm{D}}$ -32.9' (c = 1.564 (alcohol), *1* = 2, *a:* = -1.03°), the melting point of its hydriodide, 243–245°, of its methiodide, 263°, and mixed melting points of these derivatives.

Anal. Calcd. for $C_{18}H_{25}O_2N + {}^1/_2H_2O$: C, 72.92; H, 8.84. Found: C, 72.85; H, 8.81.

The reduction product sublimed with loss of its hydrate water to give the anhydrous tetrahydrodesoxycodeine of sharp m. p. 125–126° which will be further described in our next paper.

Catalytic Reduction of Dihydrodesoxycodeine-A Hydrochloride.—2.7 **g.** of pure hydrochloride (from sodium–alcohol reduction of desoxycodeine-A) in 35 cc. of water with 0.4 g. of palladium on barium sulfate took up 190 cc. of hydrogen in thirty-five

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investigation showed that the base of $[\alpha]_{\mathrm{D}}$ 0° showed a levorotation on laborious purification. **The** dextrorotatory persistent impurities do not appear when the desoxycodeine-B employed is purified to constant rotation.

minutes and stopped (calculated for one mole of hydrogen, 188 cc.); 2.5 g. of tetrahydrodesoxycodeine was obtained, which was purified as above described, melted at 143–145°, and had $[\alpha]^{21}_{D}$ −31.8" (c = 1.510 (alcohol), l = 1, a = −0.48°). In a similar reduction, 1.0 g. of dihydrodesoxycodeine-A hydrochloride prepared by sodium and alcohol reduction of desoxycodeine-B took up 85 cc. of hydrogen in thirty minutes (calculated for one mole, 80 cc.). The product was tetrahydrodesoxycodeine, m. p. 1.14–145".

Dihydrodesoxycodeine-B (m. p. 128–131°).—Three grams of desoxycodeine-C (non-phenolic, m. p. 105–106°) in 100 cc. of 20% sulfuric acid was reduced electrolytically, using an electrode of 60 sq. cm. area and a current of 8.2 amp. The reduction was carried out at 5 to 10°, and continued until a test portion was completely soluble in an excess of alkali, usually requiring three to four hours. The acid solution was filtered and treated with a slight excess of ammonia, a red oil separated, which soon solidified and could be collected on a filter. It was dissolved in 20 cc. of boiling alcohol, and water added dropwise until crystallization began. The yield was 2.4 g. of dihydrodesoxycodeine-B, melting at 117–120°. It was converted to the hydriodide, this salt recrystallized from water to constant melting point, and the free base liberated from the hydriodide, then crystallized several times from dilute alcohol. It separated in white flakes of m. p. 128–131°, and showed the rotation $[\alpha]^{20}_{D}$ −106.9° (c = 1.038 (96% alcohol), l = 1, α = −1.11°), $[\alpha]^{20}_{D}$ −69.1° (c = 0.680 (10% acetic acid), l = 1, a = −0.47°). Dihydrodesoxycodeine-B is very soluble in most organic media and soluble in alkali.

Anal. **Calcd** for $C_{18}H_{23}O_2N + {}^1/_2H_2O$: **C,** 73.43; **H,** 8.21. Found: **C,** 73.58, H, 8.19.

Reduction of Dihydrodesoxycodeine-B.—1.1 g. of the base was dissolved in 6 cc. of normal hydrochloric acid, the solution made up to 30 cc. with water, and shaken under hydrogen, using 0.3 g. of palladium–barium sulfate catalyst. In thirty-five minutes 103 cc. of hydrogen was absorbed (calcd. for 1 mole, 95 cc.). It yielded 1.0 g. of product melting at 140–145°, which after purification proved to be identical with tetrahydrodesoxycodeine in every respect, and gave a hydriodide of m. p. 245° and a methiodide of m. p. 265°.

Dihydrodesoxycodeine-C (m. p. 111°).—The starting material for the preparation of this base was chlorodihydrocodide. For the reduction of codeine, platinum oxide was found to be an excellent catalyst, 60 g. of codeine with 0.7 g. of platinum oxide took up 4750 cc. of hydrogen in sixty-five minutes, yielding 60 g. of dihydrocodeine, which was converted to chlorodihydrocodide (yields varying from 85 to 50%) by the method of *Freund*[6]

A solution of 10 g of chlorodihydrocodide in 300 cc. of 20% sulfuric acid was reduced electrolytically, using a current of 8 amp. and an electrode of 60 sq. cm. area, temperature maintained between 10 and 20°. For complete reduction, which was indicated by the alkali solubility of a small test portion, about eight hours was required. The acid reduction solution was filtered, brought to neutrality (litmus) with ammonia, and extracted with ether. The aqueous layer was acidified, and ammonia in excess added dropwise while shaking with ether. The combined ether extract was dried and distilled, yielding a reddish oil which was dissolved in hot alcohol and thrown out crystalline by slow addition of water; m. p. crude, 114–117°. The base was crystallized from dilute alcohol to constant m. p., 109–111°, yield 6 g.; 2.5 g. of tar-like residues was obtained: $[\alpha]^{24}_{D}$ −61.6° (c = 1.591 (96% alcohol). 1 = 1, α = −0.98°).

Anal. Calcd. for $C_{18}H_{23}O_2N + {}^1/_2H_2O$: C, 73.43; H, 8.21. Found: C, 73.30; H, 8.17.

Reduction of Dihydrodesoxycodeine-C.—A solution of 1 g. of the base in 30 cc. of methyl alcohol was hydrogenated in the presence of 0.05 g of platinum oxide. In seventeen minutes 80 cc. of hydrogen was absorbed (calcd. for one mole, 85 cc.). The product of the reduction was identified as "β"-tetrahydrodesoxycodeine by its melting point, 142–144°, its hydriodide of m. p. 245°, and its methiodide, m. p. 260°, none of which showed any depression of melting point with the corresponding "0"-tetrahydrodesoxycodeine derivatives. The reduction product showed the rotation $[\alpha]^{19}_{D}$ −33.1. (c = 1.544 (alcohol), l = 1, a = −0.51°).

Dihydrodesoxycodeine-D (m. p. lor^{o}).—Five grams of β-chlorococide in 100 cc. of 0.3 N hydrochloric acid was hydrogenated in the presence of 1.25 g. of palladium–barium sulfate catalyst.[28] The reduction was complete in two hours, with the absorption of 870 to 920 cc. of hydrogen (calcd. for two moles, 800 cc.). The excess absorption of 10 to 15% above the expected amount is accounted for by the formation of small amounts of tetrahydrodesoxycodeine. The reaction mixture was filtered, the mixed bases precipitated by a slight excess of ammonia, and extracted into ether. The residue from distillation of the ether was dissolved in 30 cc. of water containing approximately the amount of tartaric acid necessary for the formation of the acid tartrate, and cooled to 0°. After several hours the acid tartrate of dihydrodesoxycodeine-D separated nearly quantitatively as beautiful white needles, while the very soluble oily tartrate of tetrahydrodesoxycodeine remained in solution. The crystalline acid tartrate was further purified from hot water, and the base liberated from it with ammonia; yield, 3.5 to 4.0 g. It melts at 106–107°, and shows $[\alpha]^{20}_{D}$ −82.5" (c = 0.866 (96% alcohol), 1 = 2, a = −1.43°), (Mannich, $[\alpha]^{18}_{D}$ −81.47°).

Anal. Calcd. for $C_{18}H_{23}O_2N$: C, 75.74; H, 8.12. Found: C, 75.53; H, 8.22.

The method of preparation, melting point, rotatory power and analysis of dihydrodesoxycodeine-D show its identity with the dehydroxydihydrocodeine of Mannich.[18] The method of separation from tetrahydrodesoxycodeine given above is more effective than that described by Mannich. The tetrahydrodesoxycodeine was isolated from the mother liquors of the tartaric acid treatment by addition of excess ammonia, and purification of the crystalline precipitate from acetone; m. p. 143–145°, $[\alpha]^{25}_{D}$ −32.1° (c = 1.712 (alcohol), l = 1, a = −0.55").

Reduction of **Dihydrodesoxycodeine-D.—Two** grams of the base in 100 cc. of methyl alcohol was reduced with 12.5 g. of sodium, 100 cc. more of methyl alcohol being added during the reduction. The dark mixture was diluted with 150 cc. of water, acidified with hydrochloric acid, and a small amount of tarry material filtered out. The reduction product was isolated by precipitation with ammonia and extraction with ether. and after purification from acetone showed the m. p. 142–145' and did not depress the melting point of tetrahydrodesoxycodeine. The hydriodide melted at 243°, the methiodide at 260–263° and gave no depression with the same derivatives of known tetrahydrodesoxycodeine.

Reduction of 2.0 g. of dihydrodesoxycodeine-Din 250 cc. of 20% sulfuric acid with a current of 6 amp. on a 60 sq. cm. electrode for four hours gave a quantitative yield of tetrahydrodesoxycodeine, m. p. 144–145' (mixed m. p. 144–145").

Dihydrodesoxycodeine-D was regained unchanged from attempted hydrogenation with platinum oxide in methyl alcohol or methyl alcohol-acetic acid, or palladium barium sulfate in dilute hydrochloric acid.

Dihydrodesoxycodeine-E (m. p. 139°).—This was prepared by electrolytic reduction of bromocodeinone as described by Speyer[26] and was found to have the properties given by this author; 1.1 g. of the base in 30 cc. of 0.2 N hydrochloric acid with 0.3 g. of palladium barium sulfate took up 100 cc. of hydrogen (1 mol = 95 cc.) in thirty

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[28] Houben, "Methoden der organ. Chem.," 1925, Vol. II, p. 500; Schmidt, Ber., 52, 409 (1919).

minutes. The product, isolated in the usual way showed the m. p. 143–145°, $[\alpha]^{19}_D$ $-32.6°$ (c = **2.178** (alcohol), 1 = **1**, α = $-0.71°$), and **was** undoubtedly tetrahydrodesoxycodeine.

The salts and alkyl halides of the dihydrodesoxycodeines described above are listed in the following table.

DERIVATIVES OF THE DIHYDRODESOXYCODEINES

Substance	M. p., °C.	$[\alpha]_D$ c t, °C.	Formula	Calcd.	Found
A **Methiodide**[a]	**Brown 245. m. 250–251**	**−7 5°, water, 2 27. 20**	$C_{19}H\ _6O_2NI$	**C. 53 37 H, 6 13**	**C. 53.70 H, 6.27**
B **Hydrochloride**[b]	**154–156 (dec)**	**−76.4°, water. 1.256, 21**	$C_{18}H_{23}O_2N \cdot HCl$	**Cl, 11 03**	**Cl, 11 19**[c]
B Hydriodide[d]	**Sint 244–246, m. 255–256**	**−79 3°, 96% alc., 1.147, 19**	$C_{18}H_{23}O_2N \cdot HI$	**I, 30 72**	**1, 30 87**
B Methiodide[e]	**About 175**		$C_{19}H_{26}O_2NI$	**1, 29.71**	**I. 29.79**
C Hydrochloride[f]	Sint. 157–163, **m. 241–242**	**−3 6°, water, 2 345, 20**	$C_{18}H_{23}O_2N \cdot HCl$	**Cl, 11.03**	**Cl, 10 97**
C Hydriodide[g]	**242–243**	+52°, +51 6°, **water, 0 980, 1 666, 22**	$C_{18}H_{23}O_2N \cdot HI$	**I, 30.72**	**I, 30.66**
C Methiodide[h]	**245–246**	**+15.4°, 96% alc., 1 298, 21 5**	$C_{19}H_{26}O_2NI$	**I, 29 71**	**I, 30 19**
D **Acid tartrate**[i]	**123–125**	**−39 6°, water, 1 793, 30**	$C_{18}H_{23}O_2N \cdot C_4H_6O_6$	**C, 60.65 H, 6 71**	**C, 60 50 H, 6 87**
D Hydriodide[j]	**250–251 (dec)**		$C_{18}H_{23}O_2N \cdot HI$	**I, 30 72**	**I. 30 88**
D Methiodide	**256**				

[a] Precipitated from methanol solution with absolute ether, purified from water, white crystals. The methiodide degrades to a crystalline methine base which will be described in a later paper. [b] Precipitated as white crystals by addition of alcoholic hydrogen chloride to a hot absolute alcohol solution of the base. [c] Subst. dried in vacuum at 100°. [d] Purified from water, long white needles. [e] Cryst. from water, white needles. [f] Base in hot absolute alcohol with alcoholic hydrogen chloride; white crystals from absolute alcohol. [g] Purified from water, white prisms. [h] Excess methyl iodide boiled out of methanol solution, this diluted with an equal volume of water, and methanol distilled off; white needles separated on cooling. [i] **7.0** g. of base in **50** cc. of hot water with **4.0** g. of d-tartaric acid; recrystallized from water; soluble **4.5** g. in **100** cc. of water at 28°. [j] Crystallized from water in long yellow needles. The corresponding hydrochloride could not be obtained crystalline.

Summary

1. An exhaustive investigation of the dihydrodesoxycodeines has resulted in the preparation of certain new dihydrodesoxycodeines, and in a clarification of the confused and incorrect statements in the literature. The compound resulting from reduction of a-chlorocodide or of desoxycodeine-A with sodium and alcohol is shown to be a dihydrodesoxycodeine, and not a tetrahydrodesoxycodeine as heretofore believed. The important supposed isomerism of a-tetrahydrodesoxycodeine and β-tetrahydrodesoxycodeine which has exerted a strong influence on theories of morphine structure does not exist. The significance of this fact for other cases of isomerism believed to be of the same type, is pointed out.

2. The derivation of dihydrodesoxycodeine-A from desoxycodeine-B (formerly thought to be a dihydrodesoxycodeine) is demonstrated.

3. Dihydrodesoxycodeine-B, the electrolytic reduction product from desoxycodeine-C, is described, and its relationship to tetrahydrodesoxycodeine shown.

4. Dihydrodesoxycodeine-C, from electrolytic reduction of chlorodihydrocodide, is correctly described, and its relationship to tetrahydrodesoxycodeine shown.

5. The preparation of dihydrodesoxycodeine-D by catalytic reduction of β-chlorocodide is described, its relationship to the non-phenolic desoxycodeine-C pointed out, and its further reduction to tetrahydrodesoxycodeine accomplished.

6. The existence of dihydrodesoxycodeine-E is verified.

7. There is no evidence in the desoxycodeine series justifying the assumption of stereoisomerism due to spatial relationships on C-14. Until the existence of such an isomerism in the desoxycodeine or other series of morphine derivatives is demonstrated, it is improbable that more than six desoxycodeines can exist (three of which are known), and five dihydrodesoxycodeines, all of which have been described.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 69]

CONDENSATIONS BY SODIUM INSTEAD OF BY THE GRIGNARD REACTION. I. TERTIARY CARBINOLS

BY AVERY A. MORTON AND JOSEPH R. STEVENS

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Sodium and magnesium show many similar properties in organic reactions, for example, in the Wurtz–Fittig synthesis, in the formation of pinacones, and in the condensation of acetylene derivatives. Many investigators[1] have observed the behavior of metal alkyls and aryls which may be likened to that of the Grignard reagent. The literature[2] also indicates that sodium may be used in mixtures of the halide and carbonyl compounds[3]

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[1] Among others see Frankland, *J. Chem. Soc.*, 13, 191 (1860); Acree, *Am. Chem. J*, 29, 588 (1903); Schorigin, *Ber.*, 41, 2711 (1908); *ibid.*, 43, 1938 (1910); Schlenk and Ochs, *ibid.*, 49, 608 (1916); Schlenk and Holtz, *ibid.*, **50**, 262 (1917); Schlubach, *ibid.*, 52, 1910 (1919); Ziegler and Schnell, *Ann.*, 437, 227 (1924); Ziegler and Colonius, *ibid.*, 479, 135 (1930).

[2] For reactions run without isolation of an intermediate aryl and alkyl see (a) Kekulé, *Ann.*, 137, 181 (1866); (b) Frey, *Ber.*, 28, 2515 (1895); (c) Acree, *Am. Chem. J.*, 29, 588 (1903); (d) Schorigin, *Ber.*, 40, 3114 (1907); (e) Schorigin, *ibid.*, 41, 2711 (1908); (f) Nagai, Ogata and Takata, *J. Pharm. Soc. Japan*, No. 407, 3; *Chem. Abstracts*, 10, 1186 (1916); (g) Blicke, THIS JOURNAL, 46, 2560 (1924); 47, 229 (1925); (h) Rodd and Linch, *J. Chem. Soc.*, 2174 (1927).

[3] Schorigin, *Ber.*, 40, 3111 (1907), has definitely stated that the halogen alkyls react with esters or acid chlorides in the presence of sodium in a manner similar to the behavior of the Grignard compounds. His conclusion is based on a limited number of experiments which included bromides only, and the aromatic esters and acid chlorides.

to give the same product as if the condensation had been brought about through the intermediate formation of a metal alkyl or aryl. We have begun, therefore, a systematic study of the use of sodium in such condensations as are commonly brought about step-wise through the Grignard reagent. Our work brings out several points which deserve special consideration. Thus very good results are obtained with chlorobenzene.[4] In fact, in the preparation of triphenylcarbinol from chlorobenzene and ethyl benzoate in the presence of sodium, neariy theoretical yields of crude material were obtained. This is in striking contrast to the great difficulty of causing any reaction between chlorobenzene and magnesium.[5] Again we may use solvents other than anhydrous ether. This fact has been observed before[2a,e,h] but has never been properly emphasized. We have obtained very good yields of triphenylcarbinol in benzene and in gasoline. One other very important point is the simplicity of carrying out the reaction. In contrast to the common practice with magnesium, which includes the initial preparation of the Grignard reagent followed by the addition of the carbonyl compound and the long period of refluxing and stirring necessary to complete the reaction, we obtain the carbinol by putting the organic halide, the carbonyl compound and sodium together in a bottle with ether, benzene, or other suitable solvent and setting aside for a day or such time as is necessary for the sodium to disappear completely.

In this paper we describe the preparation of triphenylcarbinol from phenyl halides with ethyl benzoate, diethyl carbonate, or diethyl oxalate and sodium. We also record a few experiments on the synthesis of some aliphatic and mixed tertiary carbinols, using reagents such as ethyl propionate and diethyl ketone, compounds which might be expected to enolize or polymerize in the presence of sodium. No attempt has been made to obtain maximum yields by this method. The work is intended to show the strength of sodium as a condensing agent, particularly in its action with chlorides. Without doubt a study of optimum conditions for some of these reactions would lead to good preparative methods.

We are continuing our studies in the use of sodium in condensations commonly carried out by the Grignard reaction, stressing those conditions in which its use appears to be of considerable advantage, *viz.*, the use of chlorides and of solvents other than ether. The more powerful action of

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[4] The observation that chlorides may be used with sodium in these condensations has been made only once before by Rodd and Linch,[2h] who condensed chlorobenzene, chlorotoluene and similar compounds with Michler's ketone to form dyestuffs.

[5] Gilman and St. John, *Rec. trav. chim.*, 49, 717 (1930), and Gilman and Brown, THIS JOURNAL, 52, 3330 (1930), have published methods for improved yields of phenylmagnesium chloride from magnesium and chlorobenzene but the processes involve either very long heating to initiate and complete the reaction or heating in the absence of a solvent to 150–160° for three hours.

the sodium enables one to synthesize tertiary carbinols such as tribiphenylcarbinol, which have hitherto been prepared by a very long procedure, and to obtain organic acids from the reaction of carbon dioxide with chlorides. We have also studied the reaction with nitriles. The details of these and other reactions will be published in succeeding papers.

Experiments

The results in the preparation of triphenylcarbinol are grouped in Table I. The procedure was somewhat similar in all of these cases. The halide, carbonyl compound and sodium were usually put into a bottle or flask with the solvent. The container was then stoppered tightly and the mixture set aside until the sodium had reacted or longer. At the beginning some heat was evolved. It was therefore desirable to set the container in cold water for a time, although this was omitted frequently. When the reaction was completed the contents were decomposed with water (usually a little alcohol was added first to decompose any unchanged sodium) and the mixture steam distilled. Crude triphenylcarbinol was obtained in the residue, which was spread out on paper and left to dry. This crude carbinol

TABLE I

REACTIONS

Halide	Mole	Carbonyl compound	Mole	Sodium, mole	Solvent	Cc.	Time	Crude triphenylcarbinol, %
Chlorobenzene	0 2	Ethyl benzoate	0 1	0.4"	Ether	200	2 Days	73
Chlorobenzene	.2	Ethyl benzoate	.1	$.4^{b}$	Ether	200	2 Days	60
Chlorobenzene	.06	Methyl benzoate	.03	$.12^{a}$	Ether	25	2 Days	75
Chlorobenzene	.2	Ethyl benzoate	.1	$.4^{c}$	Ether	200	6 Days	98
Bromobenzene	.2	Ethyl benzoate	.1	$.4^{c}$	Ether	200	6 Days	98
Iodobenzene	.2	Ethyl benzoate	.1	$.4^{c}$	Ether	200	6 Days	85
Chlorobenzene	.2	Ethyl benzoate	.1	$.43^{c}$	Benzene	200	8 Days	84
Chlorobenzene	4.5	Ethyl benzoate	1.0	4^{a}	Gasoline	2000	3^{d} Week	67
Chlorobenzene	0 1	Diethyl carbonate	0.33	0.2"	Ether	200	24 Hours	23
Chlorobenzene	.12	Diethyl oxalate	.02	$.12^{a}$	Ether	200	4 Days	19
Bromobenzene	.02	Benzyl[6] benzoate	.01	$.022^{a}$	Ether	20	2 Days	38

[a] Sodium sand. [b] Single lump of sodium. [c] Sodium wire 1½ mm. O. D. [d] Because of the larger quantity and the heat evolved, the sodium wire was added in four portions at intervals of two days.

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[6] This experiment was suggested by the fact that Blicke, THIS JOURNAL, 46, 2560 (1924), obtained some triphenylcarbinol from bromobenzene, benzaldehyde and sodium. He also obtained benzyl benzoate from the reaction, which, as seen by our experiment, may have caused the formation of his triphenylcarbinol.

undoubtably contained some solvent and diphenyl. That it was chiefly the carbinol, however, is shown by the fact that in every case except in the product obtained from the reaction in gasoline, a single digestion with a small quantity of alcohol gave a product melting at 160° or better.

In Table II we have grouped the results obtained in the preparation of a few other tertiary carbinols. These experiments were intended to show that sodium could be used with aliphatic compounds in spite of the great tendency of the latter to enolize and condense with themseives. The runs were made with the bromide since at this stage of the work we held to the prevailing prejudice that chlorides were rather unreactive. As in the case of the preparation of triphenylcarbinol, no attempt was made to obtain optimum conditions. The solvent was 200 cc. of anhydrous ether. The reaction flask was set in an ice-bath and the mixture stirred for seven hours, after which the mass was allowed to stand overnight; 0.2 mole of sodium was used in each experiment. The usual method of isolation was to decompose the product with water, dry the ether layer over potassium carbonate and distil the product.

TABLE II

RESULTS IN PREPARATION OF TERTIARY CARBINOLS

Halide, 0.1 mole	Carbinol compound, 0.1 mole	Product	%
Bromobenzene	Diethyl ketone	Phenyldiethylcarbinol[a]	25
Ethyl bromide	Diethyl ketone	Triethyl carbinol[b]	17
Ethyl bromide	Ethyl propionate	Triethylcarbinol[b]	9
Ethyl bromide	Benzaldehyde	Phenylethylcarbinol[c]	14

[a] Boiling point 221–229°. Klages, *Ber.*, 36, 3692 (1903), records 223–224°. Distillation with a trace of hydrochloric acid formed the unsaturated compound, 3-phenylpentene-2, b. p. 104–107°. Klages records 107–108°.

[b] Boiling point 135–142°. Weigert, *Ber.*, 36,1009 (1903), records 142". When distilled with oxalic acid the unsaturated compound (b. p. 95–97°) was formed. Saytzeff, *J. prakt. Chem.*, [2] **57**, 39 (1898), records 97–98" for 3-ethyl pentene-2.

[c] Boiling point 208–214". Phenylethylcarbinol boils at 212° as shown by Schorigin, ***Ber.*, *41*,** 2721 (1908). When distilled from oxalic acid an unsaturated liquid (b. p. 175–177) was obtained. *Sym.*-phenylmethylethylene is reported by Klages, *Ber.*, 36,2574 (1903), as boiling at 177°.

Conclusions

A systematic study of the use of sodium as the condensing agent in reactions hitherto considered typical of magnesium through the Grignard reagent has been started.

Sodium has been found to be better than magnesium in the preparation of triphenylcarbinol in that chlorobenzene can be used, solvents other than ether are permissible and the reaction can be carried out in one step.

The preparation of some aliphatic and mixed tertiary carbinols by means of sodium is described.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SHARP & DOHME, INC.]

PALLADIUM CATALYST. II. THE EFFECT OF HYDROGEN CHLORIDE IN THE HYDROGENATION OF ISONITROSO KETONES

BY WALTER H. HARTUNG

RECEIVED MARCH 9, 1931 PUBLISHED JUNE 8, 1931

It has been shown that benzaldoxime and benzonitrile when reduced catalytically, with palladium on charcoal, form pure primary benzylamine if the proper amount of hydrogen chloride is present, whereas in the absence of the acid a mixture of primary and secondary bases results.[1]

Profiting by this knowledge it has been possible to prepare a series of amino alcohols of considerable physiological interest by reducing isonitroso ketones of the general formula ARCOCR=NOH under similar conditions. The oximino ketone is dissolved in absolute alcohol containing three equivalents of hydrogen chloride and is then agitated with the catalyst in an atmosphere of hydrogen until reduction practically ceases. Under these conditions all isonitroso ketones in which the aromatic portion is a hydrocarbon radical, that is, is phenyl, *m*- and *p*-tolyl, naphthyl, the reduction goes smoothly and completely to the corresponding amino alcohol.[2] In those cases where the aromatic portion of the molecule is substituted by a phenolic hydroxyl or its methyl ether, the reduction stops at the amino ketone stage and the resulting compound may be isolated and purified, as its salt, and then in aqueous solution and with new catalyst reduced to the corresponding amino alcohol. The reduction of the phenolic compounds will be described in a subsequent paper, the reason for mentioning them at this time being to emphasize the fact that in each case pure primary amine is obtained.

A second point is that under the conditions employed the oximino group apparently is a readier receptor for hydrogen than is the ketonic portion. This is shown not only in the case of the phenolic derivatives but also with isonitrosoacetophenone and in isolated cases with isonitrosopropiophenone.

Isonitrosoacetophenone, as already described,[2] is as a rule first hydrogenated to the corresponding intermediate amino ketone stage. With isonitrosopropiophenone the rule is for the reduction to proceed to the corresponding amino alcohol, but in several instances out of many only two-thirds of the calculated hydrogen was taken up and the product when isolated proved to be pure hydrochloride of phenyl-α-aminoethyl ketone, $C_6H_5COCH(CH_3)NH_2{\cdot}HCl$. Hence the evidence would seem quite conclusive that under the conditions here employed, of the two groups capable of being hydrogenated the oximino is the more susceptible.

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[1] Hartung, THIS JOURNAL, 50, 3370 (1928).

[2] Hartung and Munch, *ibid.*, 51, 2262 (1929); Hartung, Munch, Deckert and Crossley, *ibid.*, 52, 3317 (1930).

In neutral alcoholic solution, that is, in the absence of hydrogen chloride, the product isolated from the reduction of isonitrosoacetophenone was 2,5-diphenylpyrazine. But as already explained[2] this end-product results in the following manner

$$\text{Isonitrosoacetophenone} \longrightarrow \omega\text{-aminoacetophenone} \xrightarrow[\text{condensation}]{\text{spontaneous}}$$

$$\text{diphenyldihydropyrazine} \xrightarrow[\text{O}_2]{\text{atmosphere}} \text{diphenylpyrazine[3]}$$

that is to say, reduction in this case takes place at the oximino group, which is quite what one might expect in view of the foregoing discussion.

The hydrogenation of higher homologs in the absence of acid, however, follows a course that is most strikingly different, one which while theoretically possible was not anticipated because of the results already described.

A product obtained by the reduction of isonitrosopropiophenone, melting at 108–110° has been described as of unknown composition.[2] In a personal communication Dr. D. Holroyde Hey, of the University of Manchester, suggested that this product might be the oxime of phenylacetylcarbinol. Comparison with known phenylacetylcarbinol oxime supplied by him[4] indicated the correctness of this suggestion and preparation of the corresponding semicarbazone lent confirmation. This could mean only one thing, *viz.*, that in this instance the ketonic carboxyl was affected and the oximino group remained unchanged. Further proof of this was found in the fact that products similarly obtained from isonitrosobutyrophenone and isonitrosohexanophenone, hitherto also unidentified, turned out to be the oximes of phenylpropionylcarbinol and phenylvalerylcarbinol, respectively.

In neutral absolute alcoholic solution hydrogen absorption does not, as a rule, cease when one molar equivalent has been taken up, nor does it continue until three molar equivalents, the amount necessary for complete reduction to the amino alcohol, have been used. However, when reduction is stopped, of itself or deliberately, after somewhat more than one equivalent of hydrogen has been taken up, the yield of carbinol ketoxime is a maximum, approaching theory, although other products are also formed. On the other hand, if hydrogenation proceeds to any great extent beyond this point, the amount of carbinol ketoxime becomes proportionately less and the quantity of other products becomes correspondingly greater. These other products have been identified as an ammonia (odor) and a mixture of primary, secondary and tertiary amines, separated according to Hinsberg's classical method with benzenesulfonyl chloride.

Such results indicate that under these conditions the first product is that in which the ketonic carbonyl is reduced to the carbinol, and then if further

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[3] Compare also references 16, 17, 18 and 19 cited in Ref. 2.

[4] Hey, J *Chem. Soc.*, 232 (1930).

reduction does occur, the oximino group is affected, and it, in the absence of hydrogen chloride, behaves quite as one might expect from the results of previous experimenters with oximes,[5] that is, it forms primary contaminated with secondary and tertiary amines.[6]

Another striking difference between reduction in neutral medium as compared to that in a solution containing hydrogen chloride is in the rate of hydrogen absorption. This is shown in Fig. 1, by the two representative curves. The conditions were identical except that in one three equivalents of hydrogen chloride were used, and in this one practically three times as much hydrogen was taken up in about one-third the time as in the other.

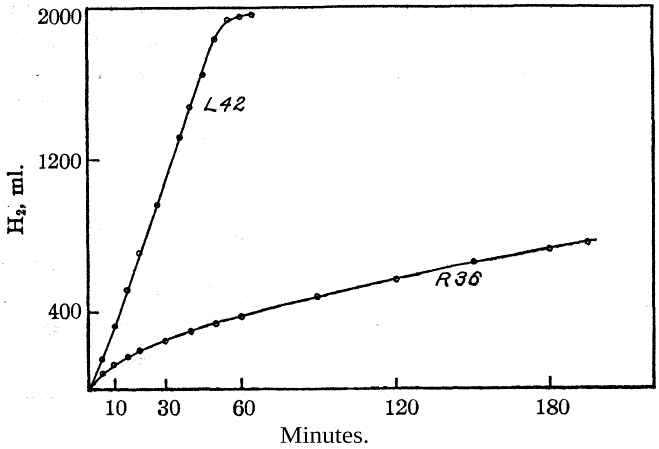
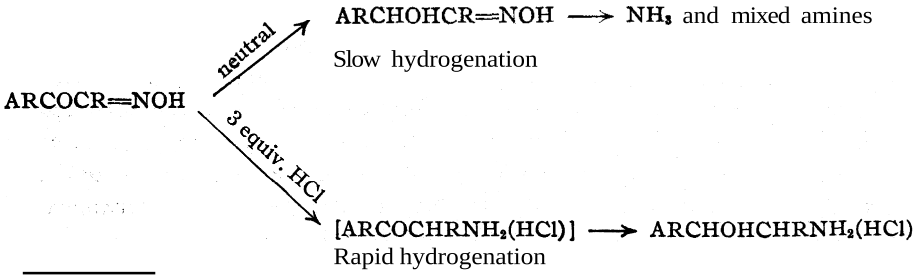


Fig. 1.—Curves showing difference in rates and extent of hydrogenation in absence and presence of hydrogen chloride. In each instance 4.9 g. of isonitrosopropiophenone (0.03 mole) in 100 ml. of absolute alcohol was used. R36 represents reduction in neutral medium and L42, in presence of 0.09 mole of hydrochloric acid.

In substance, then, the reduction of isonitroso ketones in absolute alcoholic solution may follow one of two courses



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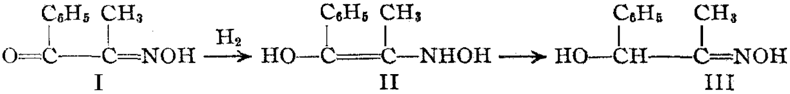
[5] See references 1, 2, 3, 4 and 5 in Ref. 1.

[6] It is of interest to note, in this connection, that Adkins and Cramer [THIS JOURNAL, 52, 4349 (1930)], with their nickel catalyst in neutral solvent, obtained pure primary amines from o-tolunitrile and isonitrosopropiophenone.

and the influence of the hydrogen chloride becomes apparent in three distinct ways. First, it is responsible for the hydrogenation of the oximino portion; second, it has a marked effect on the rate of hydrogenation; and, third, it prevents formation of contaminating secondary and tertiary bases.

In discussing the formation of the oxime of phenylacetylcarbinol, Hey[4] suggests that this need not "necessarily signify that the oximino group is less susceptible to the action of the reducing agent," for he postulates 1,4-addition with a subsequent rearrangement of the intermediate hydroxylamino-alkenol (II) to the carbinol oxime (III)



$$O{=}\overset{C_6H_5}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}NOH \xrightarrow{H_2} HO{-}\overset{C_6H_5}{\overset{|}{C}}{=}\overset{CH_3}{\overset{|}{C}}{-}NHOH \longrightarrow HO{-}\overset{C_6H_5}{\overset{|}{CH}}{-}\overset{CH_3}{\overset{|}{C}}{=}NOH$$

Such an hypothesis is inadequate in that it does not show how the first intermediate (II) rearranges to form, in the presence of hydrogen chloride and after addition of another mole of hydrogen, the amino ketone ($ArCOCHRNH_2{\cdot}HCl$); and it fails to take into account the difference in rates of hydrogen absorption in neutral and acid media.

An explanation, not inconsistent with experimental results, might be given as follows. The oximino ketone and the hydrogen chloride form *a* complex or compound in which the electronic structure is so shifted as to make the oximino portion very susceptible to the entry of hydrogen. In the case where the aryl is a hydrocarbon, the susceptibility of the ketonic carbonyl may be unaffected or possibly also increased. If the aryl contains a phenolic hydroxyl or a methoxy group, this group may modify the degree but not the nature of this shift induced by the acid, so that the susceptibility of the carbonyl to reduction is reduced. Such an explanation is conceivable and does not complicate the picture.

Experimental

The apparatus and procedure for reduction have been described in the preceding papers. The only modification that need be mentioned is that the reaction flask was wrapped in a towel so that hydrogenation proceeded in the dark. Evidence, not yet conclusive, indicates that light may have an inhibiting effect; hence, in order to maintain external conditions as reproducible as possible the reduction was carried out in the wrapped flask.

Oxime of Phenylpropionylcarbinol, $C_6H_5CHOHC({=}NOH)C_2H_5$.—Isonitrosobutyrophenone, 8.9 g., in 100 ml. of absolute alcohol, took up 950 ml. of hydrogen during 445 minutes. The catalyst was filtered off and the solvent evaporated under reduced pressure over sulfuric acid, leaving a yellow crystalline residue. After crystallization first from benzene and then from benzene–petroleum ether (60:40), the gray crystals began to sinter at 92° and melted at 97°.[7]

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[7] Tiffeneau and Lévy, *Bull. soc. chim.*, 37, 1247 (1925).

Oxime of Phenylvalerylcarbinol, $C_6H_5CHOHC(=NOH)C_4H_9$ -Products obtained four years ago by the hydrogenation of isonitrosohexanophenone in neutral absolute alcoholic solution were recrystallized from toluene and melted at 97° (corr.).[8]

Oxime of **Phenylacetylcarbinol,** $C_6H_5CHOHC(=NOH)CH_3$ ----Only two representative experiments will be given.

Experiment R *36* (see Fig. 1). Three-hundredths mole (4.9 g.) of **isonitrosopropiophenone** in 100 ml. of absolute alcohol absorbed 760 ml. of hydrogen (0.0338 mole) during the course of 195 minutes. The catalyst was filtered off and the solvent evaporated. The larger portion of the residue, after recrystallization from toluene, was identified as the oxime of phenylacetylcarbinol, m. p. 113° (corr.). The toluene mother liquors were extracted with dilute hydrochloric acid; the acid extract on benzoylation formed a small amount of crystals which were very soluble in toluene, but could be forced from it by means of excess petroleum ether. These crystals formed an opaque melt at 164° (corr.) and are suspected of being a derivative of secondary amine. The benzoyl derivative of phenylpropanolamine melts at 143.5° (corr.).[9]

Experiment R 53. A twentieth mole (8.2 g.) of isonitrosapropiophenone in 100 cc. of absolute alcohol behaved as follows.

Hydrogen, ml.	Time, min.	Rate/min.	Hydrogen. ml.	Time, min.	Rate/min.
190	10	19	Fortified catalyst by adding 0.1 g. of $PdCl_2$		
410	30	10	1520	300	4
610	60	6	1900	450	3
870	120	4	Added 0.1 g. of $PdCl_2$		
1170	210	3	2010	480	3.7
			2060 (0.0915 mole)	510	1.7

The catalyst was filtered off. The filtrate had in it the odor of ammonia. The solvent was evaporated and the residue was taken up in hot toluene. On cooling, crystals settled out (4.1 g.), which were identified as phenylacetylcarbinol oxime. The toluene mother liquors were extracted with dilute hydrochloric acid to extract the bases. These were treated with benzenesulfonyl chloride in order to separate them by the well-known method of Hinsberg.[10] The derivative of the primary amine (1 g. isolated) after crystallization from toluene melted at 127° (corr.), agreeing with the corresponding derivative prepared from known phenylpropanolamine. The derivative which should be from the secondary amine was a brown, amorphous solid. By filtering it in hot dilute alcoholic solution through charcoal, it was possible to obtain a yellow-brown product of indefinite crystalline form that melted at 110° (uncorr.). The composition of this substance is unknown. Analysis showed it to contain 4 42% nitrogen, whereas $(C_6H_5CHOHCH—CH_3)_2NSO_2C_6H_5$ should contain but 3.3% nitrogen.

The tertiary amine was isolated by extracting it from ethereal solution with dilute hydrochloric acid and evaporating this in *vacuo* over sulfuric acid and finally over phosphorus pentoxide. The residue began to sinter at 82° and melted at 88° (corr.). Its identity is also unknown. It contained 4.63% nitrogen, while the calculated nitrogen content for $(C_6H_5CHOHCH—CH_3)_3N \cdot HCl$ is 3.07%.

Hydrolysis of the oxime of phenylacetylcarbinol by warming with dilute acid gave good yields of the corresponding ketone alcohol.

Phenyl-α-aminoethyl ketone hydrochloride was obtained in one instance in very

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[8] Tiffeneau and Lkvy give the melting point 95–96'.

[9] Schmidt, ***Arch. Pharm.***, 255, 147 **(1917),** describes $C_6H_5CHOHCH(CH_3)NHCOC_6H_5$ as melting at 142°.

[10] Hinsberg, ***Ber.***, 23, 2962 (1890); 33,3526 (1900).

pure form. A catalyst, double the regular size, was being used for the third time to reduce 65.2 g. of isonitrosopropiophenone; initial hydrogen absorption was 90 ml./min; at the end of 220 minutes the rate was still 30 ml./min., but since 18,400 ml. of hydrogen had been taken up, that is, a slight excess over that calculated to give amino ketone, the reduction was purposely stopped at this point. The resulting product was purified by forcing it out of absolute alcoholic solution with ether and formed the characteristic red decomposing melt at 183.5° (corr.).[11]

Summary

The effect of the presence of hydrogen chloride during the hydrogenation of a-oximino ketones, by means of palladium catalyst, has been described. The effect is manifested in three distinct ways. (1) It promotes the reduction of the oximino group. (2) It increases many fold the rate of hydrogenation. **(3)** It prevents the formation of contaminating secondary and tertiary bases.

BALTIMORE, MARYLAND

[CONTRIBUTION PROM THE FRICK CHEMICAL LABORATORY OP PRINCETON UNIVERSITY]

DERIVATIVES OF OPTICALLY ACTIVE TRIARYLCARBINOLS AND THEIR HALOCHROMIC SALTS[1]

BY EVERETT S. WALLIS

RECEIVED MARCH 12, 1931 PUBLISHED JUNE 8, 1931

Shortly after Gomberg's discovery of triphenylmethyl, Norris and Sanders[2] made the interesting observation that colorless triphenylchloromethane forms a dark brown crystalline salt with aluminum chloride of the formula $(C_6H_5)_3CCl\cdot AlCl_3$. Kehrman and Wentzel[3] soon showed that this was a general property of triphenylchloromethane and they prepared double compounds with other metallic salts. Since then many investigators[4] have studied these halochromic salts, and today we have **a** large number of colored double compounds of triarylmethyl halides with metallic salts, acids and halogens.

The question as to the constitution of these compounds and related substances such as the triarylmethyls and triphenylmethane dyes has long been debated. The problem has been approached both from the experimental and theoretical sides in the hope that a simple explanation for the color **and** salt-like nature of these compounds could be found. Following the observation that colorless triphenylchloromethane dis-

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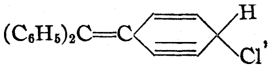
[11] Beilstein, 3d ed., Vol. III, supplement, p. 112.

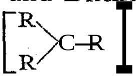
[1] Presented before the Organic Division of the Atnerican Chemical Society in Indianapolis, Indiana, April, 1931.

[2] Norris and Sanders, *Am. Chem.* J, 25, 54, 117 (1901).

[3] Kehrman and Wentzel, *Ber.*, 34, 3818 (1901).

[4] Gomberg, *ibid.*, 35, 1822 (1902); Baeyer, *ibid.*, 38,1162 (1905); Tschitschibabin, *ibid.*, 40, 1817 (1907); Meyer, *ibid.*, 41, 2576 (1908); Wieland, *ibid.*, 42, 3024 (1909); Gomberg and Cone, *Ann.*, 370, 142 (1909); Schlenk, *ibid.*, 372, 9, 25 (1910).

solved in concentrated sulfuric acid, and in liquid sulfur dioxide to give intense yellow solutions, Kehrmann[6] assumed a quinonoid constitution, , for the explanation of color. In concentrated sulfuric acid and in liquid sulfur dioxide a tautomerism of the molecule occurred, and in the halochromic double salts of the triarylmethyl compounds with metallic halides the presence of color was also due to this quinonoid modification. This theory was subsequently used to explain the formation of color in the sulfates, nitrates and perchlorates of the triarylcarbinols, and has received much attention and support especially from the work of Gomberg, Cone and Anderson.[6]

However, there are experiments[7] recorded in the literature which are difficult to explain on the basis of this theory of constitution. These results have led to a different interpretation for the formation of color in these compounds. On the basis of this "carbonium ion theory" it is assumed that triarylmethyl compounds can exist in two forms—a colorless modification in which the negative group, X, is directly bound to the central carbon atom, and a colored modification of a true salt-like character (carbonium salt). The colorless solutions of the triarylmethyl halides are of the former type. The colored solutions of these compounds as well as the colored sulfates, nitrates, perchlorates, and double salts are of the latter type. According to Hantzsch[8] and Dilthey[9] this colored form can be best represented by the formula,  $\left[\begin{matrix}R\\R\end{matrix}\!\!>C-R\right]X$, where X may be Cl, ClO_4, OSO_3H, $SnCl_5$, etc.

In the light of these two different interpretations, therefore, it seemed that it would be of interest if further investigations were made on this problem along somewhat different lines. If a triarylmethyl compound could be prepared in which the four groups around the central carbon atom were all different, the molecule would then contain an asymmetric carbon atom and it should be possible to resolve it into its enantiomorphic forms. Such a compound would still have the property of forming halochromic double salts with metallic halides, and the behavior of such salts toward polarized light could be easily studied. If the above quinonoid theory be correct for the explanation of color in halochromic salts, we would expect

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[5] Kehrmann and Wentzel, *Ber.*, 34, 3815 (1901).

[6] Gomberg and Cone, *ibid.*, 39, 3274 (1906); 42, 406 (1909); Gomberg, *ibid.*, 40, 1847 (1907); Anderson and Gomberg, THIS JOURNAL, 50, 203 (1928); Anderson, *ibid.*, 51, 1889 (1929); 52, 4567 (1930).

[7] A. Baeyer and Villiger, *Ber.*, 35, 1189, 3013, 3054 (1902); A. Baeyer, *ibid.*, 38, 569 (1905); 40, 3083 (1907); Tschitschibabin, *ibid.*, 40, 3965 (1907); Schlenk and Weikel, *Ann.*, 368, 295 (1909); Conant, Small and Taylor, THIS JOURNAL, 47, 1959 (1925).

[8] Hantzsch, *Ber.*, 54, 2573, 2613 (1921); 63B, 1181 (1930).

[9] Dilthey, *J. prakt. Chem.*, [2] 109, 273 (1925); 118, 321 (1928); 124, 81 (1929).

such salts on hydrolysis to the colorless benzenoid form to give optically inactive products due to the fact that in the halochromic state the asymmetry of the central carbon atom has been destroyed. In the investigations which I now wish to report this was found under certain conditions not to be the case.

Phenylbiphenyl-a-naphthylcarbinol was prepared according to the method of Schlenk.[10] Several attempts were made to resolve the carbinol itself by combining it directly with brucine, quinine, camphorsulfonic acid, etc., but only negative results were obtained. Experiments were carried out in an attempt to make the carbinol in the form of its chloride combine with silver salts of optically active acids, but this method of approach proved unsatisfactory. Phenylbiphenyl-a-naphthylchloromethane, however, was found to combine with thioglycolic acid giving a stable derivative which was easily resolved.[11] *l*-Phenylbiphenyl-α-naphthylmethylthioglycolic acid, $(C_6H_5C_6H_4)(C_{10}H_7)(C_6H_5)C{-}SCH_2COOH$, has the following specific rotation in carbon tetrachloride: $[\alpha]^{20}_{D}$ −13.63°; in ether, $[\alpha]^{25}_{D}$ —12.93'. Experiments with this substance show that it forms halochromic salts. Concentrated sulfuric acid, perchloric acid and mercuric chloride unite with it forming deep blue-violet halochromic compounds which on pouring into ice water yield the carbinol, $(C_6H_5C_6H_4)(C_{10}H_7)(C_6H_5)COH$, in its optically inactive form. A solution of titanium tetrachloride in chloroform when added to a chloroform solution of *l*-phenylbiphenyl-a-naphthylmethylthioglycolic acid produces a deep blue-violet halochromic salt which on decomposition with ice water yields inactive phenylbiphenyl-α-naphthylmethylthioglycolic acid. However, when a solution of ferric chloride in glacial acetic acid is added to a chloroform solution of the levo thioglycolic acid derivative, the deep blue-violet halochromic compound so formed, on pouring into ice water, produces the original Lphenylbiphenyl-a-naphthylmethylthioglycolic acid with no racemization. This is also true in the case of the zinc chloride halochromic salt. If an ether solution of zinc chloride be added to an ether solution of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid, the deep blue-violet compound so produced is optically active and on hydrolysis produces the original I-thioglycolic acid compound with no change in rotation.

If we accept the statement that the formation of color in the double salt of triarylmethyl compounds with metallic halides is caused by a tautomerism of the molecule into a quinonoid modification, the two forms of phenylbiphenyl-a-naphthylmethylthioglycolic acid would be represented by the formulas[12]

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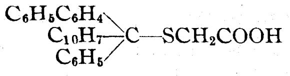
[10] Schlenk, *Ann.*, 394,196 (1912).

[11] Wallis, *Proc. Nat. Acad. Sci.*, *16, 215* (1930).

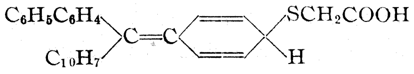
[12] Other possible quinonoid formulas can be written, but it makes no difference which group undergoes quinonoidation so far as the present discussion is concerned.



$(C_6H_5C_6H_4)(C_{10}H_7)(C_6H_5)C{-}SCH_2COOH$

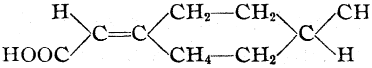
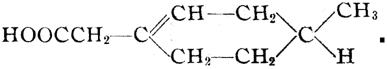
I

Colorless benzenoid



II

Colored quinonoid

On hydrolysis of the colored double salts, which according to this theory are represented by form II, compounds of type I are produced. According to theories of stereochemistry the asymmetric carbon atom in I has lost its asymmetry in form II. However, a construction of a model of the molecule of form II shows that it possesses an asymmetry of a different type known as "centroasymmetry" or molecular asymmetry, although it contains no asymmetric carbon atom. Therefore, theoretically, it could exist in two optically active modifications, but these two modifications would in all probability be produced in the rearrangement of the colorless benzenoid form, and, therefore, a racemic product would result. The question as to what will occur when an optically active substance of which the enantiomorphism of molecular configuration is associated with one particular type of asymmetry is converted into a second substance of which the optical activity arises from the exhibition by the molecule of enantiomorphism of a quite different type is not new. Perkin and Pope[13] have shown that an optically active compound whose activity is due to molecular asymmetry undergoes racemization during its conversion into the isomeride which contains only an asymmetric carbon atom. *l*-1-Methyl-cyclohexylidene-4-acetic acid,  was found by them to rearrange to dl-1-methyl-Δ^3-cyclohexene-4-acetic acid, . During the rearrangement complete racemization took place, even though the rearrangement product contains a true asymmetric carbon atom. In the light of such experiments, if the quinonoid theory for the explanation of color be correct, we would expect that a compound of Formula I on conversion into its halochromic salt and subsequent hydrolysis would be racemized, and would yield an optically inactive product.[14] That this is not the case is readily seen from the experimental results on the halochromic compounds of ferric chloride and zinc chloride.[15] In these instances not even partial racemiza-

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[13] Perkin and Pope, *Trans Chem. Soc.*, 99, 1515 (1911)

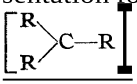
[14] Similar reasoning has been used by Phillips (*ibid* ,127, 2563 (1925)). to explain the fact that certain optically active sulphinates racemize rapidly.

[15] The fact that the double salt with titanium tetrachloride behaves differently than the double salts with ferric chloride and zinc chloride is perhaps to be expected. Titanium tetrachloride is a compound which is itself unstable in aqueous solution and is hydrolyzed with liberation of much energy and a large concentration of hydrochloric acid. Hydrolysis of the double salt of such a compound could easily be imagined to produce racemization. That this interpretation may be correct is strengthened by the

tion takes place. It therefore appears that whatever may be the cause of color in these halochromic compounds *we must not assign a structure or configuration which in any manner disturbs fundamentally the arrangement of groups around the central carbon atom.*

The alternative theory of color formation usually called the carbonium ion theory at first sight might not appear to be invalidated by these results. There is some evidence from optically active sulfonium compounds[16] that at least with a sulfur atom a positive ion maintains an asymmetric configuration. It is plausible that in both the optically active methylethylthetines and in the optically active sulfinates, the tercovalent sulfur atoms are associated with free electric charges. From this it might be imagined that a carbonium ion could maintain a structure approaching that of an asymmetric molecule. Experimental evidence[17] has been found* which seems to support this view. However, if this be true we would expect that the halochromic compounds produced by the action of sulfuric acid, perchloric acid and mercuric chloride on *l*-phenylbiphenyl-α-naphthylthioglycolic acid would produce on hydrolysis the optically active modification of the carbinol. But in these three cases the racemic compound is formed. It must be noted that the sulfonium ion if present in the thetines and sulfinates possesses a complete octet of valency electrons whereas in the carbonium ion only a sextet of valency electrons is present. Therefore the carbonium ion may possess a far less rigid structure than the sulfur atom in the thetine ion. In fact, recent evidence of Kenyon and Phillips[18] leads to the view that tercovalent carbonium ions are optically unstable.

Another argument which could be put forward against this view that a carbonium ion is always produced in the colored salts of the triarylcarbinols is the fact that the halochrornic compounds with zinc chloride and ferric chloride on hydrolysis do not produce the carbinol, but the original *l*-thioglycolic acid derivative. We should expect the carbinol to be formed if a carbonium ion were produced in the production of the halochromic salt, for hydrolysis of a compound containing the carbonium ion generally produces the corresponding carbinol.

It therefore would appear from these results on halochromic salts of an optically active derivative of a triarylcarbinol that the most likely representation for their structure is that one mentioned previously in this paper,  $\left[\begin{matrix}R\\R\end{matrix}\!\!>\!C-R\right]X$ in which the central carbon atom is coordinately un-

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fact that an acetic acid solution of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid containing hydrogen chloride racemizes.

[16] Pope and Peachey, *Trans. Chem. Soc.*, 77, 1072 (1900); Phillips, *ibid.*, 127, 2552 (1925).

[17] Jones and Wallis, THIS JOURNAL, 48, 169 (1926); McKenzie, Rogers and Wills, *Trans. Chem. Soc.*, 129, 779 (1926).

[18] Kenyon and Phillips. *ibid.*, 133, 1676 (1930).

saturated. In such a compound the molecule is heteropolar as compared with the colorless homopolar modification. The C—X bond may or may not be a true ionic linkage depending on whether the particular inorganic acid or salt used causes a complete transference of an electron to the octet of the group X, or only a partial distortion from the normal position.

Experimental Results

Preparation of *l*-Phenylbiphenyl-α-naphthylmethylthioglycolic Acid, $(C_6H_5C_6H_4)(C_{10}H_7)(C_6H_5)C—SCH_2COOH$.—*l*-Phenylbiphenyl-a-naphthylmethylthioglycolic acid was prepared according to the method of Wallis.[19] Seventeen grams of the pure levo compound was obtained from 39 g. of the brucine salt; 1.0242 g. dissolved in 25 cc. of dry ether solution gave a rotation of —1.06 at 25° in a 2-dm. tube, $[\alpha]_D^{25}$ —12.93'; 1.0020 g. dissolved in 25 cc. of carbon tetrachloride solution gave a rotation of —1.09 at 20° in a 2-dm. tube, $[\alpha]_D^{20}$ —13.63°; 0.4215 g. dissolved in 25 cc. of glacial acetic acid solution gave the following rotations at 20° in a 2-dm. tube: α_{6563} —0.23, α_{5893} —0.29, α_{5463} —0.36, α_{4861} —0.50, α_{4358} —0.70; $[\alpha]_{6563}^{20}$ —6.82, $[\alpha]_{5893}^{20}$ —8.60, $[\alpha]_{5463}^{20}$ —10.68, $[\alpha]_{4861}^{20}$ —14.83, $[\alpha]_{4358}^{20}$ —20.76°.

An ether solution of this substance on standing at room temperature for two weeks showed no change in rotation. However, a solution of this material in glacial acetic acid on standing slowly decreased in rotatory power.

The residues from the fractional crystallizations were worked up and gave 20 g. of a mixed dextro phenylbiphenyl-a-naphthylmethylthioglycolic acid,[20] $[\alpha]_D^{20}$ +10.13° in ether.

Action of Concentrated Sulfuric Acid.—Two grams of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid was dissolved in 5 cc. of concentrated sulfuric acid previously cooled to —20°. A deep violet color developed. As soon as solution was complete the contents of the flask were poured into ice water. The deep violet color of the halochromic sulfate disappeared immediately and a white precipitate was formed. This was filtered off and dried; 1.7 g. of crude product was obtained. One-half gram of this material dissolved in 25 cc. of benzene solution gave no observable rotation in a 2-dm. tube. Recrystallization of a second portion from benzine gave a compound which melted at 161–162°. A mixed melting point determination of this substance with *dl*-phenylbiphenyl-a-naphthylcarbinol showed no change in melting point.

Action of Perchloric Acid.—Two grams of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid was dissolved in 30 cc. of glacial acetic acid and cooled to the freezing point of the mixture; 10 cc. of a 60% aqueous solution of perchloric acid previously cooled to 0° was then added, and the deep violet halochromic compound was poured immediately into ice water. It melted at 138–145°; 0.5 g. of this crude product in 25 cc. of benzene solution gave no observable rotation in a 2-dm. tube. Recrystallization of the material from benzine (60–80°) gave a compound which melted at 160–161°. A mixed melting point determination with the dl-carbinol showed no change in melting point.

Action of Mercuric Chloride.—A solution of 1.0 g. of mercuric chloride dissolved in 30 cc. of dry ether was cooled to 0° and added to a solution of 1.0 g. of *l*-phenylbiphenyl-or-naphthylmethylthioglycolic acid in 10 cc. of ether. The deep violet mixture was poured immediately into ice water. The ether layer was separated, washed and dried with anhydrous sodium sulfate. A portion of this solution in a 2-dm. tube gave

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[19] Wallis, *Proc. Nat. Acad. Sci.*, 16, 215 (1930).

[20] The dextro modification was not obtained in a pure form. Fractional crystallization of the brucine salt gives only the pure 1-isomer.

no observable rotation. On partial evaporation a compound was deposited which contained ether of crystallization. It melted at 113° and contained no sulfur. The ether was removed by warming and the product crystallized from benzine (60–80°). The product so obtained melted at 160°. A mixed melting point determination of this substance with dl-phenylbiphenyl α-naphthylcarbinol[21] showed no change in melting point.

Action of Titanium Tetrachloride.—0.45 g. of titanium tetrachloride in 10 cc. of pure chloroform was cooled to 0° and added to a solution of 1.0 g. of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid dissolved in 15 cc. of chloroform. The deep violet solution was poured into ice water. The colorless chloroform layer was separated, washed three times with water and dried over anhydrous sodium sulfate. A portion of this solution in a 2-dm. tube gave no observable rotation. The chloroform was evaporated and the product crystallized from toluene. A white crystalline compound was obtained which melted at 114". This compound contained sulfur, and was identical in its properties with dl-phenylbiphenyl-a-naphthylmethylthioglycolic acid. Similar experiments at −70° gave the same results. The product formed was inactive.

Action of Ferric Chloride.—A qualitative study of the ferric chloride and zinc chloride double salts of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid showed that these compounds on hydrolysis gave solutions which were optically active. Therefore, quantitative experiments were carried out in order to determine whether partial racemization took place during the formation and hydrolysis of the double salts. The following experiments will serve as typical examples: 0.50 g. of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid was dissolved in dry ether The volume of the solution was made up accurately to 25 cc. A portion of this solution in a 2-dm. tube gave a, at 20° −0.59°. The two solutions were then carefully poured into a 50-cc. Erlenmeyer flask and cooled to 0°. All receptacles were washed with ether to insure no loss of the thioglycolic acid derivative. One gram of ferric chloride previously dissolved in 10 cc. of glacial acetic acid was added. A deep violet halochromic compound formed immediately. The mixture was then poured into ice water. The color disappeared at once. The ether layer was removed, washed with distilled water and dried with anhydrous sodium sulfate. The aqueous layer was extracted three times with ether. This extract was washed twice with distilled water and dried. The ether solutions were united and concentrated by evaporation to 20 cc. The solution was then made up accurately to a volume of 25 cc. and the rotatory power determined, $\alpha_{\rm D}^{20}$ −0.56. The solution was evaporated and the material which separated out was crystallized from benzine. The compound was found to contain sulfur. It melted at 107–108". A mixed melting point with *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid showed no appreciable change in melting point. Other experiments were carried out varying the concentrations of the reactants and the solvents, but in no case was appreciable racemization observed.

Action of Zinc Chloride.—0.61 g. of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid was dissolved in ether and the solution accurately made up to a volume of 25 cc.; $\alpha_{\rm D}^{20}$ in a 2-dm. tube was −0.73. The solution was cooled to 0° and to it was added an ether solution of 0.50 g. of zinc chloride previously cooled to 0°. The deep violet solution was poured into ice water and the colorless ether layer removed. This was washed twice with distilled water and dried. The aqueous layer was extracted with ether and the ether solution was washed and dried with anhydrous sodium sulfate. The two solutions were united and concentrated to 20 cc. The volume was then made up to 25 cc. and the rotatory power determined, $\alpha_{\rm D}^{20}$ in a 2-dm. tube, −0.70". The solution was evaporated and treated as described in the experiments on the ferric chloride

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[21] Phenylbiphenyl-a-naphthylcarbinol crystallizes from ether with ether of crystallization. This compound melts at 115–116°.

double salt. A mixed melting point determination with *l*-phenylbiphenyl-α-naphthylmethylthioglycolicacid showed no change in melting point.

Other experiments were carried out varying the amount of zinc chloride, but in no case was racemization observed.

Conclusions

Certain derivatives of triarylcarbinols containing an asymmetric carbon atom have been prepared. Phenylbiphenyl-a-naphthylmethylthioglycolic acid has been resolved into a pure levo form, $[\alpha]^{20}_{\mathrm{D}}$ $-13.63°$, and a mixed dextro isomer $[\alpha]^{20}_{\mathrm{D}}$ $+10.13°$. Experiments with this substance show that it forms halochromic compounds. Concentrated sulfuric acid, perchloric acid and mercuric chloride unite with it to form deep violet halochromic compounds which on pouring into ice water yield the carbinol in its optically inactive form. Titanium tetrachloride produces a deep violet halochromic salt which on decomposition with water yields the racemic phenylbiphenyl-a-naphthylmethylthioglycolic acid. However, the double salts with ferric chloride and zinc chloride on hydrolysis give *l*-phenylbiphenyl-a-naphthylmethylthioglycolic acid with no racemization.

A discussion of these facts is given with special reference to the quinonoid theory and carbonium ion theory of formulation for the explanation of color.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

SOME CHLORINE DERIVATIVES OF BENZYLPHENOLS. I. DICHLORO DERIVATIVES OF ORTHO AND PARA BENZYLPHENOLS

BY R. C. HUSTON AND E. F. ELDRIDGE

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This paper is the first of a series dealing with the chlorination and the chlorine derivatives of the benzylated phenols. Only a comparatively few of these compounds have been reported.

A chlorobenzyl phenol[1] was made by treating benzylphenol with sulfuryl chloride. The investigator reported that the chlorine probably entered the ring in the ortho position, giving the formula $C_6H_5CH_2C_6H_3ClOH$, but gave no proof of structure. Beilstein reports its formula as C_6H_5-$CHClC_6H_4OH$ with the chlorine on the CH_2 group. Richter's Lexicon shows the substitution in the meta position.

Sentinis prepared a benzyl chlorophenyl ether[2] by passing chlorine into an alcoholic solution of the ether to which some mercuric oxide had been added as a catalyst. This was later shown by Baw[3] to be benzyl *p*-chlorophenyl ether.

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[1] Peratoner and Vitaei, *Gazz. chim. ital.*, *28*, 197 (1898).

[2] Sentinis, *Ann.*, 161, 345 (1872).

[3] Baw, *Quart. J. Indian Chem. Soc.*, 3, 101 (1926).

Benzyl 2,4 dichlorophenyl ether[4] and benzyl 2,4,6-trichlorophenyl ether were prepared by treating the respective chlorophenol in alcohol with benzyl chloride and sodium ethoxide. The bromine derivatives were prepared in the same manner.

Benzyl pentachlorophenyl ether,[5] $C_6H_5CH_2OC_6Cl_5$, was made by warming the silver salt of pentachlorophenol with benzyl iodide.

Baw[3] prepared benzyl 2-chlorophenyl and benzyl 2,4-dichlorophenyl ethers by treating the appropriate phenols with benzyl chloride and aniline.

The work on which we wish to report here was limited to those derivatives containing two chlorine atoms. The dichloro compounds of both the ortho and para benzylphenol were prepared.

The latter, 3,5-dichloro-4-hydroxydiphenylmethane, was first made by the aluminum chloride condensation of benzyl alcohol and 2,6-dichlorophenol. The structure of this compound was proved by preparing the same compound by direct chlorination of *p*-benzylphenol in chloroform using the quantitative amounts of chlorine. Needle shaped crystals were obtained. The aluminum chloride condensation, in this case, proved to be of considerable interest as we were able to isolate from the oil obtained from the condensation 2,6-dichlorophenyl benzyl ether. This is the first time that an ether has been isolated from an aluminum chloride condensation and opens a considerable field for speculation as to the mechanism of the reaction. In order to identify this ether it was later prepared by treating 2,6-dichlorophenol and benzyl chloride with metallic sodium in methyl alcohol. The boiling point at 15 mm. was 194–195°, very near that of the phenol.

The preparation of 3,5-dichloro-2-hydroxydiphenylmethane was effected in two ways: first, by the Claisen reaction in which 2,4-dichlorophenol and benzyl chloride were treated with sodium in toluene and, second, by direct chlorination of o-benzylphenol in chloroform with the calculated amount of chlorine. The same compound was obtained in each case.

The ether, 2,4-dichlorophenyl benzyl ether,[3,4] was isolated from the Claisen reaction mixture by extraction with petroleum ether. This same compound was later prepared by the action of sodium on 2,4-dichlorophenol and benzyl chloride in methyl alcohol.

An attempt to substitute more than two chlorines into the ortho and para benzylphenols proved unsuccessful. Both benzyl phenols were treated with three molecular equivalents of chlorine and then with a large excess, but no compounds containing more than two atoms of chlorine were obtained. Apparently chlorine does not easily substitute in the benzyl group.

The benzoic, benzene sulfonic and toluene sulfonic esters of each of the

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[4] Auwers, *Ann.*, 357, 85–94 (1907).

[5] Biltz and Giese, *Ber.*, 37, 4020 (1904).

dichlorobenzyl phenols were prepared. These all proved to be crystalline substances and served to further characterize the phenols.

Experimental

Benzyl Alcohol, 2,6-Dichlorophenol and Aluminum Chloride.—Fifty grams of benzyl alcohol and 225 g. of 2,6-dichlorophenol were suspended in 250 cc. of petroleum ether. The suspension was mechanically stirred while 30 g. of aluminum chloride was added at intervals over one hour. The phenol is only slightly soluble in the ether. Stirring was continued for thirty minutes after the aluminum chloride had been added and the mixture allowed to stand overnight. At no time during the reaction did the temperature exceed 32°. The suspension was decomposed with ice and hydrochloric acid and the petroleum ether withdrawn. The water mixture was extracted with ethyl ether. (Drying with potassium carbonate was attempted in the first condensation, but later omitted as distillation of the dried mixture gave a large amount of charred material.) The solvents were distilled, the residues combined and then fractionated.

The first fractions consisted of unchanged benzyl alcohol and 2.6-dichlorophenol. Twenty-three grams of a yellow oil was obtained between 195 and 205" at 15 mm. The material from six similar condensations was combined and purified by further distillation. The boiling point at 15 mm. after three distillations was 194–196".

A determination of the chlorine content of the oil by the Parr bomb method showed a percentage of chlorine in two samples of 27.7 and 28.1. Since the theoretical amount of chlorine in 3,5-dichloro-4-hydroxydiphenylmethane is 28%, it was at first thought that the oil was that compound. Subsequent results showed that this was not entirely true.

The benzoyl derivative prepared by the pyridine method melted at 98.5–99°.

Chlorination of *p*-Benzylphenol.—Ten grams of *p*-benzylphenol suspended in chloroform was treated with two equivalents of chlorine.[6] The solvent was distilled and a yellow oil obtained which was fractionated. All but a small amount came over between 190 and 205° at 15 mm. This solidified on standing and was recrystallized from petroleum ether; m. p. 58–58.5°.

Anal. Subs., 0.1840, 0.1889: cc. of 0.1 N $AgNO_3$, 14.38, 14.95. Calcd. for $C_{13}H_{10}OCl_2$: Cl, 28.0. Found: Cl, 27.8, 28.1.

Crystals of this compound seeded in the oil prepared by the aluminum chloride condensation dissolved. The benzoyl derivative in this case gave a melting point of 98.5–99°, which was identical with that prepared from the oil.

The oil from the aluminum chloride condensation was then treated with a water solution of potassium hydroxide. An oil remained undissolved. This was withdrawn and the solution acidified with hydrochloric acid. A crystalline compound was obtained which when purified proved to be identical with the compound obtained by direct chlorination of p-benzylphenol.

Benzyl 2,6-Dichlorophenyl Ether.—Six and one-half grams of metallic sodium was allowed to react with 100 cc. of methyl alcohol. The solution was cooled and 45 g. of 2,6-dichlorophenol added. This mixture was heated on the oil-bath at 150° for thirty minutes, cooled and 35 g. of benzyl chloride added. The entire mixture was allowed to stand overnight and then heated on the oil-bath for five hours. After cooling, the oil was extracted with petroleum ether, the ether removed and the residue distilled.

A very small amount of benzyl chloride came over at 90 to 190° at 15 mm. Practically all of the remaining oil distilled between 190 and 196°. Refractionation produced a yellow oil with a boiling point of 194–196° at 15 mm. This oil solidified after standing

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[6] Houben, "Methods of Organic Chemistry," Vol. 2, p. 799.

in the ice box for three months. A crystal of the ether so prepared was seeded in the oily residue obtained from the aluminum chloride condensation. The oil solidified immediately. The melting point of both compounds was identical, 39.5–40°.

Anal. Subs., 0.2418, 0.1930: cc. of 0.1 N $AgNO_3$, 19.05, 15.1. Calcd. for $C_{13}H_{10}OCl_2$: Cl, 28.0. Found: Cl, 27.9, 27.7.

3,5-Dichloro-2-hydroxydiphenylmethane.—Sodium (11.5 g.) was suspended in 130 cc. of toluene and 81.5 g. of 2,4-dichlorophenol added. The mixture was heated on the oil-bath at 150° for thirty minutes, during which time the white sodium salt was produced. The mixture was cooled and 63.3 g. of benzyl chioride added. After standing overnight it was heated for five hours on the oil-bath (160°), cooled and treated with 250 cc. of methyl alcoholic potassium hydroxide. The solution was extracted with petroleum ether. The remaining alcoholic solution was then neutralized with hydrochloric acid and the phenol extracted with ethyl ether. After removing the ether, the residue was fractionated. The fraction between 140 and 210° at 15 mm. solidified in the receiver and yielded, after recrystallization from petroleum ether, 30 g. of pure dichlorobenzyl phenol, m. p. 77.0–77.5°.

Anal. Subs., 0.2000, 0.1895: cc. of 0.1 N $AgNO_3$, 15.6, 14.82. Calcd. for $C_{13}H_{10}OCl_2$: Cl, 28.0. Found: Cl, 27.6, 27.7.

The same compound was prepared by direct chlorination of *o*-benzylphenol. The chlorination was carried out as before using calculated amounts of potassium permanganate to produce the chlorine. The dark colored oil was fractionated and the fraction between 190–200" at 15 mm. was purified by recrystallization from high test gasoline.

Benzyl 2,4-Dichlorophenyl Ether.—This compound was prepared by treating sodium 2,4-dichlorophenylate in methyl alcohol with the equivalent amount of benzyl chloride. The crystals obtained were purified from petroleum ether. The petroleum ether extract from the previous preparation of 3,5-dichloro-2-hydroxydiphenylmethane was also purified in a similar manner. The compounds[4] were prisms with identical melting points (59.0–59.5°).

Attempt to Produce the **Trichlorobenzylphenols.**—Both the para and ortho benzylphenols were subjected to the calculated amount of chlorine for the substitution of three chlorines and later to an excess of the gas. The compounds in each case were fractionated and purified by recrystallization. Upon analysis each sample showed but two chlorine atoms and gave melting points which proved them to be the dichlorobenzylphenols previously prepared.

Esters

The benzoyl, benzene sulfonyl and the toluene sulfonyl derivatives of both dichlorobenzylphenols were prepared by the pyridine method.

Esters of 3,5-Dichloro-4-hydroxydiphenylmethane

Benzoic Ester.—Prisms from petroleum ether, m. p. 98–99"

Anal. Subs., 0.1174, 0.1844: cc. of 0.1 N $AgNO_3$, 6.4, 11.25. Calcd. for $C_{20}H_{14}O_2Cl_2$: Cl, 19.9. Found: Cl, 19.4, 19.7.

Benzene **Sulfonic** Ester.—Prisms from ethyl ether, m. p. 93–94°.

Anal. Subs., 0.2630, 0.2100: cc. of 0.1 N $AgNO_3$, 13.15, 10.55. Calcd. for $C_{20}H_{14}SO_3Cl_2$: Cl, 18.05. Found: Cl, 17.75, 17.85.

***p*-Toluene** Sulfonic Ester.—Prisms from ethyl ether, in which it is only slightly soluble, m. p. 120–121°.

Anal. Subs., 0.1743, 0.2054: cc. of 0.1 N $AgNO_3$, 8.35, 10.05. Calcd. for $C_{21}H_{16}SO_3Cl_2$: Cl, 17.42. Found: Cl, 17.15, 17.40.

Esters of 3,5-Dichloro-2-hydroxydiphenylmethane

Benzoic Ester.—Needles from 70% alcohol, m. p. 66–67°.

Anal. Subs., 0.1162, 0.1785: cc. of 0.1 N $AgNO_3$, 6.45, 9.75. Calcd. for $C_{20}H_{14}O_2Cl_2$: Cl, 19.9. Found: Cl, 19.65, 19.50.

Benzene Sulfonic Ester.—Elongated prisms from ethyl ether, m. p. 110–110.5°.

Anal. Subs., 0.2562, 0.2360: cc. of 0.1 N $AgNO_3$, 12.95, 11.85. Calcd. for $C_{20}H_{14}SO_3Cl_2$: Cl, 18.05. Found: Cl, 17.90, 17.85.

p-Toluene Sulfonic Ester.—Prismatic plates from ethyl ether, m. p. 124.5–125°

Anal. Subs., 0.2239, 0.1822: cc. of 0.1 *N* $AgNO_3$, 10.95, 8.80. Calcd. for $C_{21}H_{16}SO_3Cl_2$: Cl, 17.42. Found: Cl, 17.35, 17.20.

Summary

1. The dichloro derivatives of both ortho and para benzylphenol and their ethers were prepared by direct chlorination and by condensation of the chlorinated phenols with benzyl alcohol.

2. The aluminum chloride condensation of 2,6-dichlorophenol and benzyl alcohol gave the ether as well as the benzylated phenol.

3. No evidence was obtained of the substitution by direct chlorination of more than two chlorines in either para or ortho benzylphenol.

4. The benzoyl, benzene sulfonyl and toluene sulfonyl derivatives of each dichlorobenzylphenol were prepared.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TOXICAROL. II. SOME ACETYL DERIVATIVES OF TOXICAROL

BY E. P. CLARK

RECEIVED MARCH 19, 1931 PUBLISHED JUNE 8, 1931

Evidence has been presented to show that toxicarol is an hydroxy-dimethoxy compound, $C_{23}H_{22}O_7$.[1] The presence in the molecule of at least one hydroxyl group was demonstrated by the formation of a monobenzoyl derivative, but as the nature of four of the seven oxygen atoms was unknown, the existence of other hydroxyl groups was not excluded.

It has now been shown that a diacetyl derivative of toxicarol may be obtained, but because of the reactions which it and toxicarol undergo, it cannot be stated definitely that a second hydroxyl group exists in toxicarol per se. In fact, evidence is more in accord with the idea that the second acetyl group is introduced as a result of some reaction brought about by the reagents involved in the acetylation process.

An attempt to elucidate this point is in progress, but since the information upon the subject now available is interesting and will eventually contribute to the solution of the structure of the molecule, it is presented herewith.

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[1] Clark, THIS JOURNAL, 52, 2461 (1930).

When treated with boiling acetic anhydride and sodium acetate, toxicarol yields a diacetyl derivative, $C_{27}H_{26}O_9$. This material upon catalytic hydrogenation gives two products, dihydrodiacetyltoxicarol, $C_{27}H_{28}O_9$, and monoacetyldihydrodesoxytoxicarol, $C_{25}H_{28}O_7$. The latter substance may be readily deacetylated, giving a good yield of dihydrodesoxytoxicarol, $C_{23}H_{26}O_6$, but by the methods tried it cannot be further acetylated to a diacetyl derivative.

Catalytic reduction of toxicarol under the conditions which produced the desoxy compound from the acetyl derivative resulted in the formation of only dihydrotoxicarol, $C_{23}H_{24}O_7$.

Acetylation of dihydrotoxicarol with boiling acetic anhydride and sodium acetate gave two products, depending upon the duration of the reaction. When the components were allowed to react for ten minutes, only a monoacetyldihydrotoxicarol, $C_{25}H_{26}O_8$, was obtained, whereas if the reaction continued for two hours the entire product was diacetyldihydrotoxicarol, identical with the diacetyl derivative obtained by reducing diacetyltoxicarol.

Oxidation of toxicarol with potassium ferricyanide resulted in the loss of two hydrogen atoms, giving dehydrotoxicarol, $C_{23}H_{20}O_7$. Dihydrotoxicarol treated in the same manner gave dehydrodihydrotoxicarol, $C_{23}H_{22}O_7$. Dehydrotoxicarol was readily acetylated with acetic anhydride and sodium acetate, but under all the conditions tried only a monoacetyl derivative was obtained.

Reduction of dehydro or acetyldehydrotoxicarol gave, respectively, dihydrotoxicarol and monoacetyldihydrotoxicarol. The latter substance was the same as the acetyl derivative obtained by mild acetylation of dihydrotoxicarol.

In the process of reducing these dehydro derivatives not only was the double bond demonstrated by the catalytic hydrogenation reduced, but the structure which gave rise to the dehydro formation was regenerated. This is in sharp contrast to the corresponding dehydro derivatives of rotenone[2] and deguelin,[3] which do not reduce to the corresponding parent substance.

Dehydrotoxicarol may also be obtained by oxidizing toxicarol in an absolute alcoholic potassium acetate solution with iodine. Four atoms of iodine are readily consumed and a beautiful yellow iodo compound separates. This is undoubtedly iododehydrotoxicarol, but analysis of the compound was not satisfactory. This failure was probably due to the retention of an indefinite quantity of solvent which could not be removed under the condition to which the material was subjected. The melting point of the compound varied over a range of 30° depending upon the

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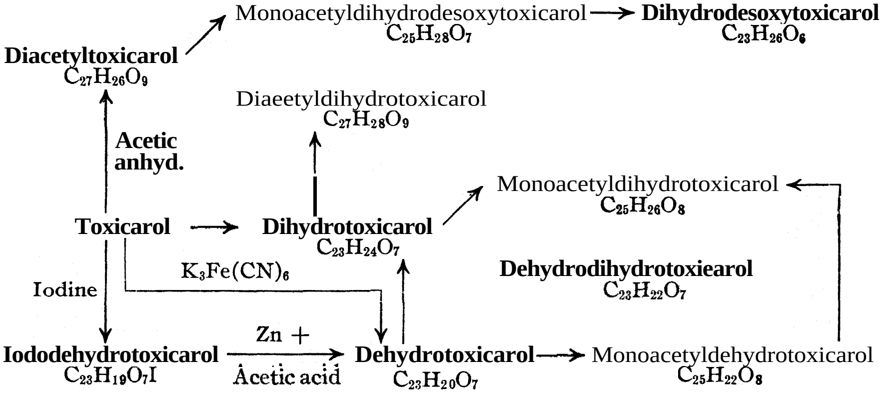
[2] LaForge and Smith, THIS JOURNAL, 52, 1094 (1930).

[3] Clark, unpublished data.

solvent used for its recrystallization, but all samples readily lost their iodine when treated with zinc dust and boiling acetic acid. Upon cooling the reaction mixture, dehydrotoxicarol separated in a relatively pure condition.

The reactions which have been discussed are represented diagrammatically in the chart.

REACTIONS OF TOXICAROL AND SOME OR ITS DERIVATIVES



In connection with the behavior of the compounds under consideration, the following facts are pertinent. Because toxicarol gives a deep green color reaction with ferric chloride, which the benzoyl derivative does not, it is concluded that the hydroxyl group which was benzoylated is phenolic. Likewise the green color is produced by dehydrotoxicarol but not by acetyldehydrotoxicarol. It would therefore be expected that dihydrodesoxytoxicarol would also give the phenolic test, but it does not.

Some work upon the oxidation of toxicarol has been under way, but it has not progressed far enough to be reported upon at this time. It may be stated, however, that when toxicarol was treated with an acetic acid solution of chromic acid, the reaction was very slow, and after twenty-four hours all that could be isolated was approximately 50% of the unchanged starting material. Diacetyltoxicarol, on the other hand, is oxidized at once, and in some experiments as many as four products have been isolated, none of which was starting material.

It therefore seems likely that in the formation of diacetyltoxicarol a new structure is developed, and although a diacetyl derivative is indicative of two hydroxyl groups, it does not seem justifiable at present to conclude that the second hydroxyl group is present in toxicarol itself.

Experimental

Diacetyltoxicarol.—A mixture of 10 g. of toxicarol, 2.5 g. of anhydrous sodium acetate and 40 cc. of acetic anhydride was boiled for thirty minutes under a reflux condenser. The resulting solution was cooled in an ice-bath, then diluted with 100 cc. of acetic acid, and allowed to crystallize. The acetyltoxicarol which separated was removed from the mother liquor by filtration and was washed on the filter first with acetic acid, then with water, and finally with methanol. The yield of crude material, whose melting point was 227–229°, was 6 g.

The mother liquors were poured into 800 cc. of water, causing a further quantity of material to separate. Salt added to the mixture caused flocculation of the precipitate, which was separated by filtration. After the precipitate was air dried it was dissolved in ether and allowed to crystallize. One and six-tenths grams of crude diacetyltoxicarol with a melting point of 195–197° was obtained. This material was recrystallized from its chloroform solution by adding five volumes of ethanol. It then melted at 226°.

The crude diacetyltoxicarol (m. p. 226–229') was recrystallized by dissolving 1 g. of the substance in 25 cc. of boiling acetic acid and adding 25 cc. of boiling water. Crystallization from the 50% acid began at once and was soon completed. Two such recrystallizations gave a pure product which melted at 233° and became clear at 236°. It consisted of thin irregularly shaped plates. In parallel polarized light (crossed nicols) the plates extinguished sharply and brilliant polarization colors were common. In convergent polarized light (crossed nicols) partial biaxial interference figures were shown only rarely: η_α, 1.500 (very common); η_β, indeterminate; η_γ, >1.740.[4]

Anal. Calcd. for $C_{27}H_{26}O_9$: C, 65.58; H, 5.30; OCH_3 (2), 12.6; acetyl (2), 17.4. Found: C, 65.71; H, 5.41; OCH_3, 12.7; acetyl, 17.2.

Reduction of Diacetyltoxicarol (Diacetyldihydrotoxicarol).—Three grams of diacetyltoxicarol dissolved in 200 cc. of hot acetic acid was reduced at atmospheric pressure and approximately 75° with hydrogen and the platinum catalyst of Voorhees and Adams.[5] After the catalyst was removed, the solution was heated to boiling and two volumes of boiling water was added. Crystallization began at once and was completed when the solution reached room temperature. The yield was 2 g. and the melting point of the crystals was 235°. It was recrystallized by dissolving the crude material in a small volume of boiling chloroform, adding approximately ten volumes of boiling methanol and maintaining the solution in a state of vigorous boiling until crystallization began. The material which separated consisted of colorless boat-shaped crystals which melted at 238° and became clear at 240°. In parallel polarized light (crossed nicols) the crystals exhibited deep purple, green and red colors: η_α, 1.480 lengthwise (common); η_β, indeterminate, and η_γ, >1.740, although many of the crystals matched a liquid of this index or showed pale blue or orange margins in white light (crosswise).

Anal. Calcd. for $C_{27}H_{28}O_9$: C, 65.31; H, 5.69; OCH_3 (2), 12.5. Found: C, 64.99; H, 5.82; OCH_3, 12.5.

Monoacetyldihydrodesoxytoxicarol.—The acetic acid mother liquors from the foregoing experiment were concentrated to a sirup under reduced pressure, and the residue was dissolved from the flask with a small quantity of boiling methanol. The solution was set aside and allowed to crystallize. The product which separated had a melting point of 155°, and the yield was usually one-third of the starting material. It was recrystallized by adding five volumes of boiling methanol to its solution in boiling chloroform and maintaining the solution in a state of vigorous boiling until the chloroform was removed. Upon cooling, the solution deposited pure colorless needles and rectangular rods whose melting point was 156°.

In parallel polarized light (crossed nicols) the material had inclined extinction and

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[4] The optical data recorded in this communication were determined by George L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture. Appreciation is gratefully expressed for this cooperation.

[5] Voorhees and Adams, THIS JOURNAL, 44, 1397 (1922).

negative elongation. In convergent polarized light (crossed nicols) the substance exhibited partial biaxial interference figures, often showing one optic axis up: , 1.547; η_β, 1.633; η_γ, >1.740; all ±0.003.

Anal. Calcd. for $C_{25}H_{28}O_7$: C, 68.17; H, 6.41; OCH_3 (2), 14.1. Found: C. 68.09; H, 6.47; OCH_3, 14.3.

When a relatively large quantity of fresh catalyst was used (1 g. of platinum dioxide for 10 g. of diacetyltoxicarol), no diacetyldihydrotoxicarol was obtained. Under these conditions, in the first crop of crystals 2.4 g. of monoacetyldihydrodesoxytoxicarol was obtained from 5 g. of diacetyltoxicarol.

Dihydrodesoxytoxicarol.—The acetyl derivative of dihydrodesoxytoxicarol was dissolved in a boiling 2.5% methyl alcoholic solution of sodium methylate. The liquid was then immediately made acid with acetic acid and set aside to crystallize. In a short time the deacetylated product separated as colorless rods. Upon recrystallization from 50% ethanol the product was pure and melted at 188". In this state it consisted of fine colorless needles having parallel extinction and negative elongation (parallel polarized light), η_α, 1.567 (lengthwise); η_β, 1.625 (crosswise); and η_γ, 1.680 (crosswise); all ±0.003. It gave no color test with ferric chloride.

Anal. Calcd. for $C_{23}H_{26}O_6$: C, 69.32; H, 6.58; OCH_3 (2) 15.6. Found: C, 69.29; H, 6.66; OCH_3, 15.6.

Dihydrotoxicarol.—Five grams of toxicarol was reduced with hydrogen as outlined under the reduction of diacetyltoxicarol. Approximately 90% of the solvent was removed by vacuum distillation, and the residue was washed from the flask with five volumes of methanol. Crystallization began at once, yielding 3.4 g. of dihydrotoxicarol melting at 205".

The crude material was recrystallized from a boiling chloroform solution by the addition of five volumes of methanol. It separated as thin hexagonal plates and occasional rods which melted at 206" and became clear at 209°. Macroscopically the preparation had a slight greenish tinge, but microscopically the crystals were colorless. In parallel polarized light (crossed nicols) most of the plates exhibited first order white, and when the stage was rotated many of the plates did not extinguish sharply. In convergent polarized light (crossed nicols) such plates showed partial biaxial interference figures frequently with one axis up: ,? 1.575; η_β, 1.627; η_γ, 1.658 (all ±0.003).

Anal. Calcd. for $C_{23}H_{24}O_7$: C, 66.97; H, 5.87; OCH_3 (2), 15.1. Found: C, 67.08; H, 5.89; OCH_3, 15.1.

Monoacetyldihydrotoxicarol.—A mixture of 0.25 g. of dry sodium acetate. 1 g. of dihydrotoxicarol and 4 cc. of acetic anhydride was boiled for ten minutes. The excess of acetic anhydride was decomposed by the cautious addition of methanol, after which eight volumes more of methanol were added. One gram of monoacetyldihydrotoxicarol with a melting point of 202° separated. It was twice recrystallized from its saturated boiling butanol solution by adding two volumes of methanol. Thus obtained it consisted of colorless prisms which began to sinter at 200° and melted at 207°. In parallel polarized light (crossed nicols) it exhibited negative elongation and straight extinction. In convergent polarized light (crossed nicols) only partial biaxial interference figures were shown: η_α, 1.583 (not common); η_β, indeterminate; η_γ, 1.655 (common crosswise). An intermediate index η_ι, 1.615, frequently occurs lengthwise on the rods (all ±0.003).

Anal. Calcd. for $C_{25}H_{26}O_8$: C, 66.06; H, 5.77; OCH_3 (2), 13.7. Found: C, 66.03; H, 5.79; OCH_3, 13.7.

Diacetyldihydrotoxicarol.—The diacetyldihydrotoxicarol was obtained by the method just given for the monoacetyl derivative except that the reaction mixture was refluxed for two hours. The solution was then cooled, diluted with an equal volume of acetic acid and allowed to crystallize. The diacetyl compound which separated melted at 235–236°. It was recrystallized by the procedure given for the same product obtained by reducing diacetyltoxicarol.

The material had the same melting point as the former product and when mixed with it there was no depression of the melting point. It also had the optical properties characteristic of the diacetyl derivative obtained by reducing diacetyltoxicarol.

Anal. Found: C, 65.32; H, 5.67; OCH_3, 12.5.

Oxidation of Toxicarol with Potassium Ferricyanide: Dehydrotoxicarol.—Five grams of toxicarol dissolved in 500 cc. of boiling ethanol was treated with 75 cc. of a hot aqueous solution of 9 g. of potassium ferricyanide and 2.8 g. of potassium hydroxide. The mixture was allowed to stand until the following day and then quickly diluted with 1500 cc. of water. Dehydrotoxicarol separated as brownish-yellow crystals, and the residual organic material, dispersed in the milky mother liquor, was carefully decanted. The crystals were then washed with water by decantation, transferred to a filter and finally washed with methanol. One and one-tenth grams of dehydrotoxicarol with a melting point of 223° was obtained.

The material was recrystallized by adding five volumes of hot methanol to its solution in chloroform. This procedure gave a product which melted at 230–231°. For analysis the compound was again recrystallized from hot cyclohexanol. In this operation a yield of 85% was obtained. The material separated as yellow rods and needles whose melting point was 234°. The crystals exhibited parallel extinction and negative elongation: η_α, 1.460 (lengthwise); η_β, 1.685 (crosswise); and η_γ, >1.740 (both ±0.003).

Anal. Calcd. for $C_{23}H_{20}O_7$: C, 67.63; H, 4.94; OCH_3 (2), 15.2. Found: C, 67.47; H, 4.97; OCH_3, 15.3.

Monoacetyldehydrotoxicarol.—The acetylation of dehydrotoxicarol was performed in the usual way with sodium acetate and acetic anhydride. The reaction mixture was refluxed for thirty minutes, then diluted with two volumes of acetic acid and allowed to crystallize. The yield was 1.6 g. from 2 g. of starting material. The crude product was recrystallized from a boiling chloroform solution upon the addition of five volumes of methanol. It separated as long light cream-colored rods and needles which melted at 231–232". The extinction was inclined and the elongation was negative: η_α, 1.563; η_β, indeterminate; η_γ, >1.740.

Anal. Calcd. for $C_{25}H_{22}O_8$: C, 66.65; H, 4.93; OCH_3 (2), 13.8. Found: C, 66.47; H, 5.05; OCH_3, 13.8.

Reduction of Dehydrotoxicarol.—Dehydrotoxicarol was reduced by the procedure given for the preparation of dihydrotoxicarol. One and six-tenths grams of dihydrotoxicarol was obtained from 2.6 g. of dehydrotoxicarol. After recrystallization the product melted at 209°. It caused no melting-point depression when mixed with dihydrotoxicarol and possessed the same optical properties that are characteristic of dihydrotoxicarol.

Reduction of Monoacetyldehydrotoxicarol.—Four and thirty-five hundredths grams of monoacetyldehydrotoxicarol was reduced in the usual manner and the resulting solution concentrated to a sirup under reduced pressure. The residue was dissolved from the flask with 25 cc. of hot methanol and allowed to crystallize. The yield was 3.5 g. of monoacetyldiiydrotoxicarol which melted at 206°. When it was recrystallized as outlined before it melted at 207° and caused no depression of the melting point when mixed with the preparation previously described. The optical properties were also identical with those characteristic of monoacetyldihydrotoxicarol.

Oxidation of Toxicarol with Iodine in an Alcoholic Solution of Potassium Acetate.—

Five grams of toxicarol and 7.5 g. of potassium acetate were dissolved in 250 cc. of boiling absolute ethanol and treated portion-wise with 100 cc. of an absolute ethanolic solution of 6 g. of iodine. The reaction mixture was allowed to stand for a day, after which the crystalline iodo compound was removed by filtration. The yield was usually 1.6 g. The product melted with decomposition at various temperatures from 198 to 204°. The crude material when recrystallized from various solvents melted with decomposition over a wide temperature range. The solvents used and the melting points of the crystals obtained from them are as follows: acetic acid, 206°; benzene and ether, 222°; pyridine and butanol, 225°; chloroform and ether, 214°; chloroform and butanol, 215°. However, various preparations obtained from the same solvents frequently showed considerable difference in the melting point. In all cases the material separated as fine yellow needles and rods.

The filtrate from the original crystals was treated with 1500 cc. of water. The precipitate formed was separated, dried, dissolved in 15 cc. of boiling acetic acid and allowed to crystallize for a day. Usually there separated 2.5 g. of iodo compound which melted at 204–205°.

Anal.[6] Calcd. for $C_{23}H_{19}O_7I$: C, 51.69; H, 3.58; I, 23.76; OCH_3 (2), 11.62. Found: C, 49.00; H, 3.53; I, 22.88; OCH_3, 11.5.

Dehydrotoxicarol from the Iodo Compound.—A mixture of 4 g. of iododehydrotoxicarol, 8 g. of zinc dust and 60 cc. of acetic acid was boiled for forty-five minutes. The clear yellow solution which resulted was decanted from the zinc and allowed to crystallize. After the crystals were removed from the mother liquors, washed with acetic acid, then water and finally methanol, 3.4 g. of crude dehydrotoxicarol was obtained. After it was recrystallized as outlined before, it melted at 235–236°. When mixed with dehydrotoxicarol prepared by the ferricyanide oxidation of toxicarol, there was no depression of the melting point. It also possessed the optical properties of dehydrotoxicarol.

Dehydrodihydrotoxicarol.—One gram of dihydrotoxicarol was treated with an alkaline potassium ferricyanide solution as outlined for the preparation of dehydrotoxicarol. There was obtained 0.11 g. of dehydrodihydrotoxicarol which melted at 254°. It was recrystallized from boiling acetic acid, from which it separated as long yellow rods whose melting point was 260°. The substance apparently is monoclinic. In parallel polarized light (crossed nicols) the extinction is usually inclined, although occasionally rods are found having straight extinction (crystals elongated parallel to the *b* axis). In convergent polarized light (crossed nicols) partial biaxial interference figures are common, frequently showing one optic axis up: η_α, 1.500; η_β, 1.680; η_γ, >1.740 (both ±0.003).

Anal. Calcd. for $C_{23}H_{22}O_7$: C, 67.30; H, 5.41; OCH_3 (2), 15.1. Found: C, 67.05; H, 5.45; OCH_3, 14.9.

Summary

1. Acetylation of toxicarol yields a diacetyl derivative which upon catalytic reduction is changed to diacetyldihydrotoxicarol and monoacetyldihydrodesoxytoxicarol.

2. Catalytic reduction of toxicarol, under the conditions used to reduce diacetyltoxicarol, yields only dihydrotoxicarol. This substance may be acetylated in such a way as to introduce either one or two acetyl groups.

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[6] The sample upon which carbon and hydrogen were determined was recrystallized from acetic acid. That upon which halogen and methoxyl were determined was obtained from chloroform and ether, melting point 210°.

3. Oxidation of toxicarol with ferricyanide yields dehydrotoxicarol involving the loss of two hydrogen atoms from the mother substance.

4. Dehydrotoxicarol is also formed by the oxidation of toxicarol with iodine in an alcoholic potassium acetate solution. In this reaction an intermediate iododehydrotoxicarol is formed which can be dehalogenated with zinc dust and acetic acid.

5. Reduction of dehydrotoxicarol or its acetyl derivative not only results in the reduction of the double bond, demonstrated by the dihydro formation, but it also regenerates the structure responsible for the dehydro formation.

6. It seems possible that the second acetyl group introduced into toxicarol is the result of some reaction brought about by the reagents involved in the acetylation process.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. XII. SOME NEW DERIVATIVES OF ROTENOL

BY H. L. HALLER AND F. B. LAFORGE

RECEIVED MARCH 21, 1931 PUBLISHED JUNE 8, 1931

When rotenone ($C_{23}H_{22}O_6$) is refluxed with zinc and alkali in alcohol solution, two products are obtained, derritol, which is soluble in alkali, and rotenol, which is alkali insoluble. Rotenol is a white compound which possesses two hydrogen atoms more than rotenone, and Butenandt[1] assumes that it is formed by the reduction of the carbonyl group to a secondary alcohol group because, unlike rotenone, it does not yield an oxime and because it liberates one mole of methane with the Grignard reagent. The presence of an hydroxyl group in rotenol has not been satisfactorily demonstrated, however, as all attempts to obtain acyl derivatives have failed, and we have lately found several new facts which contradict the assumption that it is an alcohol.

In the course of our work on the structure of rotenone it has been found that rotenol readily yields isotubaic acid on alkali fusion[2] and that dihydrorotenolic acid is readily cleaved with alkaline hydrogen peroxide, forming netoric acid[3] ($C_{12}H_{14}O_5$), which contains the original methoxyl groups.

Both these reaations are best explained by the assumption of cleavage at a carbonyl group, as is generally assumed for other derivatives of rotenone. An attempt was made, therefore, to determine whether or not rotenol possesses a ketone group or whether this group has been reduced as suggested by Butenandt.

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[1] Butenandt, Ann., 464, 253 (1928).

[2] Haller and LaForge, THIS JOURNAL, 52, 4505 (1930).

[3] Smith and LaForge, *ibid.*, 52, 4595 (1930).

We have, in fact, confirmed the observations of Butenandt in that we have been unable to form an oxime from rotenol and have not been successful in preparing an acetyl derivative. On the other hand, we have found in one important reaction an indication of the presence of a ketone group.

With Clemmensen's reagent (amalgamated zinc) isorotenol ($C_{23}H_{24}O_6$) yields a compound having the empirical formula $C_{23}H_{26}O_5$, thus indicating the reduction of a carbonyl group. Rotenol and dihydrorotenol on the other hand are not reduced with this reagent but are recovered unchanged. Rotenol, however, can be isomerized to isorotenol identical with the isorotenol obtained from isorotenone, and there is no reason to assume that the carbonyl group is involved in the process of isomerization.

As it has been shown that rotenone contains two asymmetric centers, one of which disappears when rotenone and its derivatives are isomerized with sulfuric acid to isorotenone and its derivatives, and the other in the formation of the dehydro derivatives, it would be expected that isorotenol would be optically active, especially as a new asymmetric center would be formed in the conversion of the carbonyl group to the secondary alcohol group. The fact that isorotenol is optically inactive whereas rotenol is optically active is an additional argument against its supposed alcoholic nature.

On oxidation with ferricyanide and alkali, rotenol and dihydrorotenol yield dehydro derivatives isomeric with rotenone and dihydrorotenone. Unlike all the other dehydro derivatives of rotenone, which are yellow, dehydrorotenol and dehydrodihydrorotenol are white. Molecular weight determination shows that dehydrorotenol is not a dimolecular compound. It does not yield an oxime nor an acetyl derivative. On catalytic hydrogenation dehydrorotenol yields a mixture of a dihydro compound which is identical with the dehydro derivative obtained from dihydrorotenol and an acid which has been termed dehydrodihydrorotenolic acid. This acid is quite stable to alkali and is not cleaved in alkaline solution with hydrogen peroxide as are most of the rotenonic acid derivatives. With zinc and alkali, dehydrorotenol does not add water as do other dehydro derivatives of rotenone but is reduced quantitatively to rotenol.

Dihydrorotenol also yields a dehydro derivative. This substance, dehydrodihydrorotenol, is not reduced with catalytic hydrogen, but on boiling with zinc and alkali in alcohol solution it is quantitatively reduced to dihydrorotenol.

On boiling with zinc and alkali in alcohol solution, dihydrorotenonic acid yields dihydrorotenolic acid. There is no evidence that dihydroderritolic acid is formed, as might be expected from the analogy in the case of rotenone itself.

Experimental

Dehydrodihydrorotenol.—One-half gram of dihydrorotenol was dissolved in 25 cc. of 95% alcohol and 0.9 g. of potassium ferricyanide, and 0.135 *g*. of potassium hydroxide in 7.5 cc. of water was added to the hot solution. The reaction mixture was allowed to stand overnight and then diluted with about 400 cc. of water. The precipitated substance was filtered off, washed with water and dried. Recrystallized from 95% alcohol, it melted at 171°.

Anal. Subs., 0.0870, 0.0912: CO_2, 0.2220, 0.2325; H_2O, 0.0472, 0.0499. 0.1770 subs. in 12.3 g. benzene; AT = 0.191°. Calcd. for $C_{23}H_{24}O_6$: C, 69.69; H, 6.06; mol. wt., 396. Found: C, 69.59, 69.62; H, 6.07, 6.12; mol. wt., 376.7.

Dehydrodihydrorotenol did not yield an oxime when refluxed with hydroxylamine hydrochloride and sodium acetate in absolute alcohol. When boiled with acetic anhydride and sodium acetate it was recovered unchanged.

Dehydrorotenol.—Dehydrorotenol was obtained when rotenol was treated with alkali and potassium ferricyanide in the same manner that was described for the preparation of dehydrodihydrorotenol. It was purified by crystallization from 95% alcohol. It melted at 124°.

Anal. Subs., 0.0936: CO_2, 0.2402; H_2O, 0.0465. Calcd. for $C_{23}H_{22}O_6$: C, 70.03; H, 5.63. Found: C, 69.99; H, 5.56.

Reduction of Dehydrorotenol with Catalytic Hydrogen.—1.86 g. of dehydrorotenol dissolved in 25 cc. of ethyl acetate was added to 25 cc. of ethyl acetate containing about 0.3 g. of platinum oxide catalyst, previously saturated with hydrogen, and the solution was shaken in an atmosphere of hydrogen. About 200 cc. of hydrogen was absorbed in two or three minutes, after which absorption practically ceased. The solution was decanted from the catalyst, most of the ethyl acetate was distilled off, and the concentrated solution was dissolved in ether. The ether solution was extracted with 5% sodium hydroxide, then with water. It was dried over sodium sulfate. After the ether was removed the remaining product was crystallized from 95% alcohol. It melted at 171°. When mixed with an equal quantity of dehydrodihydrorotenol, no depression in melting point was noted.

The aqueous alkaline extract was acidified with dilute sulfuric acid and extracted with ether. The ether extract was washed with water and dried over sodium sulfate. The ether was removed, and the substance was crystallized from 95% alcohol. It melted at 206°. It was named dehydrodihydrorotenolic acid.

Anal. Subs., 0.0839: CO_2, 0.2129; H_2O, 0.0474. *Titration.* Subs., 0.0328: 0.85 cc. of $N/10$ KOH. Calcd. for $C_{23}H_{26}O_6$: C, 69.31; H, 6.58. Found: C, 69.21; H, 6.32. Acid number calcd., 398; found, 386.

The potassium and sodium salts of dehydrodihydrorotenolic acid are relatively quite insoluble in dilute alkaline solution. In an attempt to oxidize this acid in alkaline solution with hydrogen peroxide by the procedure usually employed, only the unchanged material was recovered. Unchanged starting material was also obtained when the acid was treated with alkaline permanganate, although some oxidation took place.

The acid was also found to be stable on prolonged boiling in strong alcoholic potash solution.

Mixed Anhydride of Dehydrodihydrorotenolic Acid and Acetic Acid.—One-half gram of dehydrodihydrorotenolic acid was refluxed with 20 cc. of acetic anhydride and 1 g. of anhydrous sodium acetate for two hours. The solution was poured into water, the precipitate was filtered off, washed with water and dried. It was then recrystallized from 95% alcohol. It melted at 136°.

Anal. Subs., 0.0770: CO_2, 0.1919; H_2O, 0.0428. Calcd. for $C_{25}H_{28}O_7$: C, 68.15; H, 6.41. Found: C, 67.97; H, 6.22.

The substance is insoluble in cold dilute alkali and is quite stable in boiling methyl alcohol. When it is decomposed with cold alcoholic alkali, dehydrodihydrorotenolic acid can be recovered.

Reduction of **Dehydrodihydrorotenol** to **Dihydrorotenol.**—Five-tenths of a gram of dehydrodihydrorotenol was refluxed for two hours with 20 cc. of 95% alcohol, 5 cc. of 40% potassium hydroxide, and 2 g. of zinc. The hot solution was then filtered into ice cold dilute sulfuric acid. The precipitate was filtered off, washed with water and dissolved in ether. The ether solution was washed with water and dried over sodium sulfate. After the removal of the ether the substance was crystallized from 95% alcohol. It crystallized in fine needles which melted at 131–132°. The yield was 0.5 g. When mixed with an equal quantity of dihydrorotenol, the melting point was 129°. It was further identified as dihydrorotenol by an optical examination of the crystals.

Anal. Subs., 0.0785: CO_2, 0.1994; H_2O, 0.0462. Calcd. for $C_{23}H_{26}O_6$: C, 69.31; H, 6.58. Found: C, 69.28; H, 6.59.

Reduction of Dehydrorotenol to **Rotenol.**—The procedure employed was the same as that described above for the reduction of dehydrodihydrorotenol. The product obtained was recrystallized from 95% alcohol. It melted at 120° and was identified as rotenol.

Desoxyisorotenol.—Two grams of isorotenol dissolved in 80 cc. of glacial acetic acid was added to 12 g. of amalgamated zinc followed by 10 cc. of concentrated hydrochloric acid. The reaction mixture was then refluxed for two hours. The hot solution was decanted from the zinc and slowly poured into 500 cc. of water. After cooling, the precipitate was filtered off, washed with water and dissolved in ether. The ethereal solution was washed with water and dried over sodium sulfate. On removal of most of the ether the substance readily crystallized. It was recrystallized from 95% alcohol. It melted at 149°. It does not give a color with ferric chloride.

Anal. Subs., 0.0825: CO_2, 0.2189; H_2O, 0.0525. Calcd. for $C_{23}H_{26}O_5$: C, 72.25; H, 6.86. Found: C, 72.35; H, 7.07.

Isorotenol from **Rotenol.**—Three grams of rotenol (melting point 119°) was dissolved in a solution of 36 cc. of glacial acetic acid and 9 cc. of concentrated sulfuric acid. The solution was heated to 100° for five minutes, cooled and poured into 600 cc. of water. A little sodium sulfate was added, and the precipitate was filtered off and washed twice with water. The precipitate was dissolved in ether, and was washed twice with 5% potassium carbonate solution and then with water. After it was dried over sodium sulfate, the ether was removed, when the substance crystallized. The yield was 2.2 g. After repeated crystallization from 95% alcohol, it was obtained pure. It melted at 131°. It gave the same color in alcohol solution with ferric chloride as does isorotenol prepared from isorotenone. It was further identified as isorotenol by an optical examination of the crystals.

Reduction of **Dihydrorotenonic** Acid **with** Zinc and Alkali.—Two grams of dihydrorotenonic acid was refluxed for four hours in a solution of 60 cc. of 95% alcohol and 20 cc. of 15% potassium hydroxide to which had been added 4 g. of zinc. The hot solution was decanted from the zinc and filtered into cold dilute sulfuric acid. The precipitate was filtered off, washed with water, and dissolved in ether. The ethereal solution was washed with water and dried over sodium sulfate. On removal of the ether the substance readily crystallized. It was recrystallized from methyl alcohol and melted at about 90°. It was identified as dihydrorotenolic acid.

When 45% potassium hydroxide was employed, dihydrorotenonic acid also yielded dihydrorotenolic acid. There was no indication of the formation of dihydroderritolic acid.

Summary

Rotenol and dihydrorotenol on oxidation with alkaline ferricyanide yield dehydro derivatives.

Dehydrorotenol is reduced with catalytic hydrogen to a mixture of dehydrodihydrorotenol and dehydrodihydrorotenolic acid.

Dehydrodihydrorotenolic acid is not cleaved with alkaline hydrogen peroxide.

With zinc and alkali dehydrorotenol and dehydrodihydrorotenol are reduced quantitatively to rotenol and dihydrorotenol.

Isorotenol ($C_{23}H_{24}O_6$) on reduction with Clemmensen reagent (amalgamated zinc) yields a compound of formula $C_{23}H_{26}O_5$, indicating the reduction of a carbonyl group.

Dihydrorotenonic acid is reduced with zinc and alkali to dihydrorotenolic acid.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MUTAROTATION OF THE ALCOHOLATE AND ALDEHYDROL OF ALDEHYDO-GALACTOSE PENTAACETATE

BY M. L. WOLFROM

RECEIVED MARCH 23, 1931 PUBLISHED JUNE 8, 1931

The open chain or aldehydo sugar acetates synthesized in this Laboratory show mutarotation in alcohol but not in such non-hydroxylated solvents as acetylene tetrachloride. The mutarotation in alcohol is indicative of chemical combination of some kind between the solvent and the carbonyl group of the sugar acetate. In the case of galactose,[1] well-defined crystalline compounds with ethanol and water were isolated. At the time of the isolation of these two compounds, we were interested only in determining their initial rotation in chloroform and the U. S. P. grade of this solvent was used. The rotations were thus determined in chloroform containing an appreciable amount of ethanol. In both cases mutarotation curves which passed through a minimum were obtained. The unusual nature of these mutarotation curves has been pointed out to us by Professor T. M. Lowry and we have accordingly repeated the experiments using alcohol-free chloroform. In this solvent we find a minimum only in the curve for the ethanol compound (Fig. 1). Data for two experiments with the ethanol compound are given in Table I. The actual speeds for the two experiments are widely different but values identical within the limits of experimental error are obtained for the minimum and final rotations. This variation in speed is probably due to the catalytic effect of hydrogen chloride produced by the slight photochemical decomposition of the alcohol-free chloroform used, the amount of acidity present being apparently different in the two cases.

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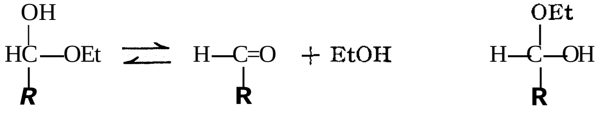
[1] M. L. Wolfrom, THIS JOURNAL, 52, 2464 (1930).

The nature of the mutarotation curve for the ethanol compound indicates a rapid initial reaction followed by a slower one and is also indicative of the presence of three substances with differing rotations. This can be adequately explained on the basis of structural theory as follows



$$\underset{(A)}{\mathrm{HC(OH)(R)}\text{—OEt}} \rightleftarrows \underset{(B)}{\mathrm{H—C(R)=O}} + \mathrm{EtOH} \qquad \underset{(C)}{\mathrm{H—C(OEt)(R)—OH}}$$

(A) (B) (C)

The fact that the free aldehyde form (B, $[\alpha]_D$ $-25°$) and the known ethanol compound (A, $[\alpha]_D$ $+1.5°$) have widely differing rotations in chloroform is proof that the ethanol is constitutionally combined and is not present as alcohol of crystallization. In the hemi-acetal structure (A) the aldehydo carbon atom becomes asymmetric and can exist in two forms, (A) and (C). From the nature of the mutarotation curve the form (C) must be more dextro-rotatory than **(A).** Experiments to find conditions for the isolation of the second form (C) are now in progress in this Laboratory.

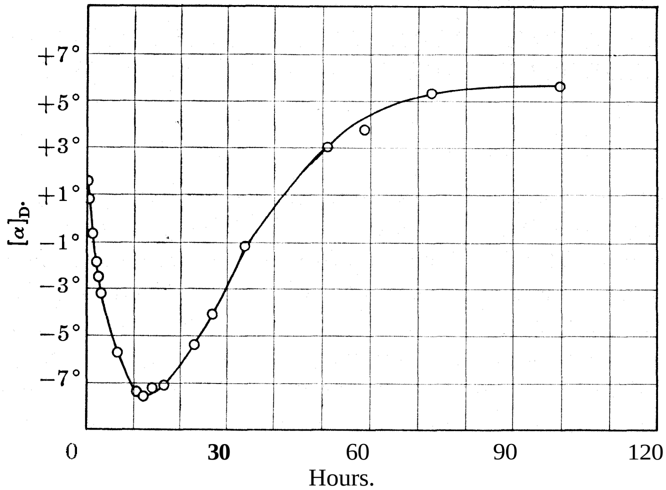
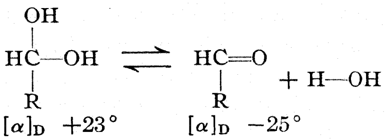


Fig. 1.—Mutarotation of the ethyl **hemi-acetal** of aldehydo-galactose pentaacetate in chloroform, Expt. 1.

The mutarotation curve obtained for aldehydo-galactose pentaacetate aldehydrol in ethanol-free chloroform is shown in Fig. 2. This is now a smooth exponential curve and differs widely in form from that obtained for the ethanol compound. In the case of the aldehydrol, the aldehydo carbon atom is not asymmetric and only one form is possible. The nature of the mutarotation is indicated by the following simple reaction



$$\underset{[\alpha]_{\mathrm{D}}\ +23^\circ}{\begin{array}{c}\mathrm{OH}\\ |\\ \mathrm{HC{-}OH}\\ |\\ \mathrm{R}\end{array}} \rightleftharpoons \underset{[\alpha]_{\mathrm{D}}\ -25^\circ}{\begin{array}{c}\mathrm{HC{=}O}\\ |\\ \mathrm{R}\end{array}} + \mathrm{H{-}OH}$$

As the rotations of both the forms indicated above are known, the data obtained may be analyzed mathematically. The data of Table II show that the reaction is a simple monomolecular decomposition, as would be predicted on the basis of an aldehydrol structure for the hydrate. The value obtained for the final rotation indicates that the change to the free aldehyde form ($[\alpha]_D$ −25°) is nearly complete. When a 4% chloroform solution of the aldehydrol was used the solution became turbid in about thirty minutes due to the separation of water.

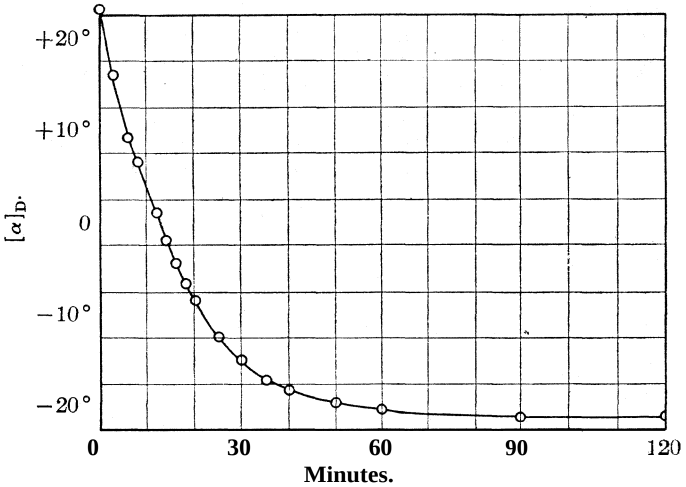


Fig. 2.—Mutarotation of the aldehydrol of aldehydo-galactose pentaacetate in chloroform.

It may be stated that the material from the equilibrated chloroform solutions of both the aldehydrol and ethyl hemi-acetal can be recovered unchanged in good yield by recrystallization from the appropriate solvents. The rotation of the free form of aldehydo-galactose pentaacetate is stable in pure chloroform solution. This is also true of the aldehydo-acetates of d-glucose[2] and of *l*-arabinose[3] recently isolated in this Laboratory. These facts show that the chloroform mutarotation of the aldehydrol and ethyl hemiacetal of aldehydo-galactose pentaacetate is not in the nature of a profound structural change involving an acetyl shift to a ring form. It is believed that the pure chloroform mutarotation of these compounds offers good evidence of their constitutional structure.

[2] M. L. Wolfrom, This Journal, 51,2188 (1929).

M. L. Wolfrom and Mildred R. Newlin, *ibid.*, 52,3619 (1930).

On the basis of the more accurate initial rotation data now reported, the specific rotation in chloroform solution of aldehydo-d-galactose pentaacetate aldehydrol is +23° and that for the ethyl hemi-acetal is +1.5°. The values previously obtained were +19.5 and −0.5°, respectively.

TABLE I

MUTAROTATION OF THE ETHYL HEMI-ACETAL OF ALDEHYDO-GALACTOSE PENTAACETATE IN PURE CHLOROFORM (*l*, 4 DM.; λ, 5892 Å.; t, 22°)

Experiment 1; *c*, 5.019			Experiment 2; *c*, 5.035		
Time, min.	**a, degrees**	**[α]D, degrees**	**Time, min.**	**a, degrees**	**[α]D, degrees**
4	+0.31	+1.6	3	−0.25	−1.2
10	.28	1.4	6	− .48	−2.4
14	.26	1.3	10	− .95	−4.7
30	.16	0.8	15	−1.24	−6.2
Hours					
1	− .04	−0.2	20	−1.35	−6.7
2	− .38	−1.9	27	−1.48	−7.4
4	− .80	−4.0	35.5	−1.56	−7.7
6.5	−1.13	−5.7	40	−1.59	−7.9
8	−1.32	−6.6	45	−1.45	−7.2
10.5	−1.47	−7.4	50	−1.40	−7.0
			Hours		
12	−1.53	−7.6	1	−1.09	−5.4
	(*l*, 2-dm.)				
14	−0.72	−7.2	1.25	−0.70	−3.5
17	− .71	−7.1	1.5	− .38	−1.9
23	− .54	−5.4	2	+ .11	+0.6
34	− .12	−1.2	3	.70	3.5
59	+ .37	+3.7	6.5	1.18	5.9
73	+ .53	+5.3	9	1.18	5.9
100	+ .56	+5.6			

TABLE II

MUTAROTATION OF THE ALDEHYDROL OF ALDEHYDO-GALACTOSE PENTAACETATE IN PURE CHLOROFORM (*l*, 4 DM.; λ, 5892 Å.; t, 23°; *c*, 2.006)

t, min.	**a, degrees**	**[α]D, degrees**	***x* (Free form)**	***a − n* (Aldehydrol)**	**k^b**
0	....	+23^a	0	1.000	
3	+1.28	16.0	0.152	0.848	0.055
4	1.14	14.2	.191	.809	.054
6	0.74	9.2	.300	.700	.060
8	.52	6.5	.359	.641	.056
10	.28	3.5	.424	.576	.056
12	.08	1.0	.478	.522	.054
14	− .16	− 2.0	.544	.456	.056
16	− .35	− 4.4	.596	.404	.057
18	− .53	− 6.6	.643	.357	.057
20	− .67	− 8.4	.682	.318	.057
25	− .99	−12.4	.769	.231	.059
30	−1.19	−14.8	.822	.178	.058

TABLE II *(Concluded)*

1, min.	α, degrees	$[\alpha]_D$, degrees	x (Free form)	$a - x$ (Aldehydrol)	k^b
35	−1 36	−17.0	0.869	0 131	0 058
40	−1.45	−18.1	.894	106	.056
50	−1.56	−19.5	.924	076	Av., 0 057 ±0.003
60	−1.62	−20.2	.939	.061	
90	−1.69	−21.1	.958	.042	
120	−1.68	−11.0	.956	.044	
240	−1.69	−21.1	.958	.042	

[a] Interpolated. [b] $k = (1/t) \log, a/(a - x)$.

The author wishes to acknowledge his indebtedness to Professor Edward Mack, Jr., for counsel in analyzing the data presented in this communication.

Summary

1. The rotation changes of the aldehydrol and ethyl hemiacetal of aldehydo-d-galactose pentaacetate have been determined in alcohol-free chloroform solution.
2. The nature of the rotation changes observed is presented as evidence for the constitutional nature of these compounds.
3. New values for the rotations of these substances in chloroform have been determined.
4. Polarimetric evidence is given for the existence of two isomeric forms of aldehydo-galactose pentaacetate ethyl hemi-acetal.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE ROTATORY DISPERSION OF SEVERAL ALDEHYDO SUGAR ACETATES

BY M. L. WOLFROM AND WALLACE R. BRODE

RECEIVED MARCH 23, 1931 PUBLISHED JUNE 8, 1931

Rotatory dispersion work in the sugar series has not been carried on to any great extent. Lowry and Richards[1] have made a very accurate study of the dispersion of sucrose in water solution and have found it to be normal and simple. In the sugar acetate series, very complete data have been obtained by Levene and Bencowitz[2] for the ring pentaacetates of *a*- and p-mannose and of *a*- and β-glucose in a number of solvents, including chloroform. In all these cases they have found the dispersion in the visible region of the spectrum to be normal and simple. Wagner-Jauregg[3] has reported

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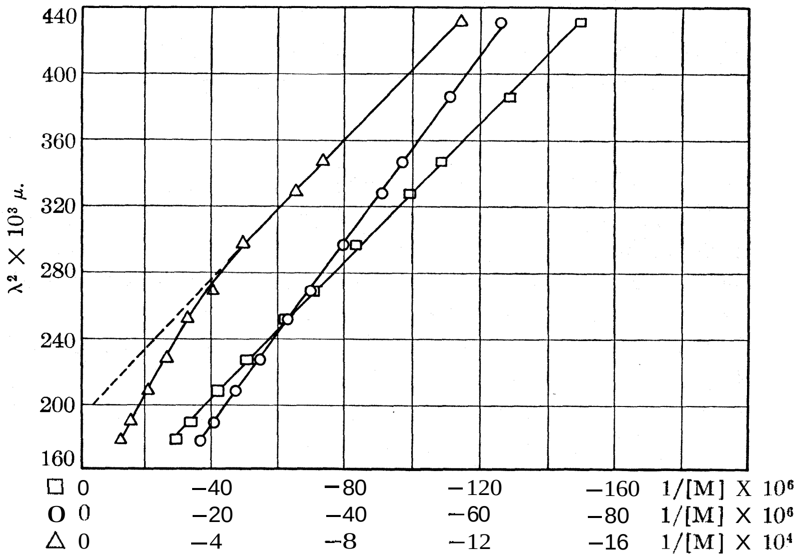
[1] T. M. Lowry and E. M. Richards, J. *Chem. Soc.*, 125,2511 (1924).

[2] P. A. Levene and I. Bencowitz, J. *Biol. Chem.*, 72, 627 (1927); 73, 679 (1927); 74, 153 (1927).

[3] T. Wagner-Jauregg, *Heb. Chim. Acta, 11,786* (1928).

the dispersions of a number of sugars in water solution and of some methylated sugars in chloroform. He has found them to be simple in every case except that of β-pentamethylglucose in chloroform, which was stated to be complex.

Optical rotations at 5892 Å. have been previously recorded for the open chain or aldehydo acetates of *d*-glucose,[4] d-galactose[5] and l-arabinose[6] in chloroform solution. We have now measured the complete optical dispersion of these substances in the visible region. This was done with the object of determining whether these compounds which are known to possess a free aldehyde group would show any unusual optical rotatory properties. The data obtained are given in Table I and an analysis of the figures obtained has been made by the graphic method. When the reciprocals of the molecular rotations are plotted against the square of the wave lengths a straight line is obtained in the case of the aldehydo-acetates of galactose and arabinose (Fig. 1). On this basis, these dispersions are then normal and simple. In the case of aldehydo-d-glucose pentaacetate, a smooth curve without a maximum or minimum is obtained when the rotations are plotted against the wave length. When the reciprocal of the molecular rotation is plotted against the square of the wave



□, Aldehydo-d-galactose pentaacetate; ○, aldehydo-*l*-arabinose tetraacetate; △, aldehydo-d-glucose pentaacetate.

Fig. 1.—Rotatory dispersion of several aldehydo sugar acetates.

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[4] M. L. Wolfrom, THIS JOURNAL, 51, 2188 (1929).

[5] M. L. Wolfrom, *ibid.*, 52, 2464 (1930).

[6] M. L. Wolfrom and Mildred R. Newlin, ibid., 52, 3619 (1930).

length (Fig. I) a deviation from a straight line appears in the violet region. The dispersion is then apparently normal and complex. The rotations for the glucose acetate are low and consequently we do not wish to place much emphasis upon this deviation, as it may represent experimental error. However, since these substances possess a carbonyl group, they would be expected to show absorption in the ultraviolet with a consequent possible effect upon the rotatory dispersion in this region of the spectrum.

In the data herein reported, a Schmidt and Haensch polarimeter with spectrometer attachment was used. The spectrometer was calibrated by a method similar to that of Bencowitz.[7] A calibration was first made against the mercury arc. This was then verified by readings on a quartz plate calibrated by the National Bureau of Standards for two lines, using the data of Lowry and Coode-Adams[8] for the dispersion of quartz. The solvent used in determining the dispersion data was alcohol-free chloroform, in which the rotations of these acetates are stable. After dispersion readings were completed, the first reading taken was always checked.

TABLE I

ROTATORY DISPERSION IN CHLOROFORM SOLUTION OF THE ALDEHYDO-ACETATES OF d-GLUCOSE, d-GALACTOSE AND l-ARABINOSE (l, 4-DM.)

	Aldehydo-d-glucose pentaacetate		Aldehydo-d-galactose pentaacetate		Aldehydo-I-arabinose tetraacetate	
	c, 4.008	**t, 27°**	**c, 4.000**	**t, 23°**	**c, 4.001**	**t, 23°**
λ, mμ	**a**	[α]	**a**	[α]	a	[α]
656.3	−0.36	− 2.25	−2.73	−17.1	− 7.96	− 49.7
621			−3.17	−19.8	− 9.03	− 56.4
589.2	− .56	− 3.50	−3.77	−23.6	−10.29	− 64.3
573	− .63	− 3.94	−4.14	−25.9	−11.04	− 69.0
545	− .83	− 5.16	−4.93	−30.8	−12.64	− 79.0
519	−1.01	− 6.31	−5.77	−36.1	−14.27	− 89.2
502	−1.26	− 7.87	−6.70	−41.9	−15.94	− 99.6
477	−1.57	− 9.81	−8.15	−50.9	−18.30	−114.5
457	−1.99	−12.44	−9.91	−61.9	−21.13	−132.1
436	−2.71	−16.95	−12.24	−76.5	−24.7	−154
423	−3.24	−20.25	−14.1	−88.2	−27.4	−171

Summary

1. The rotatory dispersion in the visible region has been determined for the aldehydo acetates of d-glucose, d-galactose and I-arabinose in chloroform solution.
2. All these substances show normal dispersion. A graphic analysis of the data shows that the dispersion of aldehydo-glucose pentaacetate is apparently complex and that the others are apparently simple.

COLUMBUS, OHIO

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[7] I. Bencowitz, *J.* Phys. Chem., 32,1163 (1928).

[8] T. M. Lowry, *Phil. Trans.*, **212A,** 261 (1912); Lowry and Coode-Adams, *ibid.*, **226A,** 391 (1927).

[CONTRIBUTION FROM THE LABORATORY OF PLANT PHYSIOLOGY, UNIVERSITY OF MARYLAND. AND THE AGRICULTURAL EXPERIMENT STATION]

THE DECARBOXYLATION OF d-GALACTURONIC ACID WITH SPECIAL REFERENCE TO THE HYPOTHETICAL FORMATION OF 1-ARABINOSE[1]

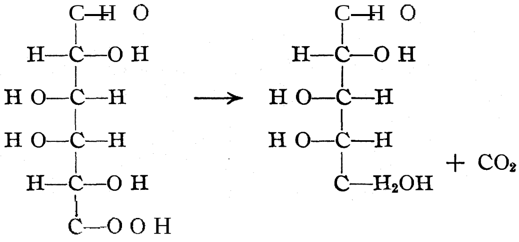
BY C. M. CONRAD

RECEIVED MARCH 24, 1931 PUBLISHED JUNE 8, 1931

Introduction

1-Arabinose has long been considered to be a component in the molecular structure of pectins.[2] Recently, several investigators[3] have cast doubt on this belief. They think that 1-arabinose may arise during dilute acid hydrolysis of pectin by decarboxylation of d-galacturonic acid.

When d-galacturonic acid is heated with 12% hydrochloric acid it decomposes into carbon dioxide and furfural.[4] Theoretically, *l*-arabinose should be formed momentarily, thus



d-Galacturonic acid *l*-Arabinose

McKinnis[5] predicted that in dilute mineral acids decarboxylation would occur and that the arabinose produced would not be decomposed. Link and Niemann[6] have shown that d-galacturonic acid (also d-glucuronic acid) actually is decarboxylated with dilute mineral acids. However, it has not been determined whether arabinose occurs among the reaction products.

Proof that arabinose or other pentoses are produced from uronic acids during the hydrolysis of plant materials would be of considerable importance with respect to carbohydrate chemistry. First, it would discredit the occurrence of arabinose, as such, in pectins. Second, it would render more

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[1] Published with the permission of the Director of the Maryland Agricultural Experiment Station.

[2] Scheibler, *Ber.,* 1, 108 (1868); von Fellenberg, *Biochem.* Z., 85, 118 (1918); Nanji, Paton and Ling, J. *Soc. Chem. Ind., 44,* 253T (1925); Ehrlich and Sommerfeld, *Biochem.* Z., 168, 263 (1926).

[3] Ahmann and Hooker, University of Missouri Agr. Expt. Sta., *Research* Bull., 77 *(1925);* McKinnis, THIS JOURNAL, 50, 1911 (1928); Willaman, in Gortner's "Outlines of Biochemistry," Chap. XXVII, p. 585.

[4] Ehrlich and Schubert, *Ber.,* 62, 1974 (1929).

[5] McKinnis, THIS JOURNAL, 50, 1911 (1928).

[6] Link and Niemann, *ibid.,* 52, 2474 (1930).

or less uncertain the occurrence of the pentoses reported in many gums, mucilages and hemicelluloses. The pentoses assumed to have been hydrolytic products could have been decarboxylation products of a complex uronide. Therefore, it is important to determine, if possible, whether arabinose is formed as a decarboxylation product of galacturonic acid in dilute mineral acids.

Experimental Part

In order to test the production of arabinose by decarboxylation it is necessary to work with galacturonic acid or with its arabinose-free derivatives. For this purpose barium galacturonate, and Ehrlich's[4] tetra acid "a" were chosen.

Preparation of Materials.—Barium galacturonate was prepared from lemon pectin,[7] according to the procedure of Link and Dickson.[8] On a dry weight basis the product yielded *16.50%* carbon dioxide when boiled with 12% hydrochloric acid and contained *25.15%* of barium. The theoretical values are *16.81* and 26.3%, respectively.

Tetra acid "a" was prepared from lemon pectin according to Ehrlich's[4] directions. One part of pectin is heated at 80° with *10* parts of 5% hydrochloric acid for six hours. The grayish white precipitate which forms is washed exhaustively, first with 1% hydrochloric acid, then with water, 95% alcohol, and finally ether. The material is sucked as dry as possible on the Büchner funnel and spread out to dry in the air. The material thus prepared contained *13.61%* moisture, 0.61% ash and yielded 24.55% carbon dioxide on the dry ash-free basis. Ehrlich found for the tetra acid "a" of sugar beets, 0.19% ash and *an* average of *24.81%* of carbon dioxide.

Apparatus.—The apparatus used to measure the extent of decarboxylation has been described previously by Conrad.[9]

Selection of 4% Sulfuric **Acid** for Decarboxylation.—Sulfuric acid has been used more than any other mineral acid for hydrolysis and isolation of sugars. This is because of the ease with which it can be removed from thr hydrolytic products. In the case of **gums,** mucilages and hemicelluloses a 4% concentration is more often employed.[10] This concentration does not appear to be very injurious to the liberated arabinose if the heating is not longer than eight to ten hours.[11] By preliminary experiments it was found that within this time sufficient decarboxylation could be obtained to detect arabinose if it is produced.

Method for the Determination of Arabinose.—Since the recovery of arabinose in crystalline condition is usually attended by much loss, it was thought preferable to obtain it as the diphenylhydrazone compound according to the method of Neuberg and Wohlgemuth.[12] Instead of using the free base, as these investigators did, the hydrochloride salt was used. This was purified by once recrystallizing the commercial prepa-

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[7] The lemon pectin was kindly furnished by Messrs. C. P. Wilson and H. W. Hall of the California Fruit Growers Exchange.

[8] Link and Dickson, J. *Biol. Chem., 86,491 (1930).*

[9] Conrad, THIS JOURNAL, 53, *1999–2003 (1931).*

[10] Abderhalden, "Handbuch der Biochemischen Arbeitsmethoden," Urban and Schwarzenberg, Berlin, 1910, Vol. II, pp. *59-64.*

[11] Anderson and Sands, *Ind.* Eng. *Chem.,* **17,** *1257 (1925);* Brown, "Handbook of Sugar Analysis," John Wiley and Sons, New York, 1912, p. *548;* Muther and Tollens, *Ber.,* 37, *298 (1904)*; Mauenbrecher and Tollens, ibid., *39, 3576 (1906).*

[12] Neuberg and Wohlgemuth, Z. *physiol. Chem.,* **35,** 31 *(1902).*

ration from 95% alcohol containing a little hydrochloric acid. It was used in 50% alcoholic solution, either with 1.5 parts of sodium acetate, or after addition of almost the calculated quantity of N sodium hydroxide.

In a few cases α-benzylphenylhydrazine hydrochloride was employed in parallel tests with the diphenylhydrazine hydrochloride. It was always used with 1.5 parts of sodium acetate in 75% alcohol.

Results

Failure to Obtain Arabinose from **Galacturonic** Acid.—When barium galacturonate is treated with 4% sulfuric acid the barium is at once precipitated as the sulfate, and the concentration of sulfuric acid is slightly reduced. The liberated galacturonic acid, on heating, yields carbon dioxide and other decomposition products. Among these, arabinose was sought in a number of experiments of which the following is a typical example.

Five grams of barium galacturonate in an Erlenmeyer flask was covered with 100 cc. of 4% sulfuric acid and gently boiled for five hours on the sand-bath. At the end of this period the evolved carbon dioxide was found to be 0.1633 g., or theoretically equivalent to 0.5565 g. of arabinose. The solution was removed from the apparatus, cooled, and treated with a very slight excess of barium hydroxide solution. The excess of alkali was immediately neutralized with a stream of carbon dioxide, and the mixture heated on the steam-bath for about an hour to enlarge the barium sulfate particles. After standing overnight the mixture was warmed with animal charcoal and filtered through a thin layer of infusorial earth. The clear filtrate was evaporated to dryness at 25-mm. pressure in a water-bath heated to 55°. The residue was dissolved in 10 cc. of water and the residual barium galacturonate precipitated with 190 cc. of 95% alcohol. The salt was flocculated by heating somewhat and separated by means of a hardened paper on a suction filter. The filtrate was clarified once again with animal charcoal and divided into two equal parts. These were evaporated to dryness, separately. To one was added 15 cc. of 50% alcoholic solution containing 0.259 g. of diphenylhydrazine hydrochloride and 0.4 g. of sodium acetate. The mixture was heated under the reflux condenser for thirty minutes and set aside. To the other portion was added 2 cc. of 75% alcoholic solution of 0.277 g. of benzylphenylhydrazine hydrochloride and 0.415 g. of sodium acetate. It was heated under the reflux condenser for twenty minutes. In both cases a dark resinous substance separated immediately on cooling. After standing for seven days no hydrazone crystals could be seen in either test. The gums dissolved completely in cold 50% aqueous pyridine and could therefore contain no hydrazone.

In a control experiment 0.4 g. of arabinose was dissolved in a mixture of 5 g. of barium galacturonate in 100 cc. of 4% sulfuric acid. The mixture was not heated, the object being only to determine how much of the arabinose would be lost due to adsorption, transfers and the like. Although the solution was not colored, animal charcoal and infusorial earth were used exactly as in the previous experiment. The final residue was not divided. It was treated with 36 cc. of an alcoholic solution containing 0.62 g. of diphenylhydrazine hydrochloride and 0.93 g. of sodium acetate. The mixture was refluxed as before and there was obtained 0.5256 g. of beautiful *l*-arabinose diphenylhydrazone, equivalent to 0.249 g. of arabinose. This is 62.3% of the amount originally added.

In a second control experiment it was sought to determine whether certain decomposition products of galacturonic acid might prevent the separation of the hydrazones. The 5 g. of barium galacturonate was boiled for five hours on the sand-bath. A quantity of arabinose, 0.556 g., equivalent to that calculated to have been produced in the principal experiment was divided into two equal portions. One portion was added at the beginning of the heating period, the other when it was half through. There was collected 0.1805 g. of carbon dioxide theoretically equivalent to 0.615 g. of additional arabinose. On removing the sulfuric acid, clarifying, concentrating, removing the remaining barium galacturonate and dividing the final alcoholic solution into two equal parts, there was finally obtained from one portion 0.3401 g. of *l*-arabinose diphenylhydrazone. Allowing for the division of alcoholic solution this accounts for 58% of the added *l*-arabinose. After purifying once from 95% alcohol and twice from 50% aqueous pyridine the hydrazone melted at 202.5° (uncorr.). From the other portion there were obtained crystals which after twice recrystallizing from 75% alcohol melted at 173–174° (uncorr.). Van der Haar[13] gives corrected values of 204 and 174°, respectively, for the diphenylhydrazone and a-benzylphenylhydrazone of *l*-arabinose. It is therefore evident that the decomposition products of galacturonic acid do not prevent the separation of these hydrazones.

Failure to Obtain Arabinose from Ehrlich's Tetra Acid "A."—According to Ehrlich and Schubert[4] tetra acid "a" is a polymer containing four units of galacturonic acid. It contains no pentose units. On heating with acids it is hydrolyzed into galacturonic acid which in turn undergoes decarboxylation.

In repeated trials arabinose was sought in the decarboxylation products from tetra acid "a." The following is a typical experiment. A 5-g. sample of tetra acid "a" in 100 cc. of 4% sulfuric acid was boiled gently for nine hours. There was collected 0.1309 g. of carbon dioxide equivalent to 0.446 g. of arabinose. The sulfuric acid was precipitated with barium hydroxide and the mixture heated for an hour on the steam-bath. It was filtered through paper pulp and the filtrate clarified with bone charcoal. The almost colorless filtrate was evaporated at 25–35-mm. pressure to about 10 cc. Barium galacturonate was precipitated with five volumes of 95% alcohol, and removed by filtration. The clear filtrate was evaporated to 2–3 cc. Some material which had separated was again removed by adding 95% alcohol and filtering. The clear filtrate was evaporated completely to dryness. The residue was extracted three times with 10, 10 and 6 cc. of hot 95% alcohol. The combined extracts were filtered and evaporated to about 2 cc. In testing for arabinose no diphenylhydrazone could be obtained, although a dark resinous substance separated.

In a control experiment 5 g. of tetra acid "a" was heated with 100 cc. of 4% sulfuric acid in a boiling water-bath (instead of the sand-bath) for fifteen and one-half hours. Only 0.0620 g. of carbon dioxide equivalent to 0.2114 g. of arabinose was obtained and no diphenylhydrazone could be recovered. Again, 15 g. of tetra acid "a" was heated with 500 cc. of 1% sulfuric acid in the autoclave at 25-lb. pressure for one hour. In this case it was impossible to measure the amount of carbon dioxide formed. After removal of the sulfuric acid and concentration as before no *l*-arabinose diphenylhydrazone could be obtained. On the other hand, the light colored sirupy residue which remained reacted with the diphenylhydrazine to give a dark colored resinous mass.

Identification of Arabinose in the Hydrolytic Products of Apple and Lemon Pectins.—McKinnis,[5] in a study of apple pulp, concluded that apple pectin contains no arabinose. In view of the results obtained above with galacturonic acid and tetra acid "a" it was of interest to subject

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[13] Van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsauren," Gebrüder Borntraeger, Berlin, 1920.

pectins to the same conditions of experimentation and determine whether arabinose is to be found among the products.

The apple pectin[14] used was prepared from "Certo" by alcoholic precipitation and thorough washing with additional alcohol. It contained 74.3% of galacturonic acid on the dry, ash-free basis. The lemon pectin was the same as that used for the preparation of barium galacturonate and tetra acid "a."

Ten grams of pure apple pectin was mixed with 200 cc. of 4% sulfuric acid in a 500-cc. Florence flask and heated on the steam-bath for a short time until dissolved. The flask was removed to the sand-bath and the solution boiled very gently for five hours. During this period 0.0688 g. of carbon dioxide theoretically equivalent to 0.2350 g. of arabinose was produced. After cooling somewhat the acids were neutralized with barium hydroxide solution. The mixture was digested on the steam-bath for a time and set aside overnight. Next morning the supernatant liquid was poured off and the residue filtered on a hardened paper in a Buchner funnel. The decanted liquid and filtrate were combined, stirred with animal charcoal, and filtered by means of suction through a thin layer of infusorial earth on a hardened paper. The clear, practically colorless filtrate was evaporated at 20-mm. pressure in a water-bath at 50° to about 200 cc. Some white substance, probably mineral, was filtered off after first adding some animal charcoal. The filtrate was now evaporated to dryness. The residue was dissolved in 10 cc. of water and barium galacturonate precipitated by addition of 190 cc. of 95% alcohol. The precipitate was flocculated by gentle heating and filtered off on a hardened paper. The clear filtrate was again evaporated to a stiff sirup under reduced pressure. The sirup was dissolved in 33 cc. of water and treated with a solution of 1.55 *g.* of diphenylhydrazine hydrochloride and 6.50 cc. of *N* sodium hydroxide in 50 cc. of 95% alcohol. The mixture was heated under a reflux condenser for thirty minutes and set aside. After two days there had separated *l*-arabinose diphenylhydrazone which, when dried and weighed, amounted to 1.151 g. This is equivalent to 0.5465 g. of arabinose or over twice the amount that could be calculated from the carbon dioxide obtained. After twice recrystallizing from 50% aqueous pyridine, the hydrazone melted, on rapid heating, at 204.2° (corr.). Van der Haar[15] gives 204° as the melting point.

Using practically the same procedure there was obtained from lemon pectin 0.0668 g. of carbon dioxide equivalent to 0.2280 g. of arabinose. However, only 0.1892 g. of arabinose in the form of the diphenylhydrazone was isolated. In this case all the arabinose found could have been produced by decarboxylation. Nevertheless, from results obtained above, its generation through decarboxylation is unlikely. The hydrazone melted at 204° (corr.).

Discussion of Results

The results of the foregoing experiments render it very doubtful that *l*-arabinose arises as an intermediate product in the decarboxylation of galacturonic acid by mineral acids. Instead there are formed one or more sirupy substances which readily react with diphenylhydrazine and α-benzylphenylhydrazine to give dark resinous products.

There is another argument which militates against the theory that

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[14] This was kindly furnished by the Pectin Sales *Co.,* since incorporated as the General Food Sales Co., of Fairport, N. Y.

[15] Van der Haar, Ref. 13, p. 178.

arabinose arises from galacturonic acid. As is well known, arabinose, when distilled with 12% hydrochloric acid, gives 70–80% of the theoretical quantity of furfural. Galacturonic acid, distilled under these conditions, loses practically the theoretical quantity of carbon dioxide.[4,16] If, in this process, arabinose is first formed and gives rise to furfural, we should expect to recover 70–80% of the theoretical amount of furfural. However, Ehrlich and Schubert[4] obtained only 41.1–42.6%[17] under these conditions and McKinnis,[5] working with digalacturonic acid, obtained only 33.3% of the theoretical yield of furfural. These results, therefore, suggest that some substance other than arabinose is formed at the intermediate stage and that this substance does not decompose into furfural as completely as arabinose does.

If d-galacturonic acid on decarboxylation with mineral acids does not give arabinose, we may well ask what is the intermediate substance. This must remain for further investigation to disclose. In the meantime we must conclude that the recovery of arabinose from the hydrolytic products of plant materials is indicative of the occurrence of arabinose as such and not of galacturonic acid.

Summary and Conclusions

1. A test was made of the theory that *l*-arabinose arises in acid decomposition of d-galacturonic acid as an intermediate product in the formation of furfural. Galacturonic acid in the form of its barium salt was decarboxylated with 4% sulfuric acid but no arabinose could be recovered.
2. Ehrlich's tetra acid "a," a polymer of d-galacturonic acid, was also studied but in no case could arabinose be recovered from the decarboxylation products.
3. Carefully conducted controls showed that added arabinose could always be recovered.
4. 1-Arabinose was found in the hydrolytic products of both apple and lemon pectins. In the case of apple pectin over twice the amount of arabinose that could have been due to decarboxylation was found.
5. The arabinose recovered from the hydrolytic products of plant substances comes from arabinose units in the substances and not from decarboxylation of galacturonic acid.

COLLEGE PARK, MARYLAND

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[16] Dickson, Otterson and Link, THIS JOURNAL, **52**, 775 (1930).

[17] Calculated by the writer from Ehrlich and Schubert's data.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH]

EXPERIMENTS ON THE ISOLATION OF THE ANTINEURITIC VITAMIN

BY ATHERTON SEIDELL AND VICTOR BIRCKNER

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In all methods used for the isolation of the antineuritic vitamin the losses of active material are so great that only meager amounts of the final concentrate are obtained. In many cases the quantities have not been sufficient even for preliminary chemical study.

Each advance in the purification of the active fraction demonstrates more clearly the minuteness of the dose of antineuritic vitamin capable of exerting a definite physiological effect. The most active preparations so far made are probably still far from chemical purity. Even the crystals isolated by Jansen and Donath[1] seem to owe their activity to admixed vitamin. This presumption is based on the fact that fractions active in distinctly smaller doses than the Jansen and Donath crystals[2] have been obtained by the procedure described in this and in previous publications[2,3] from this Laboratory.

The necessity for obtaining larger amounts of the most highly active fractions is apparent. Existing methods need to be improved both in the reduction of losses which occur at the several stages and in their application on an increasingly large scale. The experiments here recounted were made with this purpose in view.

For convenience of discussion the procedure may be subdivided into the following steps: (1) preparation of the "activated solid"; (2) extraction and concentration of the vitamin solution; (3) benzoylation and acetone precipitation of the salts; (4) extraction and acetone precipitation of the vitamin concentrate.

Preparation of the "Activated Solid."—This step of the process was first described some fifteen years ago[4] and since then various modifications of it have been introduced. The one to be described now was the result of efforts to prepare the product on a larger scale than had previously been possible. For the opportunity and equipment to do this grateful thanks are extended to M. H. Penau, Technical Director of Les Établissements Byla, located at Gentilly (Seine) near Paris, France.

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[1] Jansen and Donath, "Med. van den Dienst der Volksgezondheid in Ned.-Indie," Weltevreden, Batavia, Java, Part 1 (1927).

[2] The results of tests of a sample of the Jansen and Donath crystals given in a previous publication [Seidell and Smith, *Pub. Health Repts.*, *45*, 3191–3200 (1930)] show the minimum curative dose for rats to be 0.04 mg., whereas repeated tests of the most active sample obtained in the present series of experiments showed it to be active in 0.03 mg. doses.

[3] Seidell, *J. Biol. Chem.*, 82, 633–640 (1929).

[4] Seidell, *Pub. Health Repts.*, *31*, 364 (1916).

One hundred and sixty kilograms of pressed brewer's yeast (equal to approximately 45 kg. of dry yeast) was added quickly to about 300 liters of rapidly stirred water heated to about 80°. The mixture, after cooling somewhat, was filtered through a large filter press. To the clear filtrate 15 kg. of fuller's earth was added and the mixture mechanically stirred for one hour. It was then allowed to stand for two hours for subsidence of the fuller's earth which had now become "activated solid." A sample of the mixture which stood in a glass cylinder showed that the supernatant liquid contained a considerable amount of material in suspension. Since this suspended colloidal matter might clog the filter press and would certainly contaminate the activated solid, it was decided to remove it by decantation. The necessities of the case, therefore, led to a modification of the procedure which subsequent experiments have shown to be of decided advantage. The final concentrate resulting from this experiment, when tested on pigeons and on rats by the Smith method,[5] was found to be considerably more active than any previously made from activated solid which had been separated from the yeast solution by means of a Sharples supercentrifuge. It is believed that this simple modification effects the removal of organic constituents which interfere with subsequent steps of the process. The supernatant liquid, therefore, should be decanted from the activated solid and this latter washed with slightly acidified (1.0 cc. of concd. hydrochloric acid per liter) water one or more times.

If the extraction of the activated solid is not to be made immediately it should be filtered or separated with a Sharples supercentrifuge and thoroughly dried or else simply immersed in about 20% alcohol to prevent decomposition of its adsorbed organic matter by organisms.

Although heating yeast in water to about 80° is a very simple and effective way of liberating the vitamins from the cells, an experiment was made in one case with the use of a liquefying agent for obtaining an aqueous solution of the vitamin.

To 7.0-kg. portions of pressed brewer's yeast there was added 700 cc. of a mixture prepared according to Pirie[6] in the ratio of 80 cc. of 81% ethyl alcohol, 20 cc. of concentrated sulfuric acid and 100 cc. of ether. The yeast rapidly liquefied and, after dilution with about three times its volume of cold water, was passed through the Sharples supercentrifuge. To the nearly clear effluent 500 g. of fuller's earth was added and the resulting activated solid after decantation of the supernatant liquid was washed twice by decantation with acidified water.

The combined activated solid thus prepared when used for the remaining steps of the process yielded an aqueous extract which contained an amount of dissolved solids greater than was present in the extracts from activated solid made by the heating method. This excess of solids was also found to interfere with subsequent steps of the process, resulting in a low yield of poor quality final concentrate. .

Extraction and Concentration of the Vitamin Solution.[7]—As pointed out in previous papers the extraction of the activated solid is made by agitating it violently in approximately 0.4 to 0.5 normal sodium hydroxide solution for about five minutes and separating the alkaline liquid from the

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[5] Smith, Pub. *Health Repts.*, *45*, 116–129 (1930).

[6] Pirie, *Biochem. J.*, 24, 51 (1930).

[7] Appreciative acknowledgment is made for facilities placed at our disposal in Washington, D. C., by the Chemical and Technological Research unit of the Bureau of Chemistry and Soils, U. S. Department of Agriculture.

solid as quickly as possible by means of a Sharples supercentrifuge. The extract must be acidified quickly with sulfuric acid and adjusted to approximately *P_H* 3.0. In all cases just at this turning point a light, fluffy precipitate separates and serves as an indication that acidity has been reached. In one case a quantity of this precipitate was separated and tested for antineuritic vitamin. Its activity was found to be very little greater than the dry yeast from which it came. Since the amount of the precipitate was small the actual loss of vitamin was insignificant.

When the slightly acid extract is distilled under diminished pressure to about one-tenth its volume, a rather large amount of a brownish product separates. This is removed best by deposition in a large cup centrifuge and the nearly clear supernatant solution decanted. This, after seeding with sodium sulfate decahydrate, is kept in a cool place for crystallization of the large excess of this salt which is present.

The brown precipitate mentioned above has been found by Doctor M. I. Smith, in rat experiments,[8] to be very rich in the thermostable growth factor (B_2 or G) required as a supplement to the antineuritic vitamin for normal growth.[9] Dried samples of it are usually about five times as active as dried yeast. This product therefore furnishes a convenient source of the thermostable factor B_2 and by very simple means, designed to eliminate the sodium sulfate present, it can be concentrated to an activity of more than ten times that of the yeast from which it was derived.

The concentrated solution from which the excess of sodium sulfate decahydrate crystallizes should be treated with about an equal volume of methyl or ethyl alcohol in order to precipitate more of the inorganic salts and the organic impurities which are present.

It is a question as to just how far this alcohol precipitation should be continued. Of course, vitamin is lost if the alcoholic concentration is raised too high. Much material which interferes with subsequent purification of the vitamin is, however, eliminated and a much better final product may be obtained by sacrificing some of the vitamin at this point.

The clear approximately 50% alcoholic solution resulting from the above treatment usually contains about 30 g. of dissolved solids per liter, of which about 30% are inorganic salts. Some typical results obtained up to this point in the procedure are shown in the accompanying table (I).

It will be noted that the estimated quantity of dry yeast used per 5.0 kg. of activated solid, as shown in Table I, varied from 20.5 to **30** kg. This was due to the difficulty of estimating closely the amount of dry yeast corresponding to given amounts of fresh or even pressed yeast. There was also considerable variation in the amount of the thermostable growth vitamin (B_2) rich precipitate which separates during the distillation of the

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[8] This work is still in progress and will be described later.

[9] Smith and Hendricks, *Pub. Health Repts.*, **41,** 201 **(1926).**

TABLE I

EXPERIMENTAL DATA

Expt.	Brewer's yeast used	Est. amt. dry yeast present, kg.	Amt. activated solid made, kg.	(B_2) rich brown precipitate, g.	(B_1) rich 50% alc. soln., liters	Total grams dissolved solids in (B_1) solution	
						Organic	Inorganic
23	Fresh	28.0	5.0	230	7.0	Not detd.	Not detd.
24	Fresh	42.0	7.5	844	8.0	Not detd.	Not detd.
25	Fresh	25.8	5.0	377	7.0	Not detd.	Not detd.
27	Pressed	23.6	5.0	112	12.2	186	205
28	Com. dry (H)	22.6	5.0	300	10.5	222	83
29	Fresh	30.0	6.0	425	5.8	144	61
30	Com. dry (W)	20.5	5.0	434	5.0	121	46
31	Pressed	33.0	5.5	604	7.0	128	53

aqueous extract of the activated solid. This is due not only to a variation in the quantity of this insoluble material but also to the presence of variable amounts of sodium sulfate and other salts which separate together with it.

The volume of the alcoholic antineuritic (B_1) vitamin solution depends upon the degree to which the concentration by distillation has been carried and this cannot be accurately controlled in the large enamel lined vacuum distilling apparatus which was used.

The extent of the recovery of the antineuritic vitamin itself is not shown in the table, but estimates from experiments on pigeons made with certain of the fractions indicated that between 5 and 20% of the original vitamin of the yeast is present in the alcoholic solution. There is consequently a loss of 80 to 95% of the antineuritic vitamin up to this point. Some of this loss may be ascribed to variations in the vitamin content of different samples of brewer's yeast but, of course, the larger part is simply due to the imperfections of the fractionation procedure. In this connection it should be pointed out that the actual yield is not such an important matter as the quality of the final product obtained. Accumulated experience seems to show that the quality and yield of the final concentrate obtained by the subsequent steps of the process vary inversely with the percentage of the original vitamin present at the 50% alcoholic solution stage. The most active concentrate which has so far been made was obtained from an alcoholic solution in which there was only about 5% of the antineuritic vitamin of the yeast from which it was prepared. Apparently the removal of inactive constituents can be effected only with simultaneous considerable losses of the active compound, especially in the earlier stages of the process.

Benzoylation and Acetone Precipitation of the Salts.—The 5 to 12 liter quantities of alcoholic vitamin solution obtained by the procedure described above were usually divided into three equal portions and these separately distilled down and benzoylated. In the case of Experiments 23, 24 and 25 it was observed that the final products obtained from the three fractions of each of these solutions differed considerably in activity even though the benzoylation and acetone precipitations were conducted as nearly alike as possible. In an attempt to ascertain the effects of slight variations of reagents and technique upon the character of the final product, a series of experiments was made with the alcoholic solutions obtained in Experiments 27–31. Each of these was divided into three equal portions which were separately distilled to small volumes. They were each centrifuged to remove slight amounts of insoluble material, and the clear supernatant solutions diluted with water to the volumes shown in Table II. The quantities of sodium carbonate and benzoyl chloride recorded in the table were quickly added and the mixtures stirred with a thermometer. The highest temperature reached during the reaction was noted and about an hour allowed for the mixtures to cool. They were then extracted with chloroform and the resulting aqueous layers poured slowly into 10–15 times their volume of acetone. The weights of the precipitated salts and their nitrogen contents are recorded in the table.

Extraction and Acetone Precipitation of the Vitamin Concentrate.—The vitamin salts were extracted by rotating for twenty-four hours with a mixture of three volumes of normal propyl alcohol and one volume of concentrated hydrochloric acid, using about 3 cc. of this mixture per 1.0 g. of salts. The extract was separated by centrifugation and the residue extracted a second time in the same manner. The two extracts were distilled under diminished pressure to about 50 cc. This concentrated liquid was centrifuged to remove a small amount of salts which separate during the distillation. The clear solution was then added dropwise to about 1600 cc. of acetone. The resulting precipitate was separated by centrifugation and dissolved in about 15 cc. of methyl alcohol and this added dropwise to about 800 cc. of acetone. The precipitate is now white and in a voluminous flaky condition. It is centrifuged and then washed with acetone by centrifugation and finally dried in a vacuum. The quantities obtained in the several experiments are shown in Table II.

The activities of the 16 precipitates made in this manner were determined by Dr. M. I. Smith, using his rat method.[5] The activities of the alcoholic vitamin solutions of Experiments 28–31 were also determined in the same manner and found to correspond, respectively, to 116, 83, 55 and 87 thousand vitamin units, or minimum curative doses.

Discussion

An examination of the results in Table II shows that unaccountable variations in the yield and quality of the final acetone precipitate frequently occur. In the case of Experiment 28(a) the yield of vitamin was only about 11%, while in the case of Experiment 31(a) it was about 70%. The only intentional difference in the two cases was that the proportion of

TABLE II

EXPERIMENTAL DATA

Expt.		Organic solids present, g.	Vol. of aqueous soln., cc.	Benzoylation reagents Na_2CO_3, g.	Benzoylation reagents C_6H_5COCl, cc.	Max. temp. of reaction, °C.	Pptd. vitamin salts, g.	N in vitamin salts, %		Final acetone pptd. vitamin, g.	N in acetone pptd. vitamin, %	Minimum curative dose (rats) mg.	Total vitamin, units
27	a	63	500 (8.0)	100 (1.6)	180 (1.8)	50	119	0.54		1.19	10.5	0.1	11,900
	b	63	500 (8.0)	75 (1.2)	180 (2.4)	45	100	.69		2.01	11.4	.25	8,000
	c	60	500 (8.3)	75 (1.2)	135 (1.8)	50	97.5	.98		0.79	10.0	.3	2,630
28	a	74	500 (6.8)	150 (2.0)	275 (1.8)	60	132	.49		1.30	12.6	.3	4,333
	b	74	500 (6.8)	150 (2.0)	275 (1.8)	25	143	.59		1.58	12.0	.5	3,160
	c	74	500 (6.8)	150 (2.0)	275 (1.8)	30	120	.61		2.03	12.4	.5	4,070
29	a	46	364 (8.0)	77 (1.7)	133 (1.7)	32	72	.9		2.47	12.1	.3	8,233
	b	46	288 (6.2)	86 (1.8)	155 (1.8)	73	99.5	.23		0.675	9.3	.06	11,250
	c	46	240 (5.0)	86 (1.8)	155 (1.8)	60	84	.50		1.06	11.5	.15	7,070
30	a	40	241 (6.0)	72 (1.8)	130 (1.8)	60	70	.42		1.09	10.9	.15	7,270
	b	40	241 (6.0)	72 (1.8)	130 (1.8)	61	69.5	.37		1.09	10.0	.17	6,400
	c	40	280 (7.0)	72 (1,8)	130 (1.8)	58	76.0	.52		1.83	10.4	.25	7,320
31	a	42.7	299 (7.0)	77 (1.8)	138 (1.8)	62	77.5	.75		1.64	13.1	.08	20,500
	b	40.0	240 (6.0)	68 (1.7)	116 (1.7)	61	69.0	.59		1.09	11.9	.10	10,900
	c	40.0	280 (7.0)	80 (2.0)	144 (1.8)	67	77.0	.31		0.70	8.9	.8	8,750
22		94 (Est.)	675 (7.2)	150 (1.6)	275 (1.8)	50	160.0	.06	a b	0.074 0.120	8.2 7.0	... 0.03	 400

Of the figures in parentheses the first in each experiment shows the ratio of solution to organic solids; the second shows the ratio of sodium carbonate to organic solids, and the third the ratio of benzoyl chloride to sodium carbonate.

sodium carbonate used in the benzoylation was slightly higher in the first case than in the second. A similar diminution with increase of sodium carbonate is noted in Expt. 30(c) but in this case the quality of the final precipitate was not affected but only the quantity obtained. It is apparent that the exact ratio of reagents to organic solids in the solution being benzoylated must be very carefully controlled in order to get the best results. The optimum ratios appear to be approximately seven times as much aqueous solution as there are organic solids, 1.8 times as much sodium carbonate as organic solids and 1.8 times as much benzoyl chloride as sodium carbonate.

The experiments have definitely demonstrated the advantage of higher temperatures for the reaction. In the cases of experiments 28(b) and (c) and 29(a) the mixtures were immersed in ice water to prevent a rise in temperature, and in each case the activity and yield of the final precipitate was of a low order. The effect of higher temperatures than result spontaneously during the reaction has not as yet been studied.

The results in the table also show that the lower the percentage of nitrogen in the precipitated vitamin salts, the higher the activity of the final acetone precipitated vitamin. Attention should therefore be directed continually toward conducting the benzoylation in such a manner that as little nitrogenous material as possible remains in the acetone precipitated salts.

It is noteworthy that the samples of final acetone precipitated vitamin except those from solutions cooled during the benzoylation vary in activity, as measured by minimum curative dose, from 0.03 mg. to 0.3 mg. It will be noted that in general the more active samples have the lower nitrogen content. There is, however, no close parallelism between nitrogen content and activity. Hence, considerable amounts of non-vitamin nitrogenous compounds are probably still present even in the more active samples.

In conclusion, attention is directed to the fact that the procedure here described does not involve the use of any of the precipitating agents which form so important a part of most other methods for the concentration of the antineuritic vitamin. Even without the use of platinum precipitation, a concentrate distinctly more active than the crystals made with such extraordinary expenditure of effort by Jansen and Donath has been obtained. Furthermore, fairly large quantities may be prepared. Under favorable conditions about 1.0 g. of a product approximately equal in activity to the Jansen and Donath crystals should be obtained from each 10 kg. of dried brewer's yeast. It is hoped that with further intensive study this yield can be increased; also, that it will be possible to prepare considerably larger amounts of the product curative in 0.03-mg. doses which has, so far, been obtained only once.

Summary

The procedure involving adsorption of the antineuritic vitamin upon fuller's earth and subsequent extraction, benzoylation and acetone precipitation has yielded, without the use of any precipitating agents, final products the most active of which was curative in 0.03-mg. doses, by the Smith rat method. This is an activity about one-fourth greater than that of the jansen and Donath crystals. It is more than twice as great on the nitrogen basis. Products of somewhat lower activity were obtained in considerably larger yields. Apparently small variations of conditions at certain stages of the process may affect greatly the quantity and quality of the final product. Especial attention has been given to the effect of variation of ratio of the benzoylating reagents and of the temperature of the reaction upon the quality and yield of the final concentrate.

WASHINGTON, D. C.

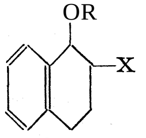
[CONTRIBUTION NO. 75 FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

NEW ALKAMINES IN THE TETRAHYDRONAPHTHALENE SERIES[1]

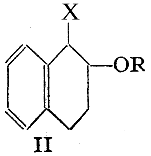
BY ERICH MOSETTIG AND ALFRED BURGER

RECEIVED MARCH 27, 1931 PUBLISHED JUNE 8, 1931

In the classic investigations of partially hydrogenated naphthalene derivatives carried out by Bamberger[2] over forty years ago, the fact was established that alicyclic β-tetrahydronaphthylamine and its derivatives exert to a considerable degree a specific pharmacological action. After studying a number of compounds, Bamberger stated the rule that this property is exhibited only when the substituted nucleus is hydrogenated, and only when the basic substituent occupies the 8-position. In more recent years, this observation was confirmed through the investigations of von Braun[3] on alicyclic amino alcohol derivatives of tetrahydronaphthalene. He was able to show that only compounds of type I have pharma-



I



II

X = NH_2, $HNCH_3$, $N(CH_3)_2$, etc. R = H or alkyl

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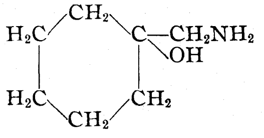
[1] This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

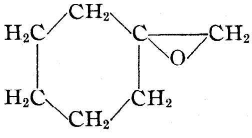
[2] E. Bamberger and W. Filehne, *Ber.*, 22,777 (1889).

[3] Von Braun, Braunsdorf and Kirschbaum, *ibid.*, 55, 3648 (1922); v. Braun and Weissbach, *ibid.*, 63,3052 (1930); *cf.* Strauss and Rohrbacher, *ibid.*, 54, 40 (1921).

cological properties resembling those of alicyclic β-tetrahydronaphthylamine, whereas derivatives of type II are comparatively inactive. The P-position of the basic group in these cases is likewise the deciding factor.

In an earlier paper[4] we described attempts to synthesize hydroaromatic alkamines of type III which had their starting point in the oxide IV,


III


IV

but which as practicable synthetic methods were unsuccessful, since the reaction of diazomethane on cyclohexanone, used for the preparation of IV, ran chiefly to ring enlargement, giving cycloheptanone and cyclooctanone. At that time the surmise was made that the corresponding naphthalene derivatives, *a*- and β-ketotetrahydronaphthalene, because of the linkage of the hydrogenated ring to an aromatic nucleus, would show far less tendency to undergo ring enlargement.

Of the isomeric ketotetrahydronaphthalenes, only β-tetralone can be induced to react with diazomethane; a-tetralone is indifferent toward this reagent. This is in general accord with the observations of von Braun and others[3] on the remarkable differences in the activity of the two tetralones. We need mention here only the relative instability of β-tetralone, and the unexplained blue color which results when this compound is exposed to atmospheric oxygen in the presence of alkali.[5] The behavior of the two ketones toward sodium bisulfite differs also; only the @-isomergives a bisulfite compound. We believe that'an analogy for this is to be found in the case of mixed aliphatic–aromatic ketones. Whereas ketones of the type $ArCOCH_3$ do not, in general, give bisulfite addition products, benzyl methyl ketones, the so-called @-ketonesof the type $ArCH_2COCH_3$, in most cases do so. In a recent investigation of ketones of this type[6] the conclusion was drawn that if a ketone forms a bisulfite compound it may be expected to react with diazomethane. The behavior of a- and β-tetralone toward diazomethane and sodium bisulfite gives additional support to this conclusion.

When carefully purified β-tetralone is acted upon by diazomethane in ether–methanol mixture, a product containing an additional $-CH_2-$ group and showing none of the properties of a ketone results. It is characterized as an ethylene oxide derivative by its facile conversion to amino alcohols. Arndt, Meerwein and Mosettig (for a bibliography, see the paper

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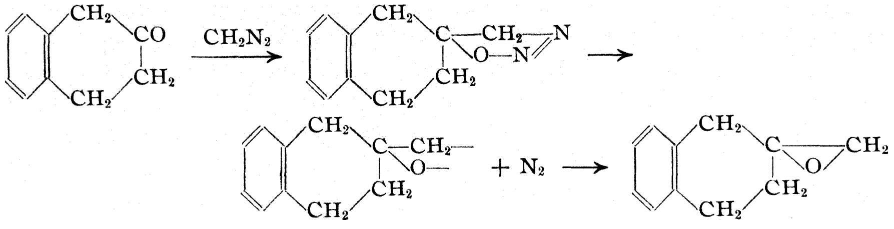
[4] Mosettig and Burger, THIS JOURNAL, 52, **3456** (1930).

[5] We have found that this color appears also in the presence of ammonia and amines, as dimethylamine, diethylamine or piperidine.

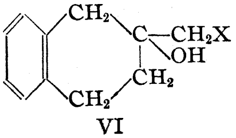
[6] Mosettig and Jovanovif. ***Monatsh..*** 53 and 54. 427 (1929).

of Mosettig and Burger, Ref. 4) have investigated thoroughly in recent years the reaction of diazomethane with carbonyl compounds, and according to their formulation the reaction under discussion may be represented as



V

where Formula V depicts the oxide obtained as the end-product. Reasoning from analogy and from the general rule that addition of amines to ethylene oxides results in an hydroxyl group on the carbon atom carrying the least hydrogen, we believe that the amino alcohols formed by addition of amines to V must have the formula VI.

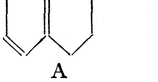


VI

$X = -N(CH_3)_2, -N(C_2H_5)_2, -NC_5H_{10}$

The oxide (V) derived from 8-tetralone could not be purified for analysis, and the dimethylamino-, diethylamino- and piperidino alcohols from it, which do not crystallize, were characterized and analyzed as the well-crystallized hydrochlorides, perchlorates and platinichlorides. It is possible that isomers of these amino alcohols, formed by addition of the amines to the oxide in the alternative way, are present in the reaction mixture, and the formation of homologs, from a theoretically possible homologous oxide, is not excluded. The mother liquors from the crystalline salts of all of these amino alcohols yielded oily fractions in considerable quantity, but in only one case (that of the dimethylamino alcohol) could a second amino alcohol be isolated in the form of well-defined salts.

In addition to the oxide (V), the reaction of diazomethane with β-tetralone gives about a 30% yield of a yellow oil which has the properties of neither a ketone nor an ethylene oxide. The substance is free from nitrogen and is monomolecular, but analytical values, which do not correspond to any plausible empirical formula, are not significant, since in spite of the narrow boiling range observed we cannot be sure that only one compound is present. The oil has an agreeable odor, recalling that of 8-naphthol methyl ether. The methoxyl determination and hydrogenation experiments were negative, which together with the high boiling point, 137–139° (1 mm.), excludes the possibility that the indifferent compound is the methyl ether



A

of the enolic form of 8-tetralone, b. p. 136° (15 mm.) (A), which has been prepared by von Braun.[7] We are at present able to make no conjecture as to the nature of the indifferent by-product.

The reaction of diazoethane with β-tetralone proceeds much more vigorously than that of diazomethane, but yields nevertheless more than half of the p-tetralone unchanged. The rest of the reaction mixture consists of a high-boiling, rather unstable, strongly colored oil, which could not be purified. The crude reaction mixture, which was believed to contain an ethylene oxide type, was treated with piperidine in an unsuccessful attempt to isolate amino alcohols. In this experiment the interesting observation was made that β-tetralone forms an addition product with piperidine on gentle warming. The addition compound is unstable and decomposes slowly on standing into its components, p-tetralone and piperidine. The decomposition, which also takes place in dilute hydrochloric acid solution, is accelerated by heating.

a-Tetralone does not give such an addition product with piperidine.

The new alicyclic alkamines from tetrahydronaphthalene described in this paper have been prepared preliminary to an extension of the synthetic method to analogous compounds involving higher ring systems. According to Bamberger's rule mentioned above, the amino alcohols prepared from p-tetralone should have a marked pharmacological action. The pharmacological report on these substances will be published (C. W. Edmunds and N. B. Eddy) from the Medical School of the University of Michigan.

Experimental Part

β-Tetralone (1,2,3,4-Tetrahydro-2-ketonaphthalene) and Diazomethane.—β-Tetralone was prepared by heating the methiodide of 1-dimethylamino-2-hydroxy-1,2,3,4-tetrahydronaphthalene according to the directions of von Braun.[8] The product obtained gave a semicarbazone which melted at 194–195° on rapid heating, 189–191° on slow heating (v. Braun gives m. p. 190–191°).

The p-tetralone, which cannot be kept unchanged for any length of time, was converted to the bisulfite compound, which was washed with ether and kept in a glass-stoppered bottle The free ketone was liberated from the bisulfite compound with sulfuric acid, just before using.

Twenty-five grams of β-tetralone was prepared by decomposition of the bisulfite compound and distilled in a vacuum, b. p. 142° (15 mm.). It was added to a solution of 15.2 g. of diazomethane (i.e., a little over two molecular equivalents) in 660 cc. of ether at —5". After addition of 200 cc. of absolute methyl alcohol, the mixture was allowed to stand at room temperature and soon began to evolve nitrogen vigorously. After the solution had stood for thirty-six hours, the ether was removed on a steam-bath and the methyl alcohol was distilled off under reduced pressure at 25–30'. The residue was purified by distillation in a vacuum. It boiled between 123–140° at 1 mm. pressure, the main portion distilling at 137–138°. The distillate consisted of 24 g. of a yellow oil The residue from the distillation was a reddish-brown resinous tar.

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[7] Von Braun and Weissbach, Ber., 63, 3055 (1930).

[8] Von Braun. Braunsdorf and Kirschbaum, *ibid.*, 55, 3659 (1922).

In another run with 74 g. of β-tetralone and 47 g. of diazomethane in 2560 cc. of ether and 500 cc. of methyl alcohol, 68 g. of the yellow distillate was obtained, of which 63 g. boiled from 135–145° at 6 mm. pressure. In this case relatively more of the non-distillable resinous substance remained in the flask.

The yellow oil gave neither a semicarbazone nor a bisulfite compound. It showed a more or less pronounced color reaction when treated with a dilute solution of alkali or strong amines. The solution turned blue although no β-tetralone could be shown to be present in the mixture. The oxide (V) formed about two-thirds of this oil, from which it could be removed by treating with amines as described below. The indifferent part (35 to 36% of the whole weight of the oil) was purified by repeated distillation. The final distillate was a yellow oil of b. p. 137–139° (1 mm.).

Anal. Subs., 0.0690, 0.0829, 0.0799: CO_2, 0.2062, 0.2477, 0.2392; H_2O, 0.0496, 0.0589, 0.0571. Found: C, 81.50, 81.49, 81.65; H, 8.04, 7.95, 8.00. *Mol. wt.* Subs., 0.3121: 13.05 g. of benzene; *Δt*, 0.680°. Calcd. for $C_{11}H_{12}O$: mol. wt. 160. Found: 179.

Amino Alcohols from the Oxide V

General Preparative Method.—These amino alcohols were prepared by heating the crude oxide with 10% more than the calculated amount of the amines (dimethylamine, diethylamine, piperidine, respectively) and the same weight of water in a sealed tube at 95–100° for five hours. The reaction mixtures were taken up in ether and washed with water to remove most of the unchanged amine. The amino alcohols were extracted with dilute hydrochloric acid from the ethereal solution, precipitated with alkali and taken up again in ether. The ethereal solution was dried and the solvent evaporated. The residues distilled in a vacuum as almost colorless oils. The original ethereal layer contained the indifferent oil mentioned above.

The oily amino alcohols were dissolved in a little ether and an ethereal solution of perchloric acid was added in small portions. An oil precipitated out which soon crystallized. The addition of perchloric acid was continued until the precipitated salt began to separate as a viscous mass. It was collected on a filter and recrystallized from alcohol-ether. The yield was about half of that expected. These perchlorates were decomposed with a solution of sodium hydroxide, and the free alkamines were taken up in ether. The dried ethereal solution was treated with ethereal hydrochloric acid and the crystalline hydrochloride recrystallized from a mixture of alcohol and ether.

The procedure outlined above was used to obtain pure dimethyl- and diethylamino alcohols, but in the case of the piperidino alcohol it was found advisable to precipitate the hydrochloride first with ethereal hydrogen chloride, interrupting the precipitation as soon as the hydrochloride no longer separated well crystallized. The mother liquors resulting from the perchlorate precipitations described above yielded a further precipitate of an oily perchlorate with more ethereal perchloric acid.[9] Only in the case of the dimethylamino alcohol could this second precipitated fraction be obtained crystalline, and from it other well-crystallized salts of the unidentified (apparently homologous) dimethylamino alcohol, which is listed second in the table, could be prepared.

β-Tetralone and Piperidine.—Four grams of β-tetralone and a solution of 3.2 g. of piperidine in an equal amount of water was heated in a sealed tube to 100° for four hours. The reaction mixture was shaken with ether and the latter washed with water until the aqueous extracts were but faintly blue. The ethereal layer was then rapidly extracted with dilute hydrochloric acid twice. This absolutely clear acid solution becomes turbid after some time. When the acid solution was warmed to 30°, 3 g. of an oil separated

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[9] The piperidino alcohol hydrochloride mother liquors were made alkaline, extracted with ether, and the extract treated with perchloric acid.

TABLE I

CONSTANTS AND ANALYTICAL DATA

Compound	B. p. (or m. p.), °C.	Formula	Calcd.. %	Found, %
Dimethylamino alcohol"	(b.) 116–118 1 mm.)	(8 g. of the crude oxide yielded 6.5 g.)		
Hydrochloride[b]	(m.) 175–176	$C_{13}H_{20}ONCl$	Cl, 14.68	14.69
Perchlorate"	(m.) 158–159	$C_{13}H_{20}O_5NCl$	Cl, 11.60	11.55
Platinum salt	(m.) 197–198 (dec.)	$C_{26}H_{40}O_2N_2PtCl_6$	Pt, 23.80	23.84
Dimethylamino alcohol (homolog?)				
Hydrochloride	(m.) 196–198	$C_{14}H_{22}ONCl$	Cl, 13.87	13.24
Perchlorate	(m.) 184	$C_{14}H_{22}O_5NCl$	Cl, 11.09	11.17
Platinum salt	(m.) 197–198	$C_{28}H_{44}O_2N_2PtCl_6$	Pt, 23.12	22 87
Diethylamino alcohol	(b.) 135–137 (1 mm.)	(6 g. of the crude oxide yielded 5.2 g.)		
Hydrochloride	(m.) 125–126[d]	$C_{15}H_{24}ONCl\cdot H_2O$	H_2O, 6.26	6.25
		$C_{15}H_{24}ONCl$	Cl, 13.15	13.09
Perchlorate	(m.) 155–156	$C_{15}H_{24}O_5NCl$	Cl, 10.63	10.53
Platinum salt	(m.) 190 (dec.)	$C_{30}H_{48}O_2N_2PtCl_6$	Pt, 22.27	22.41
Piperidino alcohol	(b.) 146–148 (1 mm.)	(8 g. of the crude oxide yielded 8.3 g.)		
Hydrochloride	(m.) 200–200.5	$C_{16}H_{24}ONCl$	Cl, 12.59	12.34
Perchlorate	(m.) 147.5–148	$C_{16}H_{24}O_5NCl$	Cl, 10.26	10.06
Platinum salt	(m.) 205–206.5 (dec.) slow heating; 214–216 (dec.) fast heating	$C_{32}H_{48}O_2N_2PtCl_6$	Pt, 21.68	21.58

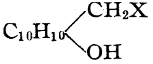
[a] The same yields were obtained when the dimethylamino alcohols were prepared by heating the oxide with a benzene solution of dimethylamine. [b] All hydrochlorides were analyzed by direct precipitation with silver nitrate. [c] All perchlorates were analyzed by the method of Hofmann, *Ber.*, 43, 1080 (1910), fusion with sodium carbonate and determination of halogen. [d] The hydrochloride of the diethylamino alcohol crystallizes from a mixture of ordinary alcohol and ether with one molecule of water of crystallization, which is given off at 92°. The halogen analysis was carried out after drying the substance at 90–95° in a vacuum.

out which was extracted into ether and was identified as pure 8-tetralone (semicarbazone, m. p. 189–190°). The acid solution contained only piperidine.

It was not possible to distil the unstable supposed addition compound under the same conditions as the piperidino alcohols described above, and no analysis could be carried out because of the rapid decomposition which took place even at ordinary temperatures. On distillation the addition compound decomposed into the components, β-tetralone and piperidine.

Summary

A series of new alkamines derived from tetrahydronaphthalene has been prepared for pharmacological study.

The alkamines of Formula  $C_{10}H_{10}\langle^{CH_2X}_{OH}$ (X = $-N(CH_3)_2$, $-N(C_2H_5)_2$, $-NC_5H_{10}$) are formed through addition of secondary amines, as dimethylamine, diethylamine or piperidine, to the ethylene oxide type of compound $\underline{C_{10}H_{10}CH_2O}$ which results from the action of diazomethane on β-tetralone.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE CLEAVAGE OF BETA DIKETONES. I. CLEAVAGE BY ORGANIC MAGNESIUM COMPOUNDS

BY E. P. KOHLER AND J. L. E. ERICKSON

RECEIVED MARCH 28, 1931 PUBLISHED JUNE 8, 1931

In a recent communication from this Laboratory,[1] it was reported that organic magnesium compounds effect a very characteristic cleavage of α-oxido ketones. We have observed a somewhat similar cleavage of β-diketones. In a study of the relative activity of the three carbonyl groups of diphenylpropane trione, we added this substance to phenyl magnesium bromide in the usual manner and obtained benzoin and triphenyl carbinol. Manifestly, these products are due to cleavage, and from the formation of triphenyl carbinol it is evident that this cleavage is anterior to the final decomposition of the magnesium derivatives with acids.

From general considerations as well as from the results published by Neufville and v. Pechmann,[2] it appears probable that the central carbonyl group in the triketone is much the most active of the three. If this is really the case, then the primary reaction between the triketone and phenyl magnesium bromide would be expected to yield phenyl dibenzoyl carbinol, a very interesting disubstitution product of a β-diketone. In the hope of discovering some means of confining the process to this first stage, we decided to make a more careful examination of the action of organic magnesium compounds on other β-diketones.

Surprisingly few β-diketones have heretofore been treated with Grignard reagents. Zelinsky[3] added acetylacetone to methyl magnesium iodide and observed a vigorous reaction, but he obtained only a very small quantity of a product, of which he states, merely, that it boiled at 101–102° under 15 mm., and that its composition corresponded approximately to $C_7H_{16}O_2$. Zerewitinoff[4] announced later that the diketone liberates one mole of methane from a solution of methyl magnesium iodide in isoamyl ether; he made no attempt to isolate any products.

More definite results were reported by Smedley,[5] who added dimethyl dibenzoylmethane to methyl magnesium iodide. She concluded that the reagent combined with each of the carbonyl groups, and that the final product was the ditertiary alcohol which would be expected as the result of such a process—$C_6H_5(CH_3)COHC(CH_3)_2C(OH)(CH_3)C_6H_5$. There is no evidence in support of these conclusions.

The only other open chained β-diketone that has been treated with a

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[1] Kohler, Richtmyer and Hester, THIS JOURNAL, 53, 205 (1931)

[2] Neufville and v. Pechmann, Ber., 23, 3379 (1890).

[3] Zelinsky, *ibid.*, 35, 2138 (1902).

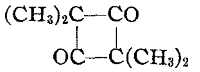
[4] Zerewitinoff, *ibid.*, 41, 2243 (1908).

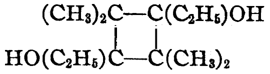
[5] Smedley, J. Chem. *Soc.*, 97, 1493 (1910).

Grignard reagent is dibenzoyl methane. Vorlander, Osterburg and Meye[6] added this diketone to phenyl magnesium bromide and proved, conclusively, that when the resulting magnesium compound was acidified, the product was β-hydroxy-β,β-diphenyl propiophenone. They, therefore, wrote the equation

$$C_6H_5COCH_2COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2C(OMgX)CH_2COC_6H_5$$

In addition to these open chained compounds one cyclic 8-diketone of an unusual type has been examined. Wedekind and Miller[7] added tetramethyl cyclobutanedione to an excess of ethyl magnesium bromide and obtained, in almost the calculated quantity, the corresponding ditertiary alcohol





If one were to judge from these meager reports one would have to conclude that the reaction between 8-diketones and organic magnesium compounds is relatively simple and uniform—far more uniform than would be expected from the varied results that have been obtained from β-ketonic esters. In reality it is neither simple nor uniform, as may be seen from the following list of diketones and the final products which we obtained from them.

I	$C_6H_5COCH_2COC_6H_5$	$(C_6H_5)_2C(OH)CH_2COC_6H_5$
II	$CH_3COCH_2COCH_3$[a]	$(CH_3)_2C(OH)CH_2COCH_3$
III	$C_6H_5COCH(C_6H_5)COC_6H_5$	$C_6H_5COCH_2C_6H_5 + (C_6H_5)_3COH$
IV	$C_6H_5COCH(CH_3)COC_6H_5$	$C_6H_5COCH_2CH_3 + (C_6H_5)_3COH$
V	$CH_3COC(CH_3)_2COCH_3$	$CH_3COCH(CH_3)_2 + (C_6H_5)_2(CH_3)COH$
Va	$CH_3COC(CH_3)_2COCH_3$[b]	$CH_3COCH(CH_3)_2 + CH_3COC_6H_2(CH_3)_3$
VI	$C_6H_5COC(CH_3)_2COC_6H_5$	$C_6H_5COCH(CH_3)_2 + (C_6H_5)_3COH$
VII	$C_6H_5COCHBrCOC_6H_5$	$C_6H_5COCH_2COC_6H_5$
VIII	$C_6H_5COCBr_2COC_6H_5$	$(C_6H_5)_2COHCHBrCOC_6H_5$
IX	$C_6H_5COCOCOC_6H_5$	$C_6H_5COCHOHC_6H_5 + (C_6H_5)_3COH$

[a] With methyl magnesium iodide. [b] With mesityl magnesium iodide.

An examination of this list shows that relatively normal products are obtained from those compounds only which are largely or entirely enolic. Even in the case of these substances the reaction is not quite as simple as it was formulated by Vorlander and his collaborators, because quantitative determinations show that they react with two moles of reagent and liberate a mole of gas. When they are added to but one equivalent of reagent, half of the material is recovered unchanged, and when, inversely, one equivalent of reagent is added to the substance, **all** of the latter is recovered. The reaction with phenyl magnesium bromide must therefore be represented as follows

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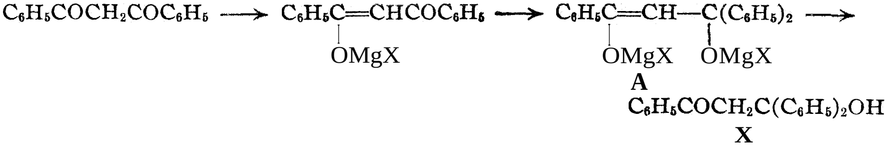
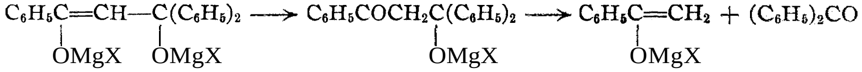
[6] **Vorländer,** Osterburg and **Meye, Ber.,** 56, 1136 **(1923).**

[7] Wedekind and Miller, *ibid.,* 44,3285 (1911).



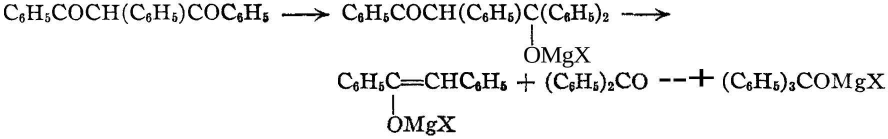
$$C_6H_5COCH_2COC_6H_5 \longrightarrow \underset{\displaystyle OMgX}{C_6H_5C}{=}CHCOC_6H_5 \longrightarrow \underset{\underset{\displaystyle \mathbf{A}}{}}{\underset{\displaystyle OMgX}{C_6H_5C}{=}CH{-}\underset{\displaystyle OMgX}{C}(C_6H_5)_2} \longrightarrow \underset{\displaystyle \mathbf{X}}{C_6H_5COCH_2C(C_6H_5)_2OH}$$

In the case of these highly enolized β-diketones the outcome is quite definite it is not possible to add more than one equivalent of the reagent, and no cleavage occurs anterior to the decomposition of the resulting magnesium derivatives with acids. It is necessary, however, to exercise great care in acidifying these magnesium derivatives, because they can pass into intermediate monomagnesium compounds that undergo cleavage with ease



$$\underset{\displaystyle OMgX}{C_6H_5C}{=}CH{-}\underset{\displaystyle OMgX}{C}(C_6H_5)_2 \longrightarrow C_6H_5COCH_2\underset{\displaystyle OMgX}{C}(C_6H_5)_2 \longrightarrow \underset{\displaystyle OMgX}{C_6H_5C}{=}CH_2 + (C_6H_5)_2CO$$

The situation is quite different in the case of the mono- and disubstitution products of these simple diketones. The monosubstitution products are too little enoliied or too feebly acidic to form copper derivatives with copper acetate; they liberate only traces of gas from methyl magnesium iodide; they nevertheless consume two equivalents of the reagent.[8] Here the first step is the addition of the reagent to one of the carbonyl groups. The resulting magnesium derivative is unstable and it decomposes in a manner that is essentially the same as that of the magnesium compounds which are formed from α-oxido ketones. The entire process, then, must be represented as follows



$$C_6H_5COCH(C_6H_5)COC_6H_5 \longrightarrow C_6H_5COCH(C_6H_5)\underset{\displaystyle OMgX}{C}(C_6H_5)_2 \longrightarrow \underset{\displaystyle OMgX}{C_6H_5C}{=}CHC_6H_5 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3COMgX$$

The extent of this kind of cleavage, and the ease with which it takes place, naturally vary with the stability of the first magnesium derivative. From the products which have been obtained with dialkyl acetacetic esters,[9] it is reasonable to infer that cleavage is less likely to occur with alkyl than with phenyl magnesium halides, and our experiments with β-hydroxy-β,β-diphenyl propiophenone show that it also takes place less readily with compounds that have less highly branched chains. These experiments with the hydroxy ketone are of special interest because in contrast with the dibenzoyl methane from which it is obtained, it can form the type of magnesium derivative that may cleave

$$C_6H_5COCH_2C{-}(C_6H_5)_2OH \longrightarrow C_6H_5COCH_2C(C_6H_5)_2OMgX$$

B

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[8] Kohler, Stone and Fuson, THIS JOURNAL, 49,3181 (1927).

[9] Slavjanoff, J. *Russ. Phys.-Chem. Soc.*, 39,140 (1907).

According to Vorlander and Meye,[10] the hydroxy ketone does not react with phenyl magnesium bromide; but they must have been deceived by the similarity in the melting points of the hydroxy ketone and that of one of the products of the reaction. In reality the substances react with great ease. One of the products is triphenyl carbinol, which shows that the magnesium compound B undergoes the usual cleavage; but in addition to this there is formed an equal quantity of the dihydroxyl compound, $(C_6H_5)_2COHCH_2COH(C_6H_5)_2$ (XI).

At times it is possible to avoid cleavage almost entirely by operating at a sufficiently low temperature. Thus by proceeding in the reverse of the usual manner, adding phenyl magnesium bromide cautiously to phenyl dibenzoyl methane while the temperature was kept below -10° and acidifying without delay, it was possible to secure a fair yield of tetraphenyl propenone—the dehydration product of the corresponding tertiary alcohol.

$$C_6H_5COCH(C_6H_5)C(C_6H_5)_2OMgX \longrightarrow C_6H_5COCH(C_6H_5)C(C_6H_5)_2OH \longrightarrow C_6H_5COC(C_6H_5){=}C(C_6H_5)_2$$

XII

As would be expected from the foregoing analysis, 8-diketones which have two substituents in the methylene group behave precisely like those which have but one. Smedley's conclusions are not in agreement with this view, but we are convinced that she was misled by her results. She subjected her product to distillation under diminished pressure and analyzed a fraction boiling at 120–125° under 55 mm. This is manifestly far too low a boiling point for the ditertiary alcohol $C_6H_5(CH_3)COHC(CH_3)_2C(OH)(CH_3)C_6H_5$. According to our interpretation, this reaction would be expected to yield the cleavage products dimethyl acetophenone and phenyl methyl carbinol. Since these substances have approximately the boiling point given by Smedley, it seems likely that she analyzed a mixture that happened to have the same composition as the ditertiary alcohol. We treated the same diketone with phenyl magnesium bromide and obtained only cleavage products.

The bromine substitution products are exceptions. They undergo the peculiar reaction of α bromo ketones which was reported many years ago by Kohler and Johnstin,[11] and which has since been observed by others.[12] The mechanism of this reaction will be considered in a later paper.

In the light of the foregoing results it is not difficult to follow the course of the reaction between phenylmagnesium bromide and diphenyl propanetrione. The most active carbonyl group combines with a molecule of the

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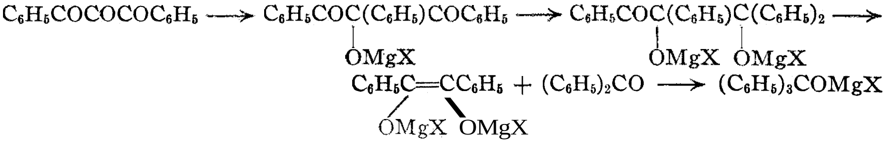
[10] **Ref.** 6, p. 1138.

[11] Kohler and Johnstin, *Am. Chem.* **J.,33,** 35 (1905).

[12] Umnova, J. *Russ. Phys.-Chem. Soc.*, 45, 881 (1913); Löwenbein and Schuster, *Ann.*, 481, 106 (1930); Fisher, Oakwood and Fuson, THIS JOURNAL, 52, 5037 (1930).

reagent and the addition product behaves like any other disubstituted β-diketone



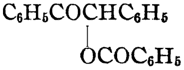
$$C_6H_5COCOCOC_6H_5 \longrightarrow C_6H_5CO\underset{OMgX}{C}(C_6H_5)COC_6H_5 \longrightarrow C_6H_5CO\underset{OMgX}{C}(C_6H_5)\underset{OMgX}{C}(C_6H_5)_2 \longrightarrow$$

$$C_6H_5\underset{OMgX}{C}{=}\underset{OMgX}{C}C_6H_5 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3COMgX$$

In *a* preliminary attempt to isolate the carbinol corresponding to the intermediate magnesium compound the reagent was added to the triketone at a low temperature and the resulting magnesium derivative was decomposed immediately. The product was a crystalline solid which had the composition of phenyl dibenzoyl carbinol XIII, but which proved to be the benzoate of benzoin XIV.

$C_6H_5COC(C_6H_5)OHCOC_6H_5$

XIII



$$C_6H_5CO\underset{OCOC_6H_5}{C}HC_6H_5$$

XIV

Experimental Part

Since many of the diketones on the list were examined by the same general procedure, it is not necessary to describe the experiments with each of these substances in detail. Experimental details will be given, therefore, only in those cases in which a special procedure was adopted or in which the reaction resulted in the formation of compounds which were not known heretofore.

The general method of procedure was to add either the diketone itself or its ethereal solution to a large excess of the Grignard reagent, warm for a few minutes to complete the reaction, decompose the magnesium derivatives either with ice and dilute acid or ice and ammonium chloride, and separate the products by whatever method seemed best.

Dibenzoyl Methane, I.—Since Vorländer and Meye's equation[e] accounts neither for the gas evolved when the diketone reacts with methyl magnesium iodide, nor for the fact that, unlike its alkyl substitution products, it is not cleaved by Grignard reagents, it was necessary to reexamine the behavior of this substance toward Grignard reagents. The true course of the reaction was established by means of three experiments with phenyl magnesium bromide.

In the first experiment the reagent was added gradually to a slight excess of the diketone, the mixture was boiled for an hour, then decomposed with iced acid in the usual manner. Of the 10 g. of diketone used all but 0.35 g. was recovered. After removing the last of the diketone in the form of its copper derivative, there remained a few drops of oil, but no triphenyl carbinol could be detected in this residue. The first step in the reaction, therefore, is the formation of the magnesium bromide derivative of the enol, and even Prolonged boiling does not result in cleavage at this stage.

In the second experiment the operation was reversed, the diketone being added to an excess of reagent. On prolonged boiling this mixture gradually deposited a gray crystalline magnesium derivative. This was collected, washed with ether, and decomposed with iced acid; it gave mainly β,β-diphenyl-β-hydroxy propiophenone (X), the substance previously obtained in the same manner by Vorländer and Meye. Some more of this hydroxyl compound was also obtained on acidifying the filtrate from the solid magnesium compound, making a total yield of 82%. The oily residue from the hydroxy ketone was composed of acetophenone—which was removed by oxidation—and benzophenone, which was separated by distillation with steam. These are decomposition products of the unstable hydroxy ketone. Since no triphenyl carbinol could be detected, there was no cleavage during the Grignard reaction.

In the last experiment **20** g. of the hydroxy ketone X was added to a solution of phenyl magnesium bromide which had been prepared from **7.0** g, of magnesium. The solid ketone was added at a rate that kept the liquid boiling gently and the mixture was boiled for fifteen minutes after all the solid had been added. The magnesium derivatives were decomposed with iced acid, and the ethereal layer washed and dried in the usual manner. After concentration, and dilution with petroleum ether, it first deposited several crops of triphenyl carbinol **(9.2 g.)** and then **7.4** g. of a different product melting at **121–123°.**

The lower melting product was purified by recrystallization from ether and petroleum ether from which it separated in flat prisms.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, **85.3;** H, **6.3.** Found: C, **85.9;** H, **6.2.**

In the machine the substance consumed approximately two moles of methyl magnesium iodide and liberated two moles of methane; it is therefore a dihydroxyl compound. A similar substance was obtained by Berberianu[13] by the action of phenyl magnesium bromide on β-hydroxy-β,β-diphenyl propionic ester. After recrystallization from alcohol our product, like Berberianu's, melts at **104°,** loses alcohol at the melting point, then resolidifies and melts again at a higher temperature.

Oxidation.—To a solution of **1** g. of the substance in glacial acetic acid was added a solution of **1** g. of chromic acid in an equal weight of water. The mixture was warmed on a steam-bath for an hour, then diluted with water, neutralized and distilled with steam. From the distillate ether extracted **0.93** g. of pure benzophenone instead of **0.96** g. calculated on the assumption that the substance is tetraphenyl propanediol (XI).

Acetylacetone. 11.—Our general procedure probably differed from that of Zelinsky[3] only in the care with which we acidified. We dribbled our magnesium compound into a mixture of ice and concentrated hydrochloric acid which was stirred vigorously and then maintained at a temperature of about $-20°$. The product was isolated by distillation under diminished pressure, and identified as diacetone alcohol by its boiling point, its composition and its conversion into mesityl oxide. The yield was 92%.

Phenyl Dibenzoyl Methane, 111.—The products obtained by the usual procedure were desoxybenzoin and triphenyl carbinol. These substances were separated by crystallization from mixtures of ether and petroleum ether and identified by comparison with authentic samples. In an "inverse Grignard reaction" an ethereal solution of phenyl magnesium bromide prepared from **0.6** g. of magnesium was added gradually to a suspension of **3.0** g. of the diketone in ether which was kept at $-10°$ by means of a freezing mixture. When the resulting solution was added to iced acid it deposited a very sparingly. soluble crystalline solid. After washing with alcohol and ether, the solid melted sharply at **150°.** It was identified as tetraphenyl propenone (XII) by comparison with a sample on hand. The yield was **67%.**

Methyl **Dibenzoylmethane, IV.—The** ethereal solution of the products was concentrated, then gradually diluted with petroleum ether until it deposited nearly all of the triphenyl carbinol. The residue on distillation yielded an oil boiling at 210–215°. When this oil was treated with semicarbazide it formed the semicarbazone of propiophenone melting at **177–178".**

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[13] **Berberianu, *Chem. Abstracts,*** 8, **1423 (1914)**

Dimethyl Acetylacetone, V.—Combes' method of preparing dimethyl acetylacetone by heating the sodium derivative of acetylacetone with methyl iodide in a sealed tube to 130°[14] is not very satisfactory. Better yields and a purer product were obtained in the following manner. To a boiling solution of 20 g. of acetylacetone and 71 g. of methyl iodide in absolute methyl alcohol was added, slowly, a solution of sodium methylate containing 9.2 g. of sodium. The solution was stirred continuously during the addition of the methylate and boiled for half an hour after all had been added. Most of the methyl alcohol was then removed by distillation under diminished pressure, and enough water was added to the residue to dissolve the sodium iodide. The aqueous solution was thoroughly extracted with ether, the ethereal solution dried over calcium chloride and evaporated.

The residue was an oil which when it was distilled under diminished pressure boiled at 69" under 12 mm. and gave a distillate that immediately solidified, giving a mass of colorless crystals melting at 21°, and having an odor resembling that of camphor. The yield was 50%.

Action of Phenyl Magnesium Bromide.—The etheral solution of the product, which was obtained in the usual manner, was dried and evaporated until almost free from ether. The residue, on dilution with a small quantity of petroleum ether, deposited a crystalline solid which melted at 81°. When this was mixed with a sample of diphenyl methyl carbinol prepared by the action of phenyl magnesium bromide on acetophenone it caused no depression of the melting point. The yield was almost quantitative.

Action of Mesityl Magnesium Bromide.—In order to prove definitely that the cleavage of the diketones occurs at the same stage as that of the oxides, dimethyl acetylacetone was also treated with mesityl magnesium bromide. The product, isolated by fractional distillation under diminished pressure, was an oil which distilled at 110–111° under 10 mm.; yield, 6 g. from 10 g. of the diketone.

For the purpose of identification 2 cc. of a 10% solution of sodium methylate was added to a methyl alcoholic solution of 0.7 g. of the oil and 0.8 g. of m-nitrobenzaldehyde. The solution was boiled for a few minutes, then diluted with enough water to produce a slight turbidity and set aside. It deposited a golden-yellow solid which, after recrystallization, melted at 82°. For comparison a sample of m-nitro benzal acetomesitylene was prepared in the same manner from acetomesitylene. The two preparations, and a mixture of both, melted at the same temperature.

Anal. Calcd. for $C_{18}H_{17}O_3N$: C, 73.2; H, 5.8. Found: C, 73.5; H, 6.0.

Dimethyl Dibenzoyl Methane, VI.—Since Smedley had reported that this diketone adds methyl magnesium iodide to form a product similar to that which is obtained from dibenzoyl methane itself, we carried out the reaction with phenyl magnesium bromide at −10°, and decomposed the resulting magnesium compounds with especial care. But when the concentrated ethereal solution of the products was cautiously diluted with petroleum ether, it deposited almost the calculated quantity of triphenyl carbinol. The mother liquor, on distillation, yielded an oil that boiled between 210–220°, and formed an oxime which melted at 59-60'—the melting point of the isobutyrophenone oxime.

Wieland and Bloch's[15] method for the preparation of diphenyl triketone, using dibenzoyl methane and nitrogen tetroxide was tried but abandoned in favor of the older method of Neufville and v. Pechmann,[16] which gave better yields and a purer product. This method involves the following steps

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[14] Combes and Combes, *Bull. soc. chim.*, [3] 7, 783 (1892).

[15] Wieland and Bloch, *Ber.*, 37, 1524 (1904).

[16] Neufville and v. Pechmann, *ibid.*, 23, 3379 (1890).

$$C_6H_5COCH_2COC_6H_5 \longrightarrow \underset{A}{C_6H_5COCHBrCOC_6H_5} \longrightarrow \underset{B}{C_6H_5COCH(OCOCH_3)C_6H_5} \longrightarrow$$

$$\underset{C}{C_6H_5COCBr(OCOCH_3)C_6H_5} \longrightarrow \underset{IX}{C_6H_5COCOCOC_6H_5}$$

The bromination of dibenzoyl methane was conducted essentially as described by v. Pechmann. The yield was 236 g. of bromo compound from 224 g. of the diketone, equivalent to 78%. For the purpose of preparing the acetate, 106 g. of the bromo ketone was added to a solution of 49 g. of freshly fused potassium acetate in 400 cc. of glacial acetic acid. The mixture was boiled for forty-five minutes, after which time the transformation was found to be complete. To the clear liquid enough water to produce turbidity was added while the solution was stirred continually and allowed to cool. It first deposited an oil which in a short time solidified to a brown mass, then colorless needles which filled the liquid. The solid was collected, washed, and recrystallized from methyl alcohol. It was then obtained in snow white crystal melting at 94". The yield was 78.5 g. or 79%.

Bromo Dibenzoyl **Carbinol** Acetate, C.—The bromination of the acetate was carried out in a manner similar to that of dibenzoyl methane. It is important to cool the solution well, to add the bromine very slowly, and to stir constantly to avoid local rise in temperature. To a solution of 77 g. of the acetate in 400 g. of chloroform was added in the course of three hours 44 g. of bromine. A stream of dry air was then passed through the solution to remove the hydrogen bromide as completely as possible.

The bromo compound may be isolated by allowing the solution to evaporate, washing the residue with alcohol and recrystallizing it from chloroform and petroleum ether; but for the purpose of making the triketone it was more convenient to operate directly with the chloroform solution as it is left after the bromination. This solution was concentrated, then transferred to a Claisen distilling flask and freed from chloroform by distillation. The flask was then heated at about 120° until the bromo acetate had decomposed and all of the acetyl bromide had distilled. The residue, which was almost pure triketone, was then distilled under diminished pressure. It was collected as a brown oil which promptly solidified to a golden-yellow crystalline mass.

The average yield of pure, redistilled triketone, boiling at 179–181° under 4 mm., was 50 g. from 77 g. of the acetate. The triketone may be recrystallized from boiling petroleum ether which has been distilled from phosphorus pentoxide. It separates in golden-yellow needles melting at 69–70". As it is extremely hydroscopic and in the air rapidly becomes coated with the white hydrate, it must be kept in a vacuum desiccator or in sealed tubes.

Reaction **with Phenyl** Magnesium Bromide.—An ethereal solution of phenyl magnesium **bromide** was prepared in the usual manner from 11.8 g. of magnesium. Meanwhile diphenyl triketone was distilled into a cylindrical dropping funnel provided with a side tube by means of which it could be connected with the distilling flask while the apparatus was exhausted through the top of the funnel. After collecting 14.5 g. of the triketone in this receiver, ether was distilled into it from the Grignard solution. In this manner it was possible to secure a solution in perfectly dry ether and in an apparatus that was convenient for the next step in the operation.

From the modified dropping funnel the ethereal solution of the triketone was added to the solution of phenyl magnesium bromide in the course of half an hour. Each drop produced a slight yellow precipitate which immediately redissolved. The mixture was boiled for an hour, then cooled and decomposed with ice and ammonium chloride. The ethereal layer was dried and concentrated. It gradually deposited crystals which melted at 131° and which were identified as benzoin by analysis and by a mixed melting point.

The mother liquor was evaporated to small volume and diluted with petroleum ether—it deposited a second crop of crystals which after recrystallization melted at 159° and which were identified as triphenyl carbinol. The yield of pure triphenyl carbinol was **9.8** g. or 62%. The same products were obtained when the magnesium derivatives were decomposed with iced acid.

Action of One Mole of Phenyl Magnesium Bromide. Inverse **Grignard** Reaction.—A solution of phenyl magnesium containing **1.82** g. of magnesium was added. gradually, to an ethereal solution of **14.30** g. of diphenyi triketone which was stirred rapidly throughout the operation. As each drop was added an insolubie magnesium compound was precipitated as a yellow solid. The mixture was decomposed with ammoniacal ammonium chloride and the ethereal solution was washed and dried in the usual manner. It yielded a colorless crystalline compound which melted at **123–124°.**

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.7; H, 5.1. Found: C, **79.8;** H, **5.1.**

The substance has the composition of phenyl dibenzoyl carbinol but when it was treated with excess of phenyl magnesium bromide it yielded products that were quite different from those which had been obtained from the triketone. Thus **0.95** g. of the substance was added to an ethereal solution of the bromide made from **0.48** g. of magnesium. The mixture was boiled for fifteen minutes and then decomposed with iced acid. The ethereal layer deposited colorless needles which melted at 164° and which were ultimately identified as triphenyl ethylene glycol by analysis and by comparison with a sample of the glycol that was prepared from benzoin by the method of Acree.[17]

The formation of triphenyl ethylene glycol suggested that our product might be the benzoate of benzoin. This substance was therefore prepared by benzoylating benzoin and a comparison showed that the two products are identical. In order to ascertain whether the benzoate is formed during the Grignard reaction or is the result of a rearrangement of the carbinol by the base used in decomposing the magnesium derivative, the experiment was repeated, but this time the mixture was treated with ice and dilute hydrochloric acid. The result was an oil which after many fractional recrystallizations was separated into benzoic acid and the same benzoin benzoate.

Summary

1. β-Diketones that have no substituents in the methylene group react with two equivalents of phenyl magnesium bromide. The product is a dimagnesium compound which on hydrolysis yields a β-hydroxy ketone.

2. β-Diketones that have one or more substituents in the methylene group likewise react with two equivalents of phenyl magnesium bromide but the result in this case is a mixture of two magnesium compounds, because the process involves a cleavage which is similar to that of oxido ketones.

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[17] Acree, *Ber.*, **37,2762 (1904).**

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE ACETOACETIC ESTER CONDENSATION. III. THE ROLE OF SODIUM IN THE CONDENSATION

BY JOHN M. SNELL AND S. M. McELVAIN

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Since the discovery,[1] in 1863, that acetoacetic ester is formed by the action of metallic sodium on ethyl acetate, periodic discussions of the role of the metal in the condensation have appeared in the literature. One group of investigators[2] has advanced the idea that sodium is not the direct cause of the condensation but serves only to generate sodium ethoxide, the active condensing agent, from traces of alcohol in the ester or from other side reactions. Another group[3] has maintained that when sodium reacts with the ester it is the metal itself which is directly responsible for the condensation. The main objections to the formulation of sodium ethoxide as the active condensing agent have arisen from the observation that sodium produces higher yields of acetoacetic ester than does sodium ethoxide,[3b,d] and that ethyl acetate from which all alcohol has been carefully removed reacts with sodium just as readily as does ordinary ethyl acetate.[3e]

A previous study[4] of the reaction of sodium with various aliphatic esters has shown that ethyl acetate and ethyl propionate are unique among this type of ester in that they are not converted by sodium into the corresponding acyloins when they are reacted with the metal in the presence of an excess of the ester. Rather, they undergo the acetoacetic ester condensation. Consequently, a study of the role of sodium in the acetoacetic ester condensation of this type of ester must necessarily be restricted to the use of ethyl acetate or ethyl propionate if complications resulting from acyloin formation are to be avoided.

This paper is a report of a study of the reaction of ethyl acetate with sodium in which a careful determination of the amounts of the reaction products, acetoacetic ester, alcohol and hydrogen, has been made. The amounts of these reaction products were determined in the reaction mixture as directly obtained from the reaction of sodium and the ester as well as after the condensation had been driven to completion as far as possible by

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[1] Geuther, *Jahresber.*. 323 (1863).

[2] Claisen, *Ber.*, 20, 651 (1887); 21, 1154 (1888); Nef, *Ann.*, 298, 320 (1897); Higley, *Am. Chem. J.*, 37,293 (1907).

[3] (a) Michael, *Ber.*, 33, 3731 (1900); (b) *ibid.*. 38, 1934 (1905); (c) Tingle and Gorsline, *Am. Chem. J.*, 37, 438 (1907); (d) *ibid.*, 40, 46 (1908); (e) THIS JOURNAL, 30, 1874 (1908); (f) Scheibler and Ziegner, *Ber.*, 55, 789 (1922); (g) Scheibler and Marhenkel, *Ann.*, 458, 1 (1927).

[4] Snell and McElvain, THIS JOURNAL, 53,750 (1931).

the removal of the alcohol produced in the reaction. Similar determinations were made with sodium ethoxide as the condensing agent under comparable reaction conditions. The results which were obtained appear to be strong evidence in favor of Claisen's original postulate that sodium is not the active condensing agent in the acetoacetic ester condensation.

Experimental Procedure and Results

In a 1-liter 3-necked flask fitted with a mercury seal stirrer, a condenser for downward distillation and a coil reflux condenser 20 cm. in length, 11.5 g. (0.5 mole) of sodium was finely powdered by heating under boiling xylene with vigorous stirring. The xylene, after cooling, was removed from the powdered sodium by decantation and the latter washed with dry ether. After pouring off this wash ether the sodium was covered with a considerable excess (2.3 moles) of carefully purified ethyl acetate.[5] The delivery end of the condenser for downward distillation was fitted with a distilling flask as a receiver. By plugging or leaving open the side arm of this receiver the ester in the reaction flask could be caused to reflux from the coil condenser or to distil into the receiver. From the top of the coil reflux condenser a tube was led to the bottom of a tower filled with porous chips which had been soaked previously in concentrated sulfuric acid. From the top of the tower a tube was led to a flask for the collection of the hydrogen evolved in the reaction.

The reaction flask was then heated in an oil-bath with stirring until the ester boiled gently. The reaction appeared to proceed quite slowly for about twenty minutes, but after this time it became so vigorous that it was necessary to remove the heating bath from the reaction flask and to cool the latter periodically with a wet towel. This more vigorous reaction continued for approximately another twenty minutes, after which time the sodium had completely disappeared and the reaction mixture was homogeneous. It was during this latter twenty minutes' reaction period that practically all of the hydrogen was evolved from the reaction. This hydrogen was collected and its volume measured.

The reaction mixture was then subjected to distillation through the other condenser attached to the reaction flask. As the ethyl acetate was removed by the distillation, pure ethyl acetate was added through the reflux condenser to the reaction mixture and the distillation allowed to proceed slowly until the distillate showed the same refractive index as that of the pure ester. As the alcohol produced in the reaction was carried out by the ethyl acetate, the reaction mixture lost its homogeneity and a voluminous salt-like precipitate, which could not be taken into solution by the pure ester, settled out.

After all of the alcohol had been removed the reaction mixture, which still had considerable excess ethyl acetate present, was treated with the calculated quantity of 35% sulfuric acid[6] to react with all of the sodium originally put into the reaction. The ester layer was then decanted from the solid $Na_2SO_4 \cdot 10H_2O$ and this salt washed with a fresh portion of ester. The combined ester portions were then washed with a solution of potassium carbonate and, after drying with solid potassium carbonate, fractionated. The ethyl acetoacetate fraction, which boiled at 70–75° (10 mm.), was collected and weighed.

Determination of Alcohol in the Distillate.—The amount of alcohol which was present in the distillate from the reaction of sodium ethoxide with various aliphatic esters has been determined from the refractive index of the distillate.[6] This method did

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[5] McElvain, This Journal, 51,3128 (1929).

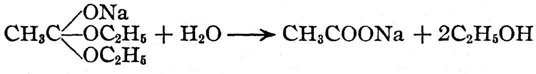
[6] Cf. Snell and McElvain, *ibid.*, 53,752 (1931).

not seem to be suitable when metallic sodium was used as the condensing agent on account of the presence in the distillate of small but unknown amounts of those liquids, xylene and ether, which were used in the preparation of the powdered sodium. For this reason the following procedure for the determination of the alcohol was adopted.

An accurately weighed aliquot (approximately 1 g.) of the distillate was heated at 100° in a sealed tube with approximately 0.6 g. of phthalic anhydride for four hours. The tube was then cooled and opened and the contents poured into a 125-cc. Erlenmeyer flask and the ethyl acetate evaporated off by heating for a few minutes on a steam-bath. The reaction tube was then washed out thoroughly with hot water and these washings added to the residue in the flask from which the ester had been evaporated. The contents of the flask, amounting to about 50 cc., was heated to boiling for about two minutes until the residue completely dissolved and then titrated with $N/5$ sodium hydroxide using phenolphthalein as an indicator. The titration was carried out as rapidly as possible and stopped when the entire solution showed the characteristic pink color of the indicator for thirty seconds. From the difference between the alkali used for this titration and the alkali equivalent of the phthalic anhydride used in the determination the amount of alcohol in the aliquot was determined. Three test solutions of alcohol in ethyl acetate containing 5.52, 10.50 and 14.25% of alcohol by weight were found by the above procedure to contain 4.51, 9.98 and 13.50% of alcohol, respectively.

The amount of alcohol in the distillates usually amounted to about 10%. All of the determinations of alcohol were made in triplicate. The average deviation from the mean was of the order of 0.05 to 0.10%. It should be pointed out that the alcohol values as determined represented minimum values as is shown by results obtained on samples of ethyl acetate containing known amounts of alcohol. This error is due, no doubt, to a slight amount of hydrolysis of the ethyl acid phthalate during the titration of the excess phthalic anhydride.

The amounts of the products of the reaction of ethyl acetate with sodium and sodium ethoxide are tabulated below. In Runs 1 and 2 the ester (2.3 moles) was allowed to react with 11.5 g. (0.5 atom) of sodium and the alcohol formed in the reaction was removed as described above. In Run 3 the same procedure was followed except that 34 g. (0.5 mole) of sodium ethoxide was used as the condensing agent instead of 0.5 atom of sodium. In Run 4 the same quantities of reactants were used and the reaction was allowed to continue only to the point at which all of the sodium had disappeared. This point was reached in about forty minutes after the ester had reached the boiling temperature. The reaction was stopped by adding a slight excess of dry hydrogen chloride dissolved in ethyl acetate to the reaction mixture. This alteration in the isolation procedure was made in order that the formation of alcohol by the reaction



$$CH_3C\begin{cases}ONa\\OC_2H_5\\OC_2H_5\end{cases} + H_2O \longrightarrow CH_3COONa + 2C_2H_5OH$$

which has been shown to take place when the reaction mixture is decomposed with 35% sulfuric acid, might be prevented. The ethyl acetate and alcohol were then distilled through a fractionating column from the reaction flask, and the amount of alcohol present in the distillate was determined by phthalic anhydride. The residue in the reaction flask was treated with water, to dissolve the sodium chloride, and ether to dissolve the acetoacetic ester. The ether layer after drying was fractionated. Run 5 was made under the same conditions as to time of reaction and method of decomposition of the reaction mixture as Run 4 except that sodium ethoxide was the condensing agent instead of metallic sodium.

The last column in the table shows the amount of residue which remained after the distillation of the acetoacetic ester.

Yields of Products from the Reaction of Ethyl Acetate with Sodium and Sodium Ethoxide

Run	Condensing agent	Hydrogen Moles per atom of Na	Hydrogen %	Alcohol Moles per atom of Na	Alcohol %	Ethyl acetoacetate Moles per atom of Na	Ethyl acetoacetate %	Residue, g.
1	Na (0 5 atom)	0.080	16	1.30	130^a	0.74	74	5
2	Na (0 5 atom)	088	17.6	1.30	130^a	.754	75.4	5
3	$NaOC_2H_5$ (0.5 mole)	..	..	1.86^b	93^c	74^b	74	4
4^d	Na (0.5 atom)	078	15.6	0.96	96^a	.49	49	4
5^d	$NaOC_2H_5$ (0.5 mole)	..	..	..	..	$.55^b$	55	1

[a] Calculated on the basis of 1 Na producing $1C_2H_5OH$, the ratio expected from the acetoacetic ester condensation when Na is the condensing agent. [b] Moles per mole of $NaOC_2H_5$. [c] Calculated on the basis of $1NaOC_2H_5$ producing $2C_2H_5OH$, the ratio expected from the acetoacetic ester condensation when $NaOC_2H_5$ is the condensing agent. [d] Reaction allowed to proceed for forty minutes. No alcohol removed from the reaction mixture and the latter decomposed with dry hydrogen chloride.

Discussion of the Experimental Results

The most striking feature of the results that are summarized in the above table is the relative amounts of alcohol and acetoacetic ester which are obtained when sodium reacts with ethyl acetate. When the alcohol is removed from the reaction (Runs 1 and 2), the ratio of alcohol to acetoacetic ester is about 1.7 to 1 and in the case (Run 4) where the alcohol is not removed the ratio is about 2 to 1. Obviously the simple equation

$$2CH_3COOC_2H_5 + Na = CH_3CONaCHCOOC_2H_5 + C_2H_5OH + H$$

which is often used to express the course of the reaction is inadequate, for according to this equation the ratio of alcohol to keto ester is 1 to 1. The alcohol in excess of that which is produced by the acetoacetic ester condensation must be formed by the reduction of some of the excess ethyl acetate. The low yield of hydrogen (about 16% of the theory) supports such a conclusion.[7] The sodium equivalent of the hydrogen that is given off from the reaction is obviously lost for reduction, but from the remainder of the sodium the amount of alcohol produced by reduction can be estimated if it be assumed that it is derived from ethyl acetate. Thus in Run 1, since a 16% yield of hydrogen is obtained, only 84% of the sodium that was used in the reaction is available for reduction. Therefore 0.42 mole of alcohol per atom of sodium should have been formed through reduction. There is left 1.30–0.42 = 0.88 mole of alcohol per atom of sodium which is due to the acetoacetic ester condensation. This yield (88%) of alcohol is quite comparable to the yield **(93%)** of alcohol obtained when sodium ethoxide was the condensing agent (Run **3**). Similarly it is seen from Run 4

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[7] Von Meyer and Friessner [*J. prakt. Chem.*, **65**, 528 (1902)] reported a **33%** yield of hydrogen from the action of sodium on ethyl acetate and concluded that the missing hydrogen, by reduction, induced side reactions that lowered the yield of acetoacetic ester. The lower yields of hydrogen obtained in the present work were due, no doubt, to the fact that very finely divided sodium was used in the reaction.

that approximately 0.42 mole of alcohol per atom of sodium is produced by reduction, leaving 0.96 − 0.42 = 0.54 mole of alcohol per atom of sodium which may be attributed to the acetoacetic ester condensation. This yield (54%) of alcohol parallels quite closely the yield (49%) of acetoacetic ester in this particular run. Obviously, the method of determination of the amounts of acetoacetic ester formed in these reactions is not as accurate[8] as the method used for the alcohol determination, so it is not surprising that the yields of the latter compound are generally somewhat higher than those of the former.

The manner in which the reduction of the ester takes place is of considerable interest. If it is assumed that "nascent hydrogen" can cause such a reduction, then there can be no argument against the contention that sodium is the direct cause of the acetoacetic ester condensation when ethyl acetate is reacted with the metal, for the sodium could in some manner condense the ester with the liberation of "nascent hydrogen" which would reduce more of the ester, thus

$$8CH_3COOC_2H_5 + 4Na \longrightarrow 4CH_3CONaCHCOOC_2H_5 + 4C_2H_5OH + 4H \qquad (1)$$
$$CH_3COOC_2H_5 + 4H \longrightarrow 2C_2H_5OH$$

Such a formulation, however, does not seem probable in view of some recent work on the mechanism of sodium reductions. Willstatter, Seitz and Bumm[9] have demonstrated that the mechanism of the reduction of phthalic acid by sodium amalgam in aqueous solution does not proceed with the "nascent hydrogen" but rather it involves the primary addition of the alkali metal to the carbon to carbon double bond followed by the hydrolysis of the organo-alkali compound. More recently, Wooster and Smith[10] showed that a similar mechanism was followed in the reduction of naphthalene by sodium or potassium in liquid ammonia. If sodium assumes such a role in the reduction of a carbon to carbon double bond it would seem safe to conclude that it functions similarly in the reduction of the carbon to oxygen double bond of an ester. As a matter of fact, the formation of an acyloin by the action of sodium on an ester is a reduction that follows such a mechanism.[4]

On the basis of such a conclusion it is difficult to see how sodium can be directly responsible for the acetoacetic ester condensation. It would seem more in accord with the experimental facts to postulate the condensation as taking place through the agency of sodium ethoxide resulting from the

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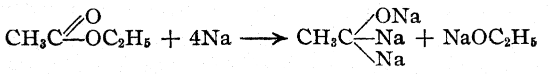
[8] The residue left after the distillation of the acetoacetic ester represents a considerable loss in the yield of the keto ester, since it undoubtedly results from the self-condensation of some of the acetoacetic ester during distillation into β-(β′-ketobutyryloxy)-aotonate and dehydroacetic acid [*cf.* Adkins and Connor, THIS JOURNAL, 52, 5193 (1930)].

[9] Willstatter, Seitz and Bumm, *Ber.*, 61, 871 (1928).

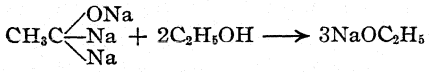
[10] Wooster and Smith, THIS JOURNAL, 53, 179 (1931).

reduction of the ethyl acetate by metallic sodium. The steps in the condensation could be represented as follows



$$\mathrm{CH_3C}\begin{smallmatrix}/\!\!/\mathrm{O}\\ -\mathrm{OC_2H_5}\end{smallmatrix} + \mathrm{4Na} \longrightarrow \mathrm{CH_3C}\begin{smallmatrix}/\mathrm{ONa}\\ -\mathrm{Na}\\ \backslash\mathrm{Na}\end{smallmatrix} + \mathrm{NaOC_2H_5} \qquad (2)$$

$$\mathrm{2CH_3COOC_2H_5 + NaOC_2H_5 \longrightarrow CH_3CONaCHCOOC_2H_5 + 2C_2H_5OH} \qquad (3)$$



$$\mathrm{CH_3C}\begin{smallmatrix}/\mathrm{ONa}\\ -\mathrm{Na}\\ \backslash\mathrm{Na}\end{smallmatrix} + \mathrm{2C_2H_5OH \longrightarrow 3NaOC_2H_5} \qquad (4)$$

$$\mathrm{6CH_3COOC_2H_5 + 3NaOC_2H_5 \longrightarrow 3CH_3CONaCHCOOC_2H_5 + 6C_2H_5OH} \qquad (5)$$

At present there is no experimental evidence for reactions (2) and (4). They simply represent the reduction of the ester through the intermediate formation of an organo-sodium compound followed by alcoholysis in accordance with the suggestion of Willstatter, Seitz and Bumm.[9] It may be that (2) represents the sum of two or more previously occurring reactions.[11]

The sum of (2), (3), (4) and (5) would be the same as the sum of the reactions shown above in (1), *viz.*

$$\mathrm{9CH_3COOC_2H_5 + 4Na \longrightarrow 4CH_3CONaCHCOOC_2H_5 + 6C_2H_5OH} \qquad (6)$$

The hydrogen which is given off in the reaction would result from the following reaction

$$\mathrm{2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2} \qquad (7)$$

It is seen from reaction (6) that **1.5** moles of alcohol are produced in the reaction for each mole of acetoacetic ester. As pointed out above the acetoacetic ester condensation went to the extent of 88% on the basis of the alcohol yields and about 75% on the basis of the keto ester yields in Runs **1** and **2.** If, however, the residue obtained in these runs after the distillation of the acetoacetic ester is considered as derived from acetoacetic ester (cf. footnote ref. 8), the yield of keto ester would be raised to about 0.85 mole per atom of sodium[12] (85%). Thus the ratio of alcohol to keto ester obtained from the reaction mixture would be 1.30/0.85 = **1.53** to 1, which compares quite closely to the ratio established by reaction (6).

In the above discussion an attempt has been made to show that a semi-quantitative consideration of the reaction products in the light of the most probable mechanism of sodium reductions leads to the conclusion that

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[11] It is quite probable that such a reduction mechanism could be tested experimentally if it were possible to find an acetate, $\mathrm{CH_3COOR}$, of such a nature that RONa did not cause the acetoacetic ester condensation of it. Work along this line is now in progress in this Laboratory.

[12] The question might well arise as to why it is not possible to raise the yield of keto ester even higher if the alcohol produced in the condensation is removed. **A** very probable reason why this is not possible is that as the alcohol is removed from the reaction mixture the sodium salt of acetoacetic ester precipitates and in so doing carries with it some of the active condensing agent, sodium ethoxide, possibly as the addition product,

$\mathrm{CH_3CONaCHC}\begin{smallmatrix}/\mathrm{ONa}\\ -\mathrm{OEt}\\ \backslash\mathrm{OEt}\end{smallmatrix}$.

sodium is not directly responsible for the acetoacetic ester condensation, but serves only to generate sodium ethoxide, which is the active condensing agent. In further support of this contention another important observation should be emphasized, *viz.*, that sodium ethoxide produces practically the same amount of condensation (Runs **3** and 5) and just as readily (Run 5) as does metallic sodium. This observation is not in agreement with the findings of some of the earlier investigators of the reaction, but it is in accord with the results recently reported by Kutz and Adkins.[13]

Summary

A study of the reaction of sodium and ethyl acetate has been made in which the amounts of the reaction products, acetoacetic ester, alcohol and hydrogen have been determined. The amount of alcohol found in the reaction mixture is approximately the sum of that produced by the acetoacetic ester condensation and that resulting from the reduction of the ester by the sodium used in the reaction. It has also been shown that sodium ethoxide brings about the condensation just as readily and completely as does metallic sodium. These results lead to the conclusion that the role of sodium in the acetoacetic ester condensation is to generate, by reduction of the ester, sodium ethoxide, which is the real condensing agent.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. **6581**

A QUANTITATIVE STUDY OF THE INFLUENCE OF ACETATE AND OF PHOSPHATE UPON THE ACTIVITY OF THE AMYLASE OF ASPERGILLUS ORYZAE

BY M. L. CALDWELL AND M. G. TYLER

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Recent work[1] has emphasized anew the importance of maintaining the optimal hydrogen-ion activity in studies of enzyme action and has also shown that this is not necessarily a fixed value, but may and often does differ with changes in the environmental conditions under which the enzyme acts. Important among the factors which have been found to influence enzyme action is the kind and concentration of electrolyte present. The experiments reported briefly here were undertaken to establish quantitatively the relations of acetate and of phosphate to the saccharogenic activity (formation of reducing sugar, chiefly maltose)[2] of the amylase

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[13] Kutz and Adkins, THIS JOURNAL, **52,4393 (1930).**

[1] (a) Sherman, Caldwell and Adams, ibid., 49, **2000 (1927); 50, 2528, 2529, 2535 (1928);** **(b)** Sherman, Caldwell and Boynton, *ibid.*, 52, **1669 (1930);** and other references therein contained.

[2] Sherman and Punnett, ibid., **38, 1878 (1916).**

of *Aspergillus oryzae* and to the hydrogen-ion activities which favor its action.

Experimental

The general plan of this work was: first, to establish the optimal hydrogen-ion activities for the enzyme in the presence of each of several different concentrations of acetate or of phosphate: by a series of parallel measurements of the activity in starch systems in which the hydrogen-ion activities differed at close intervals but in which the concentration of acetate or of phosphate was kept constant and all other conditions were strictly comparable; second, to make direct comparisons of the activity of the enzyme in the presence of the different concentrations of each buffer when the systems were in each case adjusted to the optimal hydrogen-ion activity as previously determined; and, third, to compare the activity of the enzyme in the absence of either buffer, with its activity in the presence of the most suitable concentration of phosphate or of acetate, each solution being adjusted to the most favorable hydrogen-ion activity. In these parallel experiments the control systems containing neither acetate nor phosphate were adjusted to closely graded hydrogen-ion activities by the use of graded concentrations of sodium hydroxide.

All reagents were carefully purified. Merck's soluble potato starch according to Lintner was used. It was repeatedly washed with distilled and finally with redistilled water, air dried, and moisture determined. The salts, sodium acetate and the mono- and disodium phosphates, which were of the best commercial chemically pure grade, were recrystallized twice from distilled and once from redistilled water. They were then air dried and moisture determined. Redistilled water was used for all solutions. The preparation of the amylase was obtained from a commercial product[3] by the method of Sherman and Tanberg.[4] Fresh portions of this preparation were weighed out for each experiment but the concentration was kept constant throughout the work. The activity of the enzyme (the formation of reducing sugar, chiefly maltose,[2] from starch) was determined under accurately controlled constant conditions by a slight modification of the gravimetric copper-reduction method previously described.[5] The enzyme acted for thirty minutes at 40 ± 0.02° upon 2% starch containing the concentrations of acetate or phosphate under consideration. When one concentration of a buffer at different hydrogen-ion activities was being studied, the total concentration of acetate or of phosphate was kept constant but the proportions of equimolar acetic acid and sodium acetate or of equimolar mono- and disodium phosphates were changed, the proportions depending upon previous electrometric titrations of similar starchacetate or starch–phosphate systems. The hydrogen-ion activities of all solutions were verified by electrometric measurements with a saturated calomel electrode and a hydrogen electrode of the type described by Wilson and Kern."

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[3] Courtesy of Parke, Davis and Company.

[4] Sherman and Tanberg, THIS JOURNAL, 38, 1638 (1916).

[5] Sherman, Kendall and Clark, ibid., 32, 1073 (1910); Sherman and Walker, *ibid.*, 43,2461 (1921).

[6] Wilson and Kern, *Ind. Eng.* Chem , **17**, 74 (1925).

Results

Interrelation of Hydrogen-Ion Activity, Concentration of Acetate or of Phosphate and Activity of the Amylase of Aspergillus **Oryzae.**—The average of several determinations of the influence of hydrogen-ion activity upon the amylase activity of this enzyme in the presence of each of several concentrations of acetate or of phosphate gave the following results: the maximum enzymic activity occurs under the observed conditions at hydrogen-ion activities of *P*H 5.3 to 5.5, ***P*H** 4.9 to 5.5, ***P*H** 4.7 to 5.3 and PH 4.8 to 5.2 in the presence of 0.01, 0.03, 0.06 and 0 10 M sodium acetate, respectively; and at hydrogen-ion activities of ***P*H** 5.3 to 5.5, *P*H 5.0 to 5.3, ***P*H** 4.9 to 5.1 and ***P*H** 4.7 to 5.2 in the presence of 0.01, 0.03, 0.06 and 0.10 M phosphate, respectively. In both series of experiments there is a tendency for the maximum activity of the amylase to occur in slightly more acid solutions as the concentration of acetate or of phosphate is increased from 0.01 to 0.10 M. Similar results have also been noted with pancreatic and malt amylases.[1,7]

Influence of the Concentration of Acetate or of Phosphate upon **the** Activity of the Amylase of Aspergillus **Oryzae.**—When the activities of the amylase in the presence of each of the four concentrations of acetate, with each system adjusted to the optimal hydrogen-ion activity as previously determined, were compared, it was found that there was a consistent but very small decrease in the activity of the enzyme as the concentration of acetate was increased from 0.01 to 0.10 M. Thus, the average amylase activity expressed in terms of reducing power calculated to maltose[2] was found, in twelve strictly comparable determinations, to be 211, 209, 207, 206 mg. of maltose in the presence of 0.01, 0.03, 0.06 and 0.10 M acetate, respectively.

Similar experiments with the four concentrations of phosphate under optimal conditions of hydrogen-ion activity for each system showed that there was no measurable difference in the activity of the amylase as the phosphate concentration was increased from 0.01 to 0.10 M. Thus, the average amylase activity expressed in terms of reducing power calculated to maltose was found in six strictly comparable determinations to be 213, 212, 213, 213 mg. of maltose in the presence of 0.01, 0.03, 0.06 and 0.10 M phosphate, respectively.

A Comparison of the Saccharogenic Activity of the Amylase of **Aspergillus** Oryzae in the Absence and in the Presence of Acetate or **Phosphate.**—In view of the results discussed above a concentration of 0.01 M acetate and of 0.01 M phosphate was chosen for the comparison of their influence upon the activity of the enzyme. The amylase acted simultaneously upon 2% starch alone, 2% starch containing 0.01 M acetate at the optimal hydrogen-ion activity of ***P*H** 5.5, 2% starch containing

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[7] Sherman, Caldwell and Dale, THIS JOURNAL, 49,2596 (1927).

0.01 M phosphate at the optimal hydrogen-ion activity of P_H 5.3, and upon a series of 2% starch systems to which graded concentrations of sodium hydroxide had been added, resulting in a series of hydrogen-ion activities from P_H 4.4 to 5.5, the optimal amylase activity under these conditions occurring at about P_H 5.1. It was found that under these conditions the activity of the amylase was the same in the presence of 0.01 *M* acetate as in the presence of 0.01 *M* phosphate, that this was consistently higher than its activity in the unbuffered unadjusted aqueous starch systems and slightly lower than the highest activities obtained in the unbuffered systems in which the hydrogen-ion activities were adjusted by the use of sodium hydroxide instead of by acetate or phosphate buffers. The average values of several parallel determinations under these conditions in which the activity of the amylase is expressed in terms of reducing power calculated to maltose, were 196, 203, 203,207 mg. of maltose, respectively, for the unadjusted unbuffered starch, 0.01 *M* acetate, 0.01 *M* phosphate starch systems and for the average of the highest activities in the systems adjusted only with sodium hydroxide. In the latter unbuffered systems, however, the results were very irregular, probably due to the impossibility of obtaining quantitatively reproducible hydrogen-ion activities.

These results show that if the most favorable conditions for each case are maintained, the saccharogenic activity of the amylase of *Aspergillus oryzae* is the same in the presence of 0.01 *M* acetate or of 0.01 *M* phosphate. While the activity of the enzyme is slightly lower in the presence of these buffers than that which may be obtained in their absence, the differences are very small and may, in our opinion, be considered negligible, as they would be more than offset in usual measurements of amylase activity by the advantage of having well buffered systems so necessary for reproducible and comparable results. For this reason also, acetate is preferable to phosphate for use in the measurements of activity of the amylase of *Aspergillus oryzae*, as it is a much more efficient buffer at the hydrogen-ion activities at which this amylase is most active.

Summary

The optimal hydrogen-ion activities for the action of the amylase of *Aspergillus oryzae* in the presence of different concentrations of acetate or phosphate have been quantitatively established, and found to be dependent both upon the kind and concentration of the buffer used.

The highest amylase activity of this enzyme in the presence of either of these buffers occurs in systems of slightly lower hydrogen-ion activity as the concentration of either is increased from 0.01 to 0.10 *M* (measurements at 40° for thirty minutes in presence of 2% starch).

Increasing the concentration of acetate from 0.01 to 0.10 *M* causes a slight decrease in the activity of the amylase. The decrease in activity

of the amylase in the presence of 0.01 M acetate is negligible and is more than offset by the increase in reproducibility of results over those obtained in unbuffered systems.

Changes in the concentration of phosphate from 0.01 to 0.10 M do not influence the activity of the enzyme if the hydrogen-ion activities of the systems are suitably adjusted.

If the hydrogen-ion activities of the systems are suitably adjusted, the activity of this amylase is the same in the presence of 0.01 M acetate or of 0.01 M phosphate.

In measurements of the activity of the amylase of *Aspergillus oryzae*, acetate is preferable to phosphate because of its more efficient buffer effect in the region of hydrogen-ion activities which are optimal for the action of this amylase.

In measurements of thirty minutes at 40° with 2% starch containing 0.01 M acetate, the amylase of *Aspergillus oryzae* is most active saccharogenically at hydrogen-ion activities of P_H 5.3 to P_H 5.5.

NEW YORK CITY

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE "YELLOW COMPOUNDS" RESULTING FROM THE DECOMPOSITION OF ROTENONE IN SOLUTION

BY HOWARD A. JONES AND H. L. HALLER

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The literature on *Deguelia* (Derris) contains numerous references to "yellow compounds" which are obtained in the process of isolating the active insecticidal principles, or which result from the treatment of rotenone ($C_{23}H_{22}O_6$, m. p. 163°), the most important constituent, with various reagents.[1]

Greshoff's[2] derrid, described as an amorphous material melting at 61°, and decomposing at 160°, was probably a mixture of rotenone and certain yellow materials. The same investigator later reported the melting point of pure derrid as 204°.[3]

Van Sillevoldt[4] obtained from the roots of *Deguelia elliptica* a pale yellow substance melting at 73° which he also called derrid. This, on treatment with an alcoholic solution of hydrogen chloride, gave yellow needles

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[1] Clark, *Science*, 71, 396 (1930), has isolated a yellow crystalline material, toxicarol, from the root of Deguelia *sp.* and it is possible that other yellow compounds are associated with rotenone in this root. This paper, however, deals primarily with such yellow compounds as result from the decomposition of rotenone in solution.

[2] Greshoff, *Ber.*, 23, 3537 (1890).

[3] Greshoff, *Meded. 'Slands Plant.*, 25, 47 (1898).

[4] Van Sillevoldt, *Arch. Pharm.*, 237, 595 (1899).

melting at 214°, which he called anhydroderrid. He stated that this material was also present in crude derrid.

Power,[5] on treatment of the resin from the chloroform extraction of stems of *Deguelia trifoliata* (*Derris uliginosa*), obtained a material identical with the anhydroderrid of Van Sillevoldt.

In the course of a chemical investigation of the constituents of *Deguelia elliptica* root, Tattersfield and Roach[6] obtained, in addition to rotenone: three yellow crystalline compounds. These materials were formed on fractionation of the alcoholic extracts of the root. One of these compounds corresponded to the anhydroderrid of Van Sillevoldt, another melted at 222–224°, and the third decomposed at 280°. They crystallized in the form of long, yellow needles and were only slightly soluble in organic solvents. These investigators were unable to obtain anhydroderrid from derris extract which had been freed of rotenone. They concluded that all three yellow compounds were secondary products of the extraction process.

Butenandt,[7] by treatment of rotenone with mild oxidizing agents, obtained a yellow crystalline compound melting at 218°, which he called dehydrorotenone and which he showed has the empirical formula $C_{23}H_{20}O_6$. LaForge and Smith[8] obtained a melting point of 225° for this compound.

Takei[9] obtained, on oxidation of rotenone with chromium trioxide in glacial acetic acid, a yellow compound melting at 298°. This he named rotenonone. Butenandt[7] also prepared this compound and assigned to it the formula $C_{23}H_{20}O_7$; whereas LaForge and Smith[8] assigned it the formula $C_{23}H_{18}O_7$. The latter investigators have shown that rotenonone can be obtained from dehydrorotenone and that dehydrorotenone precedes the formation of rotenonone from rotenone. Butenandt has suggested that dehydrorotenone and rotenonone are possibly the "yellow compounds" which are so frequently mentioned in the literature as accompanying rotenone. These two compounds are practically non-toxic to fish and insects.

During an investigation of the solubility of rotenone it was noted that solutions of rotenone in certain organic solvents changed, on standing, from colorless to various depths of yellow.[10] This change does not occur with equal rapidity in all solvents. Thus at room temperature pyridine solutions become deep amber in color within a few days, chloroform and ethylene dichloride solutions exhibit this change more slowly, in acetone and diacetone alcohol the change takes place only very slowly and in benzene and alcohol the change is almost imperceptible. This alteration in

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[5] Power, *Pharm. Arch.*, 5, 145 (1902); 6, 1 (1903).

[6] Tattersfield and Roach, Ann. *Appl. Biol.*, 10, 1 (1923).

[7] Butenandt, Ann., 464, 253 (1928).

[8] LaForge and Smith. THIS JOURNAL, 52, 1091 (1930).

[9] Takei, *Biochem. Z.*, 157, 1 (1925).

[10] Jones, *Ind.* Eng. *Chem.*, 23, 387 (1931).

color is accompanied by a change in the optical rotation of the solution, the rates of the two changes being roughly proportional. The solutions also lose their toxicity to fish and insects.[11]

Pyridine solutions of rotenone on standing for several days deposited long, yellow, needle-like crystals. Solutions in acetone, amylene dichloride, chloroform, diacetone alcohol and other solvents gave similar yellow crystals. However, the crystals did not separate spontaneously from these solvents, as was the case with the pyridine solutions, but only after long standing and final boiling and evaporation of the solutions to a small volume.

The present investigation has proved conclusively that the changes occurring in solution are a result of the oxidation of the rotenone by air. Thus the change is accelerated by greater exposure to air, but when rotenone is dissolved in pyridine through which nitrogen has been passed and the solution kept in an atmosphere of nitrogen, no color change takes place and no deposition of crystals is to be observed even on long standing The change is not influenced by differences in light intensity.

A chemical examination of the yellow crystalline product of the decomposition has shown it to be a mixture of dehydrorotenone and rotenonone,' both oxidation products of rotenone. The proportion of the two materials in the product deposited seems to depend upon several factors, chief of which are temperature, access of air and the length of time the solution is allowed to stand. The first product deposited seems to be dehydrorotenone, and as the decomposition progresses rotenonone is formed. These crystalline materials are only the initial products of the decomposition. The reaction continues beyond the formation of these two compounds, resulting in a complex mixture of other oxidation products of rotenone.

A sample of the yellow crystalline material removed from a pyridine solution of rotenone soon after the deposition of crystals began was found to melt at about 225°. This same material in chloroform solution had an optical rotation of $[\alpha]^{20}_{\mathrm{D}}$ $-43°$. Butenandt and Hildebrandt[12] obtained $[\alpha]^{18}_{\mathrm{D}}$ $-40.5°$ for dehydrorotenone in chloroform solution. Samples of yellow crystalline material separating at early stages from other pyridine solutions had melting points ranging from 220 to 240°. Probably rotenonone was present in some of these samples.

That rotenonone is present in increasing amounts in the mixture separating from pyridine solutions after longer standing or on more severe treatment (increased temperature or bubbling of air through the solution) was also established. Thus a sample of crystalline material, separated from a pyridine solution which had been allowed to stand over a long period of time, melted at about 280°. Several recrystallizations of this material

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[11] Davidson and Jones, *J. Econ. Entomol.*, *24*, 257 (1931).

[12] Butenandt and Hildebrandt. *Ann.*, 477, 246 (1930).

from acetic acid (no doubt causing further decomposition) raised the melting point to 298°. When mixed with an equal quantity of pure rotenonone it caused no depression of the melting point. Another sample of yellow material separating from a pyridine solution was recrystallized twice from ethyl acetate. Its melting point was found to be about 290°. The minimum and the intermediate indices of refraction[13] of both these samples were identical with those of pure rotenone. The maximum index was higher than that of the readily available reference liquids.

The yellow crystalline material separating from a pyridine solution of rotenone was found to be non-toxic to goldfish.[14] Both dehydrorotenone and rotenonone are practically non-toxic to fish.

The needle-like, yellow crystals obtained from amylene dichloride and diaeetone alcohol solutions of rotenone also appeared to be mixtures of dehydrorotenone and rotenonone.

The yellow material melting at 222–224° obtained by Tattersfield and Roach as a result of boiling alcohol solutions of rotenone was no doubt principally dehydrorotenone and the material decomposing at 280° was probably largely rotenonone.

It was also found that dihydrorotenone (in which the double bond in the side chain has been reduced) behaves similarly to rotenone in pyridine solution, as does isorotenone (in which the double bond has migrated). The pyridine solutions of these materials become deep yellow in color and needle-like, yellow crystals separate, which in the case of dihydrorotenone are no doubt a mixture of dehydrodihydrorotenone and dihydrorotenonone, and in the case of isorotenone probably consist of dehydroisorotenone and isorotenonone

Gimlette,[15] describing work done by Durham, states that crystals of rotenone are altered and reddened by exposure to light. The material in this case was no doubt impure or perhaps contained solvent of crystallization. A sample of pure, crystalline rotenone exposed to ordinary light conditions in this Laboratory showed no change in color after standing for more than a year. No change was observed in melting point, specific optical rotation or toxicity against fish and insects.

Conclusions

1. Rotenone in solution in various organic solvents decomposes, the rate of this decomposition depending on the solvent, temperature, access of air and other factors.

2. This change is an air oxidation of the rotenone, the initial products

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[13] Crystallographic examination was made by George L. Keenan of the Food and Drug Administration.

[14] Piscicidal tests were made by W. A. Gersdorff of the Insecticide Division.

[15] Gimlette, "Malay Poisons and Charm Cures," London, 1923, 2d ed., 260 pp.

of the decomposition being the yellow, crystalline compounds dehydrorotenone and rotenonone.

3. Similar changes are undergone by dihydrorotenone and isorotenone in pyridine solution, analogous compounds no doubt being formed.

4. Dry, crystalline rotenone undergoes no change on long standing.

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STUDIES ON LEVULINIC ACID. I. ITS PREPARATION FROM CARBOHYDRATES BY DIGESTION WITH HYDROCHLORIC ACID UNDER PRESSURE[1]

BY RALPH W. THOMAS AND H. A. SCHUETTE

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Priority of discovery of the fact that dilute mineral acids acting upon hexoses or any carbohydrate yielding them on hydrolysis cause the formation, among other substances, of levulinic acid must be accorded to Mulder[2] in that the compound which he isolated from such a reaction mixture and described as glucinic acid was later found by Grote and Tollens[3,4] to be identical with the substance which they obtained from inulin under similar conditions.[4] It is to the latter investigators that the common name for this keto acid is due.

The traditional equation for the formation of this acid

$$C_{12}H_{22}O_{11} = 2CH_3COCH_2CH_2COOH + 2HCOOH + H_2O$$

by no means represents a complete picture. Subsidiary reactions take place to such an extent that the best yields[5] of levulinic acid which have been reported as a direct result of studied attempts so to guide the course of this reaction that a greater conversion of carbohydrate might be rapidly

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[1] This paper, and others already published by R. W. Thomas on the general theme of the sugars as chemical raw materials [THIS JOURNAL, 52, 2028, 3010 (1930)], forms part of a thesis presented to the Graduate Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[2] Mulder, *J. prakt. Chem.*, 21, 219 (1840).

[3] Grote and Tollens, *Ber.*, 7, 1375 (1874).

[4] Mulder's discovery has been many times verified. Since his day the following carbohydrates have been made to yield this acid: starch [Grote and Tollens, *Ber.*, 7, 1379 (1874)]; dextrose, levulose [Grote, Kehrer and Tollens, *Ann.*, 206, 228 (1881)]; lactose [Rodewald and Tollens, *ibid.*, 206, 231 (1881)]; galactose [Kent and Tollens, *ibid.*, 227, 228 (1885)]; raffinose [Rischbiet and Tollens, *ibid.*, 232, 193 (1886)]; sorbose [Wehmer and Tollens, ibid., 243, 320 (1888)]; Smith and Tollens, *Ber.*, 33, 1286 (1900); and mannose [Fischer and Hirschberger, *ibid.*, 22, 370 (1889)].

[5] (a) McKenzie, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1929, Vol. IX, p. 50; (b) Sah and Ma, THIS JOURNAL, 52, 4880 (1930).

and conveniently brought about are approximately 23% of the theoretical when sugars serve as raw material, starch yielding lesser amounts. Berthelot and André,[6] in studying the decomposition of dextrose by phosphoric acid, and Ost and Brodtkorb,[7] in following the action of dilute sulfuric acid upon this sugar at temperatures up to 145°, in a sense pointed out a way for the development of an improved procedure for the preparation of levulinic acid, This fact has apparently been overlooked until now although it is true that the statement''' has been recently made, without supporting data, that the action will proceed rapidly if the temperature of the solution be raised to 110°.

The best current practice for preparing levulinic acid consists in digesting sucrose or dextrose with dilute hydrochloric acid (1 + 4)'' or (1 + 1)[5b] for ten to forty-eight hours on a boiling water-bath, filtering off the humus material, either fractionating the filtrate[5]".' or concentrating it and finally extracting the acid with a suitable solvent. An alternative procedure[5a] is to evaporate the reaction mixture to dryness before extracting the acid. These methods, however, are uneconomical in that they are time-consuming and productive of even at best but comparatively low yields, and for this reason were not well suited for the preparation of levulinic acid in the quantity needed for carrying out an investigation under way[8] in this Laboratory on sucrose as a chemical raw material. The hope that a study of the effect of altering the acid concentration and time and temperature of digestion might lead to improvements in the technique of preparing this acid, to the end that the process would be shortened and the yields increased, was realized in so far as the latter have been increased by approximately 100% over those obtainable by heretofore existing methods. How these objectives have been reached is herein communicated.

Experimental

Materials.—Commercially pure (99.85%) sucrose, levulose (moisture, 3.1%, $[\alpha]^{25}_{D}$ −79.0°), dextrose (moisture, 6.9%, $[\alpha]^{25}_{D}$ +49.5°), and ordinary domestic corn starch were used in this study.

Procedure.—The carbohydrate in question was treated with dilute hydrochloric acid in a two-liter beaker, the whole transferred to a four-liter copper autoclave containing water and digested for varying periods of time and at various temperatures as indicated in the accompanying tables. The reaction mixture[3] was then evaporated to dry-

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[6] Berthelot and André [Compt. rend., 123, 567 (1896)] heated dextrose and phosphoric acid in sealed tubes kept at 100° for 168 and 648 hours, respectively. On measuring quantitatively the products of reaction they found 37 10% of levulinic acid in the first case and 39.88% in the second.

[7] Ost and Brodtkorb, *Chem.-Ztg.*, 35, 1126 (1911).

[8] Schuette and co-workers, THIS JOURNAL, 48, 3163 (1926); 52, 2028, 3010 (1930).

[9] It was found that ether removed practically nothing from the humus material formed in the reaction and, since its presence gave to the dried residue a porous character which proved an aid to extraction, it was not filtered off.

ness on a steam-bath and the levulinic acid extracted from it with diethyl ether. The latter operation required approximately forty-eight hours when carried out in a continuous extractor. After recovery of the ether the residual oily liquid was distilled, the fraction boiling at 120–130° (4.5 mm.), collected and redistilled. The final product boiled at 106–108° (2 mm.), n^{40} 1.4342, average deviation for all runs being $+0.0004$. This latter value, which is new, was obtained on a product twice recrystallized and one which did not turn yellow after liquefaction and standing in the light for several years. It was used as a criterion of purity for each batch of levulinic acid made.

All yields recorded herein represent the mean of duplicate runs. They were found to be easily reproducible within two to three per cent.

Results and Discussion

Table I shows the effect of the temperature of digestion on the amount of sucrose converted to levulinic acid. The advantage of carrying out this reaction at high temperatures is clearly shown, the yields steadily increasing to 162°, which was the maximum obtainable with the apparatus available for this study. If per cent. yield is plotted against temperature, a curve is obtained which, although rising, begins to flatten out at the higher temperatures, thus indicating that above 162° there would result a relatively smaller increase in yield per degree rise in temperature.

TABLE I

EFFECT OF TEMPERATURE OF DIGESTION ON CONVERSION OF SUCROSE TO LEVULINIC ACID

Sucrose, g.	HCl, (1 + 5) cc.	Digestion data Time, hrs.	Temp., °C.	Pressure, atm.	Levulinic acid Yield g.	%
250	600	1	120	2.0	30.5	10.2
250	600	1	130	3.6	53.6	31.6
250	600	1	145	4.3	58.2	34.3
250	600	1	162	7.0	72.5	42.7

In Table II are set down the data pertinent to the effect that time of digestion was found to exert upon the amounts of sucrose, dextrose, levulose and starch converted to levulinic acid. It appears that equilibrium is practically reached in one hour at a temperature of 162°, longer periods of digestion producing no appreciably larger yields. The same holds true at a temperature of 145°.

Continuing the digestion of levulose, dextrose or starch with hydrochloric acid for periods longer than one hour actually resulted in decreased yields of levulinic acid, the effect decreasing in the order named. These results were not entirely unexpected, however, because of the sensitiveness of the hexose sugars to heat and continued action of the mineral acid.

That the yields of levulinic acid depend to some extent upon the concentration of the hydrochloric acid used is shown in Table III, in which the data as recorded were obtained by using always the same volume of acid solution (600 cc.), its strength being so adjusted as to give the value indicated in the second column. Hydrochloric acid diluted in the proportion

TABLE II

EFFECT OF TIME OF DIGESTION ON CONVERSION OF SUCROSE, DEXTROSE, LEVUMSE AND STARCH TO LEVULINIC ACID

Carbohydrate, g.	HCl (1 + 5), cc.	Digestion data			Levulinic acid Yield	
		Time, hrs.	Temp., °C.	Pressure, atm.	g.	%
			Sucrose			
250	600	1	162	7.0	72.5	42.7
250	600	2	162	7.0	73.6	43.4
250	600	5	162	7.0	72.7	42.9
250	600	1	145	4.3	58.2	34.3
250	600	2	145	4.3	61.5	36.2
250	600	5	145	4.3	55.0	32.4
			Dextrose			
250	600	1	162	7.0	61.0	37.8
250	600	2	162	7.0	53.0	32.9
			Levulose			
200	480	1	162	7.0	50.2	39.0
200	480	2	162	7.0	37.5	29.1
			Starch			
250	600	1	162	7.0	65.4	36.5
250	600	2	162	7.0	60.2	33.6

of one volume to five of water (6.5%) is of ample strength, a greater concentration being not only unnecessary but undesirable in that it was found to complicate the purification of the final product.

TABLE III

EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID UPON CONVERSION OF SUCROSE TO LEVULINIC ACID

Sucrose, g.	Concentration of HCl, %	Digestion data			Levulinic acid Yield	
		Time. hrs.	Temp.. °C.	Pressure, atm.	g.	%
250	3.5	1	162	7.0	59.0	34.8
250	6.5	1	162	7.0	72.0	42.4
250	10.7	1	162	7.0	70.0	41.3
250	4.2	1	145	4.3	62.0	36.5
250	6.5	1	145	4.3	60.0	35.4
250	10.7	1	145	4.3	63.0	37.1

Not much further need be said about these data except that they clearly show that a readjustment of the experimental conditions heretofore recommended is desirable not only because, by the use of high temperatures, economies as to time and materials are effected but also that the course of the fundamental reaction involved in the preparation of levulinic acid from hexoses is hereby directed away from its empirical feature to a closer approach to stoichiometrical conditions. The large increase in yields of acid so obtained points to these conclusions.

In the light of the information gained by this study the following procedure appears to warrant recommendation as a modified practical method for preparing levulinic acid.

Dissolve sucrose in dilute hydrochloric acid solution (1 + 5) in the proportion of 250 g. (0.73 mole) to 600 cc. of acid. Heat the mixture, contained in a beaker, for one hour in an autoclave after the temperature has reached 162°. If the beaker be surrounded by water, which is a very necessary condition here, the total pressure will rise to approximately seven atmospheres at this temperature. Break up the cake of humus material which has formed in the reaction mixture and transfer the whole to an evaporating dish, taking it to dryness on a steam-bath. Extract the dry residue with diethyl ether until the levulinic acid is completely removed. Drive off the ether by distillation at atmospheric pressure and then fractionally distil the residual oily liquid in *vacuo,* collecting for redistillation (106–108°, 2 mm.) that fraction boiling at 120–130° (4.5 mm.); yield, 42%.

Equally satisfactory yields may be obtained by filtering the reaction mixture, washing the humus material well with water and fractionally distilling the combined filtrates. While this latter procedure materially shortens the process, it has a disadvantage in that a tarry residue is left in the distillation flask which is very difficult to remove. Proceeding according to this modification, levulinic acid may be prepared in yields exceeding 40% in a period of five to six hours.

If a product of high degree of purity is desired, the acid may be crystallized in an ice-bath. To that end stir the liquefied acid to induce the formation of small crystals, remove them from the mother liquor by centrifugal force, and wash the crystalline mass several times with small portions of cold diethyl ether, which is in turn removed by centrifuging. Remove the last trace of ether by evaporation at room temperature and reclaim the acid in the washings by distillation. A product prepared in this way (n^{40}, 1.4342) may be kept in the liquid state without the appearance of the slightly yellow tint that is characteristic of the fractionally distilled acid.

Summary

As the result of a study of the action of dilute hydrochloric acid on certain carbohydrates, during the course of which the three variables concentration of acid, time and temperature of digestion were altered, there has been developed a modification of existing procedures for preparing levulinic acid to the end that a larger conversion of carbohydrate to this acid is now possible than by heretofore existing methods. The recommended procedure is to digest sucrose under pressure for one hour with dilute hydrochloric acid at 162° in the presence of water vapor. Details of a method leading to the preparation of a very pure product are given.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

REDUCTION PRODUCTS OF NAPHTHACENEQUINONE

BY LOUIS F. FIESER

RECEIVED APRIL 3, 1931 PUBLISHED JUNE 8, 1931

Naphthacenequinone is the most interesting of those few anthraquinones which fail to give the characteristic red vat when treated with hyposulfite and alkali in the usual manner. The failure of the Liebermann reaction cannot be attributed to steric interference, as in the case of the poly-α-substituted anthraquinones,[1] and the substance is simpler in structure than its benzologue, *lin.*-dibenzanthraquinone, which presents the same anomaly.[2] It is not generally known that naphthacenequinone belongs to this exceptional class of substances, for although the discoverers[3] made the highly interesting observation that the quinone forms an eosin-red solution on reduction in glacial acetic acid solution, they did not study the alkaline reduction, and the compound has received no attention since the time of their work. Further study perhaps has been delayed by the statement of Mills and Mills[2] that naphthacenequinone reacts in the usual manner with zinc and alkali. This unfortunate statement is probably an incorrect quotation from the paper of Gabriel and Leupold, for there is no indication that the English investigators studied the compound themselves. That there is this error in the very meager literature of the subject, became apparent to the present author in the course of an attempt to measure the reduction potential of naphthacenequinone. This attempt met with no success, and the failure appeared to be due to the unusual instability of the immediate reduction product.

Before any extensive study of the unusual behavior of naphthacenequinone could be conveniently undertaken, it was necessary to find a more suitable method of preparation than those which involve the very unsatisfactory hydrogen iodide–phosphorus reduction of hydroxy-[4] or dihydroxynaphthacenequinone.[3] Such a method was found in the dehydrogenation of 2,3-tetralanthraquinone with bromine. Pure naphthacenequinone can be obtained in 80% yield by this method in the course of a few hours. It is of interest that the hydrocarbon, naphthacene, results from the zinc-dust distillation of 2,3-tetralanthraquinone.

The reduction of naphthacenequinone has been studied under a variety of conditions, and the main results are summarized in the accompanying chart. Boiled in glacial acetic acid solution with tin, the quinone, I, first gives a deep red solution of the hydroquinone, II, and the latter substance

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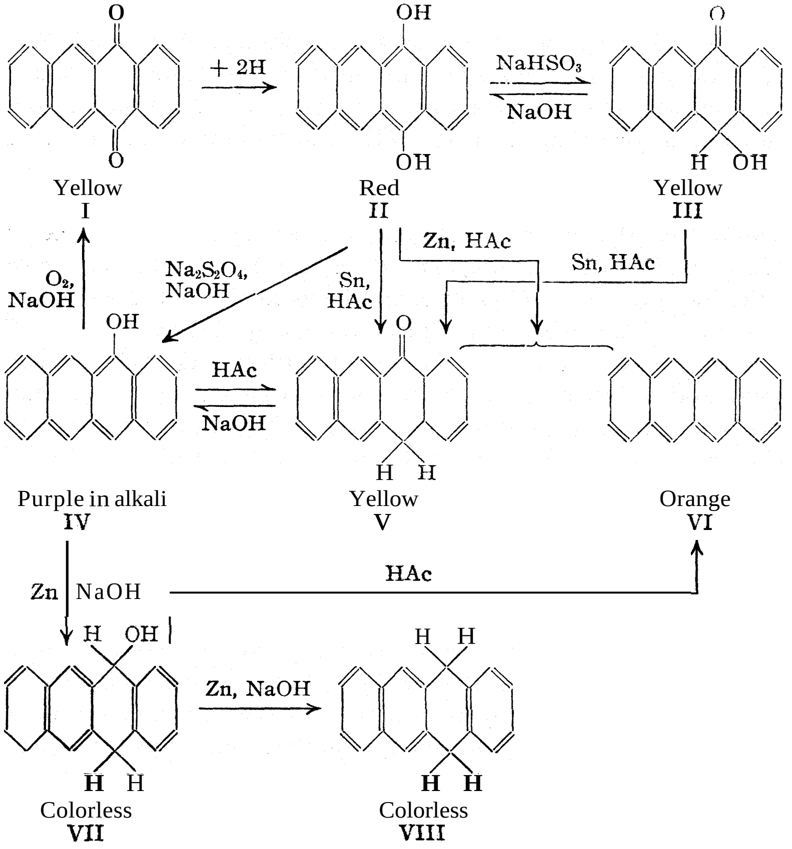
[1] (a) Seer, *Monatsh.*, **33**, 535 (1912); (b) Seer and Ehrenzweig, *ibid.*, **43** (1912); (c) Seer, *ibid.*, **34**, 579 (1913); (d) Philippi and Seka, *ibid.*, **43**, 617 (1922).

[2] W. H. Mills and M. Mills, *J. Chem. Soc.*, **101**, 2194 (1912).

[3] Gabriel and Leupold, *Ber.*, **31**, 1277 (1898).

[4] Deichler and Weizmann, *ibid.*, **36**, 547 (1903).

is then slowly converted into 2,3-benz-9-anthrone, V, and the reaction stops at this point. With the more active metal zinc, a mixture of the anthrone and naphthacene, VI, is obtained and, since the anthrone cannot be converted into naphthacene under similar conditions, it is concluded that the hydrocarbon is produced by the direct reduction of the hydroquinone. In order to prepare the diacetate of the hydroquinone in good yield, it is necessary to modify the standard method of reductive acetylation by substituting tin for zinc. Otherwise the product is contaminated with the anthrone and the hydrocarbon.



Crystalline naphthacenequinone may be boiled indefinitely with alkaline hyposulfite solution without developing the red color characteristic for most anthraquinones. When it is prepared in a finely divided condition by pouring a solution in concentrated sulfuric acid into boiling water, the quinone rapidly dissolves in alkaline hyposulfite solution and the latter acquires a deep green color. The usual red vat is obtained only by the use of alcohol as the solvent. When hyposulfite solution and a rather large quantity of alkali are added to a suspension of the quinone in boiling alcohol, the material dissolves in a few minutes to give a deep red solution of naphthacene hydroquinone, II. The color then slowly changes to an intense purple for which the anthranol, IV, is responsible. On acidification, the substance ketonizes and is obtained in the form of the anthrone.

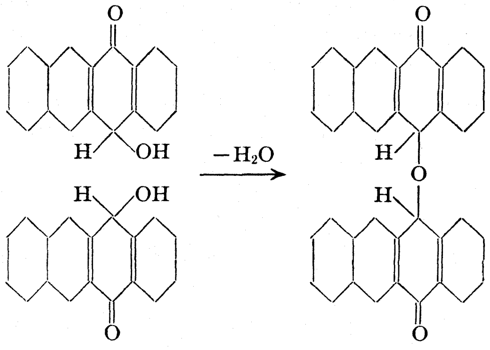
While the anthrone, V, is a very stable substance, the enol form, IV, is sensitive to both oxidation and reduction. The purple solution in alcoholic alkali oxidizes readily in the air to give naphthacenequinone. It is not attacked by hyposulfite, but it is easily reduced by zinc in the presence of alcoholic alkali to the dihydro-anthranol, VII, which in turn is converted by the same reagent into dihydronaphthacene, VIII. The dihydroanthranol, VII, very easily loses the elements of water with the formation of naphthacene, VI. The dehydration takes place instantly in a boiling alcoholic solution on adding a trace of a mineral acid, and it is likely to occur in the process of crystallizing the compound from alcohol or ligroin unless a trace of a basic substance such as pyridine is added to stabilize it.

Naphthacenehydroquinone (II) is unstable in solution not only because it is easily reduced by the reagents ordinarily used to produce it, but also because it easily undergoes two other reactions, na'mely, disproportionation and ketonization. In a solution of the substance prepared by the hydrolysis of its diacetate, in order to eliminate the possibility of reduction, the hydroquinone undergoes mutual oxidation and reduction with the formation of the quinone and the anthrone. The reaction is quite rapid in an alcoholic solution which is either strongly acidic or weakly alkaline; it is very slow in a strongly alkaline medium. The striking color changes accompanying the disproportionation are described in the Experimental Part.

Under conditions which are not easily specified, naphthacenehydroquinone ketonizes and passes into 2,3-benz-9-hydroxyanthrone, III. The keto form may be obtained quantitatively from the quinone by adding hyposulfite solution and a certain small quantity of alkali to *a* boiling alcoholic suspension of the quinone. The deep red solution of naphthacenehydroquinone which first results suddenly changes within a few minutes to brown and then to a pale pink and the solution is now found to contain the hydroxyanthrone as the sole product. With more alkali present, the substance remains in the enolic form until it is slowly converted by reduction into the anthranol. The keto form can be enolized by the action of pyridine or, more slowly, by alcoholic alkali. Although the equilibrium appears to favor the keto form in neutral or acid solution, the quantitative ketonization of the hydroquinone bas not been accomplished except in the course of the preparative method described. When working in the absence of reducing agents, the disproportionation reaction appears to be more rapid than the ketonization.

The failure of naphthacenequinone to form a red vat in an aqueous medium is probably due in large part to the great instability of naphthacenehydroquinone.

One other reduction product, and one of an unusual type, was isolated by H. D. Newman in the course of some preliminary experiments described in the Experimental Part. It was later found that the same compound may be produced in quantity by the oxidation of 2,3-benz-9-anthranol, IV, in alcoholic alkaline solution by the action of sulfur. The substance has the molecular formula $C_{36}H_{22}O_3$. It yields naphthacenequinone on oxidation and 2,3-benz-9-anthrone on acid reduction, and it corresponds in the state of oxidation to naphthacenehydroquinone. The substance is obviously composed of two C_{18} residues, but an adequate basis for a choice between several possible formulas was only furnished by the results of a quantitative study of the action of the Grignard reagent. This showed that the compound has no active hydrogen atoms, but that it adds this reagent. From these facts it was concluded that the substance has the structure of di-(2,3-benz-9-anthronyl)-ether, X. If this formula is correct,



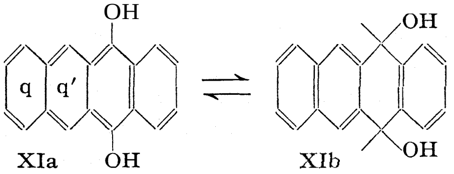
IX X

it should be possible to obtain the compound by the dehydration of two molecules of 2,3-benz-9-hydroxyanthrone, IX, and this was indeed found to be the case. The conversion is easily brought about by the action of acetic anhydride and a trace of sulfuric acid. The ether structure is thus confirmed, and the compound represents a type which is probably novel in the anthraquinone series.

The Theoretical Significance of the Results.—When the various naphthacene derivatives here described are compared with the corresponding derivatives of anthracene, it becomes apparent that there is a marked difference between the two series. Naphthacenehydroquinone, II, is more easily reduced than is anthrahydroquinone, and it has a much greater tendency to ketonize. This statement applies equally well to 2,3-benz-9-anthranol (IV); it readily forms a dihydride on reduction, and the ketonization takes place with such facility that the isomerization can only be reversed by the action of alcoholic alkali. Pyridine and aqueous alkali, reagents which readily enolize anthrone, are without effect on 2,3-benz-9-anthrone, V In each of the instances cited it is seen that the naphthacene derivatives possess an enhanced tendency to react in such a way as to produce derivatives of dihydronaphthacene. A further example of the greater stability of the dihydride structure in the naphthacene as compared with the anthracene series is that, while dihydroanthranol becomes dehydrated in alkaline solution to give anthracene, its 2,3-benz-derivative (VII) does not lose water under similar conditions, but retains the dihydride structure and is easily reduced to dihydronaphthacene.

The disproportionation of naphthacenehydroquinone is a reaction-which may be classed with those already cited. While anthrahydroquinone reacts in a similar manner only on prolonged boiling in an alcoholic solution containing hydrochloric acid,[5] naphthacenehydroquinone is completely decomposed in a few minutes even in a weakly alkaline solution. Here again a substance having a completely aromatic structure appears to be peculiarly unstable and it undergoes mutual oxidation and reduction to form products which, in their most stable condition, possess the dihydride structure.

The ortho quinonoid structure for anthracene and its benzologues furnishes the simplest explanation of the facts observed. As compared with anthrahydroquinone, naphthacenehydroquinone, XIa, has, in place of a single ortho quinonoid ring, two rings which are quinonoid. The combined system presented by rings q and q' is similar to that of the unknown 2,3-naphthoquinone, and the lack of stability of this substance shows that such a system is one of great strain or of great reactivity. This furnishes an adequate interpretation of the pronounced tendency of the compound in question to pass into substances having the dihydride structure either by ketonization, reduction or disproportionation, for the condition of strain in the molecule is thereby relieved. The striking colors of those naphthacene derivatives which have the completely aromatic



XIa XIb

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[5] K. H. Meyer, *Ann.,* **379,** 61 (1911).

structure may also be attributed to the quinonoid grouping, though the relationship of the different substances is not clear (see chart).

One may also regard naphthacene as a substance having a conjugated system of six double bonds and with consequent enhanced reactivity[6] at the meso carbon atoms, which are at the ends of this long system. Regarded thus as a condensed derivative of o-phenylenedodeca-hexa-ene, the orange hydrocarbon corresponds well in color with diphenyl-dodeca-hexa-ene, which is brown-orange.' There is also a rough correlation between the aromatic and aliphatic compounds having systems of eight conjugated double bonds with phenyl groups at the two ends, for Clar and John[s] have described *lin.*-dibenzanthracene as a blue hydrocarbon, while Kuhn and Winterstein[7] have found diphenyl-hexadeca-octa-ene to be bluish copper-red.

Since the o-quinonoid formula and the poly-ene formula are one and the same, the two points of view regarding the anthracene hydrocarbons are in no way antagonistic, but they rather supplement each other.

Clar and John[8] have recently advanced evidence to show that their blue *lin.*-dibenz-anthracene has the properties of a bivalent radical. According to their views, naphthacenehydroquinone in solution should consist of an equilibrium mixture containing the radical XIb. Naphthacene itself can hardly be formulated as a bivalent radical, for it is not attacked by moist oxygen in high-boiling solvents in the manner characteristic of the pentacyclic hydrocarbon. There is reason to believe, however, that the hydroxyl or metal-oxyl groups of naphthacenehydroquinone would promote radical dissociation at the meso carbon atoms. The red color of acid solutions of the substance is unusual among the anthrahydroquinones, and the suggestion that the color is due to the presence of a certain quantity of the bivalent radical is an attractive one. The reactions by which the compound stabilizes itself also find a ready explanation in terms of this hypothesis.

It may be pointed out in this connection that the assumption of free radicals furnishes the basis for a comprehensive interpretation of the alkaline oxidation of anthrahydroquinones and anthranols. It is generally agreed that the oxidation of sodium anthranolate to dianthrone by reagents other than oxygen proceeds through the intermediate formation of a univalent oxygen radical. The reaction with molecular oxygen must follow a different course, for the product is anthraquinone and not dianthrone. If the solution consists of an equilibrium mixture containing the trivalent carbon radical, this could form a peroxide which, by loss of sodium hydroxide, would yield anthraquinone. The reactions may be formulated as follows

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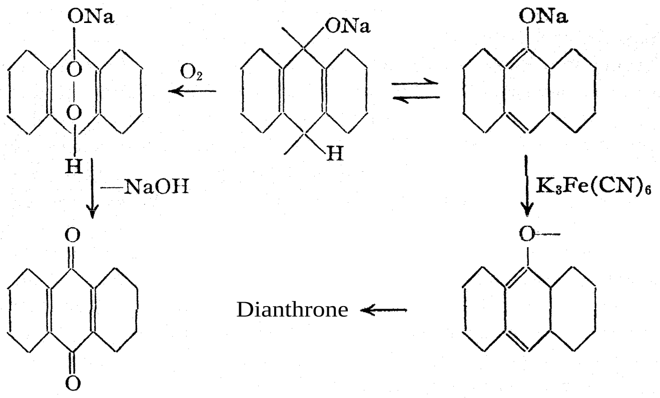
[6] Wittig and Wiemer, Ann., 483, 144 (1930).

[7] Kuhn and Winterstein, *Helv. Chim. Acta*, 11, 87 (1928).

[8] Clar and John, *Ber.*, 63, 2967 (1930).



Applied to the action of oxygen on anthrahydroquinone in alkaline solution, the same mechanism may serve to account for the great speed of the reaction,[9] and it agrees well with the facts. The peroxide in this case would yield anthraquinone by the elimination not of sodium hydroxide but of sodium peroxide, and it is well known that this is one of the reaction products.

It must be recognized that the results presented in this paper neither confirm nor contradict the interesting hypothesis that anthracene derivatives partially isomerize to substances with trivalent meso carbon atoms and that the isomerization increases with the number of linear rings. Since any isomerization to radicals must be the result of a strained condition within the molecule for which the ortho quinonoid structure may be considered responsible, the ortho quinonoid theory may be extended to include the possibility of radical formation, and it is thus both the sounder and the more fundamental of the two views.

Experimental Part

2,3-Tetralanthraquinone.—As a result of the preparation of large quantities of this material, the following procedure can be recommended as representing some improvement of Schroeter's procedure for the preparation of *o*-[tetroyl-2]-benzoic acid.[10] A mixture of 250 g. of phthalic anhydride, 350 g. of tetralin, 1200 cc. of benzene and 400 g. of aluminum chloride was stirred and heated at the boiling point for three hours. After cooling, the benzene layer was decanted from the addition product and discarded. The addition product was decomposed by adding ice and 400 cc. of concentrated hydrochloric acid, and then treated with steam until most of the adhering benzene and tetralin was removed. After removal of the aqueous solution, the product was treated with a solution of 150 g. of sodium carbonate monohydrate and digested with steam until all but a small residue had dissolved and the remaining tetralin was evaporated. The solution yielded 459 g. (97%) of good product on acidification.

In the condensation to the tetralanthraquinones, it was found expedient to use two

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[9] Fieser, This Journal, 46, 2639 (1924).

[10] Schroeter, *Ber.*, 54, 2242 (1921).

to three times the quantity of sulfuric acid employed by Schroeter, though there was no improvement in the yield.

Naphthacenequinone.—A boiling solution of 50 g. of *lin.*-tetralanthraquinone in 350 cc. of glacial acetic acid was treated with 65 g. of bromine in the course of one-half hour. Most of the solvent was removed by distillation and the thick sirup which remained was washed out while still hot into a distilling flask with sealed-on receiver. The remaining solvent was distilled off, and the heating was continued cautiously in order to promote the evolution of hydrogen bromide. The reaction should be carried out as slowly as possible, for it easily becomes too vigorous. As the formation of naphthacenequinone reached completion, the contents of the flask suddenly solidified. The product was then distilled under diminished pressure with the use of an oil pump, and then redistilled. The crude product (44 g.) is best crystallized from tetxachloroethane, which has marked solvent power for the polycyclic quinones and hydrocarbons. A single crystallization gave 37 g. of the pure quinone, while a further 3-g. portion was recovered from the mother liquor; yield (pure), 81%.

Naphthacenequinone forms yellow needles from tetrachloroethane, very long yellow or orange-yellow needles from glacial acetic acid. The purest samples melted at 285°. Gabriel and Leupold[3] have described the characteristic color tests with concentrated sulfuric acid and with glacial acetic acid and zinc dust

2,3-Benz-9-anthrone (5-Oxo-naphthacene), V.—The best method of preparing the anthrone from naphthacenequinoneis by reduction with tin in glacial acetic acid solution. Zinc is too energetic in its action and invariably leads to the production of some naphthacene. It is of interest that the hydrocarbon produced by reduction with zinc and acetic acid does not come from 2,3-benz-9-anthrone, for this substance, though easily reduced when in the anthranol condition (alkaline solution), is not affected by prolonged boiling in glacial acetic acid solution with zinc and hydrochloric acid. It thus must result above from the reduction of benz-anthrahydroquinone.

Four grams of naphthacenequinone was suspended in 100 cc. of glacial acetic acid and boiled under the reflux with 8 g. of granular tin. The quinone slowly dissolved with the formation of a deep red solution; the color faded to a pale yellow-brown in about one hour, when the reduction was complete. The solution was filtered, treated with 10 cc. of concentrated hydrochloric acid, concentrated to half its volume, and allowed to cool. The anthrone separated in nearly pure condition (3.5 g.).

A second satisfactory method of preparing 2,3-benz-9-anthrone is by reduction in alkaline solution with sodium hydrosulfite. This will be described below.

The anthrone is readily soluble in glacial acetic acid or benzene and moderately soluble in alcohol. It forms yellow needles melting at about 196°, the temperature being dependent upon the rate of heating.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.49; H, 4.96. Found: C, 88.21; H, 5.16.

The solution of the anthrone in concentrated sulfuric acid is bright red. The compound is not soluble in aqueous alkali, but dissolves readily in alcoholic sodium hydroxide solution. The solution is intensely purple; when shaken with air it rapidly loses this color and naphthacenequinone precipitates. The anthrone is not enolized by pyridine, for the material was recovered unchanged after boiling a pyridine solution with acetic anhydride.

Naphthacenehydroquinone Diacetate **(9,10-Diacetoxy-2,3-benz-anthracene).**—Liebermann's method of reductive acetylation with zinc dust, sodium acetate and acetic anhydride gave a very poor yield in the present case owing to the great ease of reduction of naphthacenehydroquinone. The desired product was invariably contaminated with the anthrone and with naphthacene. A satisfactory preparation was found in the substitution of granular tin for zinc and proceeding in the usual manner. A pure product was thus easily obtained in good yield. The substance crystallizes well from glacial acetic acid, forming orange needles melting at 269°. Dilute solutions of the substance are yellow with a green fluorescence. The hydrolysis of the diacetate will be described below.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.72; H, 4.60. Found: C, 76.33; H, 4.98.

2,3-Benz-9-hydroxyanthrone (5-Hydroxy-12-oxo-5,12-dihydronaphthacene), III.—This compound was first obtained by adding successive portions of sodium hyposulfite solution to *a* boiling alcoholic suspension of naphthacenequinone. Each addition of reagent caused the solution to take on a red color which, however, disappeared suddenly in the course of a few minutes (ketonization of the hydroquinone); but even after several hours the reduction of the quinone was not complete. It was then found that the presence of a limited quantity of alkali materially assists in the reduction and in the formation of the desired compound. With a still larger quantity of alkali present the reduction does not stop at the hydroxyanthrone stage but converts this into the anthranol. The hydroxyanthrone also may be reduced with tin in glacial acetic acid solution, forming the anthrone.

To a suspension of 6 g. of naphthacenequinone in 400 cc. of boiling alcohol, there was added a concentrated aqueous solution of 12 g. of sodium hyposulfite and 10 cc. of 6 N sodium hydroxide. The quinone rapidly dissolved, giving a deep red solution having the appearance characteristic of an anthraquinone vat. After about two minutes, the color suddenly changed to a dark greenish-brown and then as suddenly cleared to a pale pink, with the separation of inorganic salts. The inorganic material, together with a small amount of unreacted quinone, was removed by filtering the hot solution and the latter was poured into an equal volume of water to precipitate the reaction product. The material was pale pink in color and very nearly pure. The yield depends somewhat upon the character of the starting material. If a crystalline sample of the quinone is used, about 10% of it is recovered unchanged. When the naphthacenequinone is prepared in finely divided condition by pouring a sulfuric acid solution of the substance into boiling water, the conversion is quantitative.

When the above procedure was altered only to the extent of using twice the specified quantity of alkali the course of the reduction was entirely different. The red, vat color persisted for about one-half hour, when a change to reddish-purple became apparent. After one hour the solution had the purple color characteristic of the anthranol salt, and it showed no further change on prolonged reaction. On acidifying and diluting the solution, 2,3-benz-9-anthrone was obtained in excellent yield. Reduction in an alcoholic medium in the presence of a large amount of sodium carbonate also led to the formation of the anthrone. When in a finely divided condition, naphthacenequinone may be reduced with hyposulfite and alkali in an aqueous medium. The solution first becomes deep green; the color then suddenly fades and a mixture of the anthrone and the hydroxyanthrone separates.

2,3-Benz-9-hydroxyanthrone dissolves readily in benzene or glacial acetic acid; it is moderately soluble in alcohol and sparingly soluble in ligroin. It forms excellent, long, hair-fine, yellow needles and decomposes at about 230°. A characteristic test for the compound is furnished by the deep red color which it imparts to alcoholic sodium hydroxide solution (see below). It is insoluble in aqueous alkali.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.05; H, 4.65. Found: C, 82.55; H, 4.57.

This benz-hydroxyanthrone enolizes readily in boiling pyridine solution and the solution rapidly acquires the deep red color characteristic of naphthacenehydroquinone. The color fades on shaking with the air and naphthacenequinone crystallizes from the solution. When heated with a mixture of equal parts of pyridine and acetic anhydride, the benz-hydroxyanthrone is converted largely into naphthacenehydroquinone diacetate,

m. p. 269°, though a part of the naphthacenehydroquinone becomes oxidized to the quinone before it can be acetylated.

2,3-Benz-9,10-dihydro-anthranol (5-Hydroxy-5,12-dihydronaphthacene), VII.—This compound has been obtained as the first product of the reduction of 2,3-benz-9-anthrone in alcoholic alkaline solution with zinc dust, but it is most readily prepared directly from naphthacenequinone. The velocity of reduction increases very rapidly with an increase in the concentration of alkali. Under the conditions of the experiment 2,3-benz-9,10-dihydro-anthranol is in turn easily reduced to dihydronaphthacene, and the formation of a small amount of this material could not be avoided. The best yields were obtained in the following manner.

A suspension of 1 g. of naphthacenequinone in 100 cc. of alcohol and 10 cc. of 25% sodium hydroxide was boiled with 5 g. of zinc dust for one hour. The quinone rapidly dissolved to give a deep red solution; this became deep green within a few minutes and then the color slowly faded. At the end of the time specified the solution was pale greenish-yellow. It was cooled and the residue, consisting chiefly of zinc, was washed with water, dried and extracted with benzene. The benzene extract contained dihydronaphthacene (0.2 g.). The 2,3-benz-9,10-dihydro-anthranol was precipitated with water from the alcoholic solution. In order to remove a trace of zinc hydroxide and dihydronaphthacene, the crude product was dissolved in alcohol containing one drop of sodium hydroxide; the solution was cooled well, filtered and the product was precipitated with water. The material cannot be further purified by crystallization from pure solvents such as alcohol or ligroin because it is partially converted by the boiling solvents into naphthacene. A trace of an alkaline reagent, however, prevents this dehydration. The substance thus crystallizes well from benzene–ligroin containing a drop of pyridine. The solvent completely removes an otherwise persistent yellow color, and the compound forms colorless silken needles which form cottony clusters of great beauty.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.40; H, 5.75.

The benz-dihydro-anthranol has no melting point but decomposes even on very gentle heating with the formation of naphthacene. The dehydration occurs slowly on boiling an alcoholic solution of the substance, and it is completed within a few seconds if a trace of mineral acid is added. This is a good way of preparing pure naphthacene.

Dihydronaphthacene, **VIII.**—A good method of preparing this substance consists in reducing naphthacenequinone with zinc dust and alcoholic alkali in exactly the manner described above, with the exception that the heating is continued for six hours. Water is added to the now pale yellow solution and the product is extracted from the zinc with benzene. The purified material was yellow and melted at 207°. Like Gabriel and Leupold,[3] I was unable to remove the colored impurity.

Naphthacene.—This hydrocarbon was obtained both from 2,3-benz-9,10-dihydro-anthranol and by the zinc dust distillation of 2,3-tetralanthraquinone. The zinc serves to hydrogenate one part of the molecule, while it dehydrogenates another part.

One gram of 2,3-tetral-anthraquinone was dissolved in benzene in a small distilling flask and treated with 50 g. of zinc dust. After evaporation of the benzene, a further 25 g. of zinc dust was added and the flask was strongly heated. The distillate (0.5 g.) crystallized from tetrachloroethane, forming orange plates melting at 331°; it was identical with naphthacene.

Di-(2,3-benz-9-anthronyl) Ether, X.—This compound first made its appearance when a mixture of naphthacenequinone and naphthanthraquinone was being separated by vatting the latter compound with alkaline hyposulfite solution. Naphthacenequinone does not vat in the usual way, but as a result of the repeated treatment with hyposulfite, a small portion of the material was converted into the new ether. The substance concentrated in the mother liquors from the crystallization of the naphthacenequinone from glacial acetic acid. It was later found that the substance is produced in good yield when a very weakly alkaline solution of 2,3-benz-9-anthrone in alcohol is boiled for about one week in an atmosphere of nitrogen in a three-necked flask carrying rubber stoppers. The observation that the anthrone solution is perfectly stable when boiled in an all-glass apparatus led me to suspect that the observed reaction is an oxidation brought about by the sulfur in the stoppers. This was confirmed by experiment, and a suitable method of preparation thus became available.

Three grams of 2,3-benz-9-anthrone was dissolved in 450 cc. of alcohol, the solution was swept free of oxygen, and 1 g. of sulfur was added. A few drops of alkali were added to produce a purple solution, and more was added later to maintain a weakly alkaline solution. Crystals of the ether soon began to deposit on the walls of the flask and the reaction was complete in about three hours. The product was collected from the hot solution, which was very dark in color, and smelled of hydrogen sulfide. The material so prepared was very nearly pure; yield, 2 g.

The ether is very sparingly soluble in alcohol or benzene. It is very soluble in chloroform, but dissolves quite slowly. It may be purified by dissolving in chloroform, concentrating the solution and precipitating the product with petroleum ether. Good crystals are formed from glacial acetic acid, though the substance dissolves very slowly in this solvent and crystallizes only after considerable concentration. Thus naphthacenequinone, which crystallizes first from a mixture with the ether, can be dissolved out of such a mixture with glacial acetic acid, without dissolving the ether. The latter substance also crystallizes well from pyridine, in which it is very soluble. The ether forms small, salmon-colored plates melting at 295°. Crystals from chloroform are colorless, but acquire the above color on drying. A characteristic property of the ether is its color in concentrated sulfuric acid. The cold solution is bright red; on standing, or on gentle heating, it changes to an intense, pure blue.

Anal. Calcd. for $C_{36}H_{22}O_3$: C, 86.03; H, 4.42. Found: C, 86.03, 86.22; H, 4.79, 4.50. *Mol. Weight.* Calcd.: 502.2. Found (Rast): 498,496.

In the modified Zerewitinoff "machine" of Kohler[11] the substance showed no active hydrogen atoms, but added well over one mole of Grignard reagent in five minutes, even though it did not completely dissolve. The ether is converted quantitatively into naphthacenequinone by chromic acid, or into 2,3-benz-9-anthrone by tin and glacial acetic acid.

The relationship of the ether to 2,3-benz-9-hydroxyanthrone was established by the following experiment. To a suspension of 0.6 g. of the latter compound in 5 cc. of acetic anhydride a drop of concentrated sulfuric acid was added. The material rapidly dissolved to give a dark brown solution and crystals of the ether soon began to separate. After heating for one-half hour on the steam-bath, the product was collected and purified. It formed the characteristic salmon-colored plates melting at 295°, and was identical with the material prepared previously.

The Properties **of Naphthacenehydroquinone (II).**—This substance is the primary reduction product of naphthacenequinone in acid or alcoholic alkaline medium, and it imparts a red color to the solvent in either case. The solution in alcoholic alkali is deep blood-red; the alcoholic or glacial acetic acid solution is only slightly brighter. The action of zinc dust and acetic acid on naphthacenequinone produces only an eosin-red solution, because the hydroquinone is reduced further nearly as rapidly as it is formed, but by the substitution of tin for zinc a solution can be obtained which approaches in intensity the usual anthraquinone vat color. Because of its sensitivity to further reduction, solutions of the hydroquinone are best prepared from its diacetate or from its ketonic modification, though in neither case is it possible to prepare an unquestionably

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[11] Kohler and collaborators, THIS JOURNAL, 49,3181 (1927); 51,3736 (1930).

pure solution, for the substance very readily undergoes a disproportionation. The reaction is best described by quoting a few experiments.

A suspension of 0.5 g. of naphthacenehydroquinone diacetate in 150 cc. of alcohol was boiled in an all-glass apparatus in an atmosphere of nitrogen and then cooled to room temperature, when only a part of the material remained in solution (yellow). On adding 15 cc. of 6 N sodium hydroxide the solution became deep green. In a few seconds this changed to blue and this as rapidly changed to reddish-purple. On warming, the solution became deep red. These striking color changes are interpreted as follows. The blue solution probably contains the monoacetate, which is a derivative of 2,3-benz-9-anthranol and which might well exhibit a similar color. The final red color is without doubt due to the presence of the hydroquinone salt or ion. The green and purple solutions thus represent mixtures of the diacetate and monoacetate and of the monoacetate and the hydroquinone. The red color was not permanent but changed in the course of three to four days (at the boiling point) to the intense purple characteristic of solutions of the anthranol. When this solution was acidified, it became pale yellow at once and it was found to contain naphthacenequinone and the corresponding anthrone. The experiment shows that disproportionation of the hydroquinone takes place slowly in strongly alkaline solution.

In another experiment the diacetate was hydrolyzed in exactly the same manner, but as soon as the solution reached the pure red stage (five minutes) it was acidified with an excess of hydrochloric acid. The color changed from the deep, vat red to a less intense, bright red. This rapidly faded and in fifteen minutes it had become pure yellow. The alcoholic solution was found to contain about equal parts of naphthacenequinone and the anthrone. This shows that the disproportionation of the hydroquinone takes place much more rapidly in acid than in alkaline solution. The fading of the red solution of the hydroquinone as the result of the disproportionation was less rapid in the presence of acetic acid.

When a much smaller amount of alkali (1–2 cc.) was used to hydrolyze the diacetate (0.5 g.) in alcoholic suspension, the solution became green, then blue and finally purple, and the red color characteristic of the anthrahydroquinone was never reached. The acidified solution was only faintly pink and it contained the usual products of oxidation and reduction. The conclusion drawn from this observation is that the disproportionation occurs as rapidly in a weakly alkaline solution as in the presence of acids. The anthrahydroquinone disappears about as rapidly as it is produced by hydrolysis.

The benz-anthrahydroquinone may also be produced in solution by the enolization of 2.3-benz-9-hydroxyanthrone by alcoholic alkali, but the process is so slow that some of the material is probably destroyed by disproportionation during the period required. Thus when a boiling solution of 0.5 g. of the material in 150 cc. of alcohol was treated with 15 cc. of 6 N sodium hydroxide, the solution became deep brown and only acquired the intensely red color after one and one-half hours. On adding hydrochloric acid, the bright red solution which rapidly changes to yellow was again obtained. An observation for which I cannot account is that the addition of a few drops of alkali to an alcoholic solution of the hydroxy-anthrone produces at once a light red solution, while with a large amount of alkali the solution changes from red to brown to red only slowly. The light red solution can hardly contain a large amount of the anthrahydroquinone, because it undergoes disproportionation only after several days.

Summary

A satisfactory method of preparing naphthacenequinone consists in the dehydrogenation of 2,3-tetralanthraquinone with bromine. By choosing suitable reagents and conditions, naphthacenequinone may be converted

in good yield into any one of the following reduction products: the keto form of the hydroquinone, the anthrone, a di-anthronyl ether, the dihydroanthranol, naphthacene or dihydronaphthacene. Naphthacenehydroquinone, known only in solution or in the form of derivatives, is a remarkably unstable substance. It may be reduced with great ease, it ketonizes readily and it also undergoes a disproportionation.

All of the naphthacene derivatives which have a completely aromatic structure show a marked tendency to pass into derivatives of dihydronaphthacene. This is interpreted in terms of the ortho quinonoid structure for anthracene. The theory of bivalent radical formation is also discussed.

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THE PREPARATION AND SOME PROPERTIES OF THE CHLOROMANDELIC ACIDS, THEIR METHYL ESTERS AND AMIDES

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In connection with another research[2] some derivatives of the chloromandelic acids were desired. Apparently only the ortho[3] and para[4] acids and the para[5] amide have been described heretofore. It was thus decided to prepare the three acids with the corresponding methyl esters and amides.

The method of Karrer,[3] in which o-chloromandelic acid was obtained from the aldehyde through the cyanohydrin, was employed. Certain modifications described in the experimental part, however, greatly increased the yield. For the esterification the method of Fischer and Speier[6] was employed. The amides were obtained by treating alcoholic ether solutions of the esters with anhydrous ammonia. The reactions are

$$ClC_6H_4CHO \xrightarrow{HCN} ClC_6H_4CHOHCN \xrightarrow{H_2O} ClC_6H_4CHOHCOOH \xrightarrow{CH_3OH}$$

$$ClC_6H_4CHOHCOOCH_3 \xrightarrow{NH_3} ClC_6H_4CHOHCONH_2$$

Experimental

Preparation of **the** Chloromandelic Acids.—Into a 500-cc. Claisen flask standing in an ice-bath were placed 100 g. of the chlorobenzaldehyde, 48 g. of 96–98% potassium

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[1] Grafflin Scholar, 1930–1931.

[2] To be published.

[3] Karrer, *Helv. Chim. Acta*, *4*, 144 (1921).

[4] Collet, Bull. *soc. chim.*, [3] *21*, 70 (1899); Straus, Ann., **393**, 320 (1912).

[5] Rule, J. *Chem. Soc.*, **113**, 17 (1918).

[6] Fischer and Speier, *Ber.*, 28, 3252 (1895).

TABLE I

PROPERTIES OF THE CHLOROMANDELIC ACIDS, METHYL ESTERS AND AMIDES

	Best solvent for crystallization	M. p., °C. (corr.)	Appearance	Soly. in 100 cc. of benzene at 22°, g.
Ortho acid	Bz–pet. ether (10:1)	85–85.5"	Needles	0.877
Meta acid	Benzene	115–115.5	Rosets of short needles	.271
Para acid	Benzene	120.5–121[b]	Short needles	.470
Ortho methyl ester		B. p. 134–136° (6 mm.)	Colorless viscous liquid	
Meta methyl ester	Bz–pet. ether (4:1)	84	Tufts of small needles	
Para methyl ester	Bz–pet. ether (2:1)	55.6	Tufts of small short needles	
Ortho amide	Benzene	87.5	Plates	.244
Meta amide	Benzene	126.5	Scales	.021
Para amide	Benzene	125.5[c]	Plates	.044

[a] Karrer,[3] 84–85°. [b] Collet,[4] 112–113°; Straus,[4] 119–120°. [c] Rule,[5] 122–123°.

cyanide, finely powdered, and 150 cc. of ether. Seventy-five cc. of concentrated hydrochloric acid was added from a dropping funnel during forty-five minutes, while the solution was being rapidly stirred mechanically. The ice-bath was removed after thirty minutes more and the stirring continued for two hours longer at room temperature. Since cyanohydrins, in general, are unstable, no attempt was made to isolate them. The ether solution containing the nitrile was decanted from the potassium chloride directly into 500 cc. of concentrated hydrochloric acid. The acid mixture was heated on a boiling water-bath for five hours with vigorous mechanical stirring. The cooled solution was made slightly alkaline with 30% sodium hydroxide and extracted twice with 150-cc. portions of ether to remove unchanged material. The purified solution of sodium chloromandelate was then treated wth 75 cc. of concentrated hydrochloric acid and again extracted twice with 150-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate after which the ether was distilled and the crude chloromandelic acid recrystallized from benzene. (See Table II for yields and analytical data.)

The ortho and para chlorobenzaldehydes used in this work were purchased from the Eastman Kodak Company, the former being the practical grade. The *m*-chlorobenzaldehyde was prepared from m-nitrobenzaldehyde according to the method of Erdmann and Schwechten.[7]

Preparation of the Methyl Esters.[6]—Fifty grams of acid, 300 cc. of absolute methyl alcohol and 15 cc. of concentrated sulfuric acid were refluxed for five hours, after which 225 cc. of the alcohol was distilled off. The remaining liquid was made slightly alkaline with 10% sodium carbonate solution and extracted twice with 100-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate and the ester obtained by distilling off the ether.

The ortho ester was purified by fractionation *in vacuo* since it could not be induced to crystallize. The meta and para esters were obtained pure by crystallization from benzene–petroleum ether (b. p. 30–60°) solution.

Preparation of the Chloromandelamides.—The amides were prepared by dissolving 25 g. of the esters in 50 cc. each of anhydrous ether and absolute alcohol. The solution

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[7] Erdmann und Schwechten, Ann., 260, 53 (1890).

was cooled to 0° and treated with anhydrous ammonia for ten hours At the expiration of this time most of the amide had crystallized out. The alcohol and ether were evaporated under reduced pressure, after which the amide was pulverized and washed with ether. This treatment gave a product sufficiently pure for most purposes. The pure amides were obtained by recrystallization from benzene.

TABLE II

YIELDS AND ANALYTICAL DATA

Chloromandelic acid	Yield, %	Analysis Calcd. Cl, 19.01% Found (Parr bomb), Cl	 Calcd. neut. equiv., 188.5 Found
Ortho	41[a]	19.03	186.3
Meta	67	19.30	184.9
Para	82	19.28	187.6
Ester		Calcd., Cl, 17.68% Found (Parr bomb), Cl	Calcd. ester no.. 279.7 Found
Ortho	85	17.83	280.9
Meta	95	17.49	279.5
Para	83	17.87	280.9
Amide		Calcd. Cl, 19.11% Found (Parr bomb), Cl	Calcd. N, 7.55%
Ortho	90	19.06	7.56
Meta	90	19.19	7.64
Para	90	19.21	7.69

[a] Karrer reported 18 g. of this acid from 50 g. of o-chlorobenzaldehyde or 28%.

In conclusion the writer wishes to thank Dr. E. Emmet Reid for his interest and valuable suggestions.

Summary

1. A convenient method for the preparation of the monochloromandelic acids has been described.
2. The complete series of acids, methyl esters and amides was obtained and some properties of these compounds are given. Six new compounds were prepared in the course of this work.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE VIRGINIA POLYTECHNIC INSTITUTE]

THE ACTION OF SODIUM ON CELLULOSE IN LIQUID AMMONIA

BY PHILIP C. SCHERER, JR., AND ROBERT E. HUSSEY

RECEIVED APRIL 8, 1931 PUBLISHED JUNE 8, 1931

The action of sodium hydroxide solutions upon cellulose to form a compound of cellulose which has attained commercial importance in the viscose process has long been known.[1] The constitution of the compound formed in this reaction has never been definitely established although, reasoning from analogy with the ordinary alcohols, it has been assumed to be of a sodium alcoholate type in which the hydrogen atom of one, or possibly more, hydroxyl groups is replaced by sodium. Definite proof of such a compound is, however, lacking and the authors in this research have attempted to supply some evidence of it.

Kraus and his students[2] have shown that when an alcohol is treated with sodium in liquid ammonia, a sodium alcoholate results and an atom of hydrogen is liberated according to the general reaction

$$ROH + Na = RONa + \tfrac{1}{2}H_2$$

In applying this general reaction to cellulose several points were investigated. First, the amount of hydrogen obtainable from a definite amount of sodium reacting with cellulose was carefully determined and was found to agree very closely with the above reaction. Second, the final product was examined and found to possess in full the property of normally prepared soda cellulose, of reacting with carbon bisulfide to form xanthates completely soluble in water or alkali. This reaction is treated in more detail in another paper.[3] Third, it was found that there was no appreciable amount of sodium amide formed as a product of the reaction of the sodium with the solvent. The hydrogen evolved in the experiments, then, could only have come from the reaction of the sodium upon the cellulose. Fourth, it was found that one atom of hydrogen per $C_6H_{10}O_5$ group was rapidly and easily displaced. The succeeding atoms of sodium entered very slowly, due possibly to the formation of a film of rather insoluble soda cellulose about the fibers. This slower rate of reaction might also be due to lesser affinity of the secondary alcohol groups for the sodium or to an overloading of the molecule with such a strongly positive atom as sodium. No matter in what excess nor for how long a time such an excess of sodium was allowed to react upon cellulose, no more than three atoms of sodium per $C_6H_{10}O_5$ group could be introduced into the molecule. This reaffirms

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[1] Cross and Bevan, *Chem. News*, 63, 66 (1891).

[2] Kraus and White, THIS JOURNAL, 45, 768 (1923).

[3] Hussey and Scherer, "Rate of Reaction between Carbon Disulfide and Soda Cellulose."

previous evidence from acetylation and nitration of the presence of only three hydroxyl groups per $C_6H_{10}O_5$ group.

A consideration of the above described results leads to the conclusion that cellulose reacts in liquid ammonia as a typical tribasic alcohol and that, by analogy, the product of its reaction with solutions of caustic soda is probably sodium cellulose alcoholate. The number of hydroxyl groups so converted by sodium hydroxide solution probably depends upon the conditions of the reaction. Soda cellulose prepared by the action of metallic sodium in liquid ammonia is being used in this Laboratory as a material for an investigation of its reactions with other reagents.

Experimental Part

Apparatus.—As indicated in the sketch, the reaction tube consisted of a Pyrex glass test-tube (A), 32 by 300 mm., immersed in a Dewar tube (B) containing liquid ammonia boiling at atmospheric pressure. Tube (C) which passed through the rubber stopper of the reaction tube was a T tube in which the sodium to be added could be suspended by means of the movable rod (D). This tube also served to connect the reaction vessel to either the manometer (F) or the eudiometer (G) through the two-way stopcock (E). The manometer served as a mercury seal to the apparatus and to supply the pressure necessary to condense ammonia in (A). The hydrogen evolved was collected over water in order to remove the gaseous ammonia.

The ammonia was dried by passing over fused potassium hydroxide in the two towers (K) and then through a tube (J) packed with carefully dried Bentonite and the train was kept free of moisture and air by the mercury seals (I).

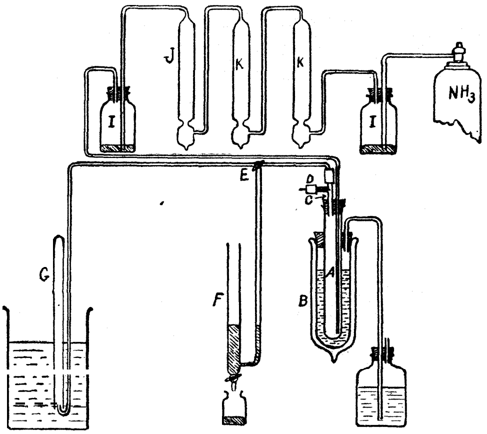

Fig. 1.

Procedure and Materials.—In order to prove the absence of water in the condensed and gaseous ammonia, about 50 cc. of ammonia from the train was condensed in **(A)** and 0.1 g. of freshly cut sodium was suspended in tube (D). After all gases had been blown out by a rapid current of ammonia, the sodium was dropped into the condensed ammonia. Absolutely no hydrogen was collected even after several hours.

The sodium used in the experiments was freshly cut under low boiling petroleum ether, weighed in Nujol, washed carefully in petroleum ether and then introduced into tube (D).

The cellulose used in these experiments was of three types. The first was a standard cellulose prepared from absorbent cotton according to the method described by Corey and Gray.[4] This contained 98.7% alpha cellulose and 0.10% ash.

The wood pulp cellulose was prepared by finely dividing and carefully drying Brown Company alpha pulp containing 94.67% alpha cellulose and 0.136% ash.

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[4] Corey and Gray, *Ind. Eng. Chem.*, 16, **853** (1924).

The regenerated cellulose used was prepared by finely dividing and carefully drying bleached and desulfurized viscose rayon prepared from Brown Company alpha pulp.

In all the experiments a sample of cellulose, accurately weighed in a weighing bottle, was placed in the reaction tube and about 50 cc. of ammonia condensed on it under a pressure of about 15 cm. of mercury in the manometer. The pressure was released by running mercury from the manometer and, with a rapid stream of ammonia passing, the tube (D) was opened and the weighed sodium suspended therein. The tube was closed and the apparatus was freed of traces of air and petroleum ether by a current of ammonia. By means of the two-way stopcock the apparatus was connected to the eudiometer and the sodium was dropped into the reaction vessel. A vigorous reaction ensued which was timed from the first addition of the sodium to the disappearance of all trace of the characteristic blue color of free sodium. After careful sweeping, the collected gas was measured and analyzed.

The residue in the reaction tube was allowed to settle and was washed several times by condensation of fresh portions of ammonia upon it. The liquid was removed each time by suction and evaporated under reduced pressure. After warming to drive out ammonia, the infinitesimal residue was dissolved in water and was of sufficient alkalinity to turn phenolphthalein. One drop of $N/10$ sulfuric acid was sufficient to turn the solution acid and it was concluded that no sodium amide resulted from the reaction The cellulosic residue, as described in another paper,[1] gave typical xanthates.

Results

The results were compiled into tables for ease of comparison and are given herewith.

EXPERIMENTS WITH STANDARD CELLULOSE

Ratio cellulose/sodium	Cell, g.	Sodium, g.	Time, min.	Atoms of H_2 per atom of sodium
1:0.228	1.8432	0.0596	4	0.983
1:0.504	0.4215	.0299	3	1.049
1:0.750	.6868	.0731	13	1.022
1.1.000	.3556	.0505	...	1.020
1:0.984	.4408	.0616	7	1.019
1:1.24	.4208	.0741	28	1.002
1:1.25	.3520	.0625	35	0.991
1:1.50	.3045	.0650	90	.974
1:2.03	.2381	.0682	240	.919
1:2.99	.1420	.0603	200	.960
I: excess	.2476	.1977	420	2.979[a]

EXPERIMENTS WITH WOOD PULP CELLULOSE

Ratio cellulose/sodium	Cell, g.	Sodium, g.	Time, min.	Atoms of H_2 per atom of sodium
1:0.250	1.6243	0.0577	2	0.983
1:0.494	0.7712	.0544	...	.997
1:0.760	.7414	.0800	4	.962
1:0.949	.7054	.0950	5	1.003
1:0.990	.5284	.0743	9	0.990
1:1.23	.3533	.0617	...	.958
1:1.47	.2471	.0515	...	1.044
1:1.68	.3393	.0809	...	0.993
1:1.99	.1948	.0551	120	.934
1:3.00	.1608	.0686	137	.963
1: excess	.1518	.1288	337	3.050[a]

EXPERIMENTS WITH REGENERATED CELLULOSE

Ratio cellulose/sodium	Cell, g.	Sodium, g.	Time, mm.	Atoms of H_2 per atom of sodium
1:0 250	1.8262	0.0648	...	1.000
1:0.496	0.8726	.0615	2	1.003
1.0 832	.4995	.0531	...	1.035
1:1 01	.4496	.0644	5	1.005
1:1 50	.2761	.0587	24	1.013
1:1.97	.1815	.0508	30	1.014
1:2 47	.1976	0692	113	0.961
1:2 93	.1358	.0564	150	.925
1:excess	.2532	.2310	240	2.949[a]
			General average	0.990

[a] These values give the atoms of hydrogen replaced per $C_6H_{10}O_5$ group, the general average of which is 2.993 atoms.

Summary

1. The action of metallic sodium on cellulose in liquid ammonia has been studied.

2. One atom of sodium enters the molecule rapidly, whereas the second and third enter very slowly.

3. A maximum of three atoms of sodium per $C_6H_{10}O_5$ group enters the molecule.

4. The reaction corresponds in general to the ordinary alcoholate reaction, ROH + Na = RONa + $\frac{1}{2}H_2$.

3. It is concluded that cellulose acts as an alcohol in liquid ammonia and probably does so in its other reactions in other solvents.

BLACKSBURG, VIRGINIA

[JOINT CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, AND MICROANALYTICAL LABORATORY, FOOD AND DRUG ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE IDENTIFICATION OF MESACONIC ACID[1]

BY H. H. MOTTERN AND G. L. KEENAN

RECEIVED APRIL 9, 1931 PUBLISHED JUNE 8, 1931

During an investigation of the occurrence of organic acids in plant material, interest was aroused in the true melting point of mesaconic acid, and also in the preparation and physical and chemical properties of some new derivatives which might prove useful in its identification. Of the derivatives commonly used, the amide is the only one which previously has been reported, but since the hydrazide is the most easily prepared, when the ester is available, it has been the derivative most commonly used in this Laboratory for the identification of naturally occurring organic acids.

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[1] Food Research Division Contribution No. 103.

Mesaconic acid and two of its derivatives, the hydrazide and *p*-nitrobenzyl mesaconate, being definitely crystalline, readily lend themselves to a microscopical study by the optical immersion method. The optical data given are of considerable importance in the rapid and accurate identification of small amounts of these substances. They have not been reported heretofore.

Experimental

Mesaconic Acid.—Mesaconic acid was prepared from citraconic anhydride by the method of Fittig.[2] Citric acid was distilled at atmospheric pressure and the oily layer obtained in the distillate was separated from the aqueous layer and redistilled; 40 g. of citraconic anhydride thus obtained was dissolved in 80 cc. of water containing 12 cc. of concentrated nitric acid, and the solution was boiled until fumes of nitrogen tetroxide appeared. When the solution had cooled, mesaconic acid crystallized out and was separated from the mother liquor by filtration. The acid was purified by recrystallization from water and was dried at 100°. It melted at 204.5° corrected When sublimated in a Hortvet sublimator it showed no change in melting point. Mesaconic acid obtained from Kahlbaum melted at 204°. The melting point is variously stated in the literature to be from 200.5 to 208°, 202° being the most commonly accepted temperature.

The melting points were taken on two different types of melting point apparatus, including the electrically heated apparatus of Sando.3 Anschiitz and Wheeler total immersion thermometers with Bureau of Standards corrections were used. All determinations were by the capillary method and were taken slowly, as the compound does not show any decomposition at this temperature within the ordinary time of taking a melting point. It is concluded therefore that 204.5" represents the melting point of mesaconic acid more closely than any figure previously reported.

Optical Properties.—Mesaconic acid, sublimed, is colorless and rod-like in habit, usually occurring in laminated, fibrous masses. With crossed nicols (parallel polarized light), the rods show parallel extinction, and the elongation is positive or negative. The double refraction apparently is very strong. The minimum index of refraction (immersion method) is considerably less than $n = 1.445$. The acid is soluble in all the oily mixtures available. The maximum refractive index (γ) was found to be 1.740 (methylene iodide) but occurs infrequently. The most significant refractive index for the substance is that shown when the elongated crystals are oriented with their long axis parallel to the vibration plane of the lower nicol. In this position the rods frequently match a liquid with $n = 1.690$ (apparently the β-value). This liquid is most useful for determinative purposes since the intermediate value occurs so frequently and is always shown lengthwise on the rods. The liquid used for this purpose consisted of a mixture of monochloronaphthalene and methylene iodide in proportions to give the refractive index desired.

A sample of mesaconic acid obtained from Kahlbaum, and one prepared from citric acid showed the same optical constants as the sublimed material.

Diethyl Mesaconate.—Fifteen grams of mesaconic acid prepared as previously described was refluxed for eighteen hours on a steam-bath with 300 cc. of absolute alcohol containing 2% of dry hydrogen chloride. The alcohol was then distilled off and the ester was dissolved in ether and washed in a separatory funnel with dilute sodium hydroxide solution until the wash water remained alkaline, then dried with anhydrous

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[2] R. Fittig, ***Ann.***, 188, 73 (1877).

[3] C. E. Sando, Ind. ***Eng. Chem., Anal. Ed.*, 3**, 65 (1931).

sodium sulfate. The ether was distilled off and the ester distilled under reduced pressure. The diethyl mesaconate so obtained boiled at 93–95° under 10 mm. pressure. The boiling point under reduced pressure has not been previously reported.

Mesaconic **Hydrazide.**—The hydrazide of mesaconic acid was prepared from the ester as follows. One cc. of 42% hydrazine hydrate in water was added to a solution of 0.7 g. of the ester in 5 cc. of absolute alcohol. After standing overnight the hydrazide crystallized out in the form of clear. glassy rods. It was soluble in water and insoluble in alcohol. On recrystallization from dilute alcohol the hydrazide melted with decomposition at 217–218°, corrected.

Anal. Subs., 0.0982, 0.0969: CO_2, 0 1377, 0.1866; H_2O, 0.0550, 0.0560 Subs., 0.0438, 0.0435: N, 0.0157, 0.0157. Caled. for $C_5H_{10}N_4O_2$: C, 37.96; H, 6.37; N, 35.43. Found: C, 38.25, 38.18; H, 6.27, 6.47; N, 35.85, 36.09.

Optical Properties.—When examined at a magnification of 15 diameters, mesaconic hydrazide, crystallized from dilute alcohol, is seen to consist of clear, glassy rods. For microscopical examination by the immersion method, the substance is pulverized into a fine powder, producing irregular fragments. When examined with crossed nicols (parallel polarized light), most of the fragments extinguish sharply and show colors of first and second order. Occasionally fragments occur which do not extinguish sharply, remaining essentially bright when the stage is rotated, and showing a partial biaxial interference figure with the optic axis up when the material is examined in convergent polarized light (crossed nicols). The refractive indices are: n_α 1.583; n_β 1.610; n_γ 1.680; all ±0.003.

p-Nitrobenzyl Mesaconate.—The p-nitrobenzyl ester of mesaconic acid was prepared by the method of Reid.[4] On recrystallization from dilute alcohol it melted sharply at 134° corrected.

Optical Properties.—p-Nitrobenzyl mesaconate crystallizes in rods and plates. With crossed nicols, the extinction is parallel and the elongation negative. The refractive indices are $n_\alpha = 1.610$, occurring frequently lengthwise on rods; $n_\beta = 1.627$, frequently shown crosswise on rods; $n_\gamma = 1.680$, also shown crosswise on rods but not as common as α and β; all ±0.003. In identifying the substance by the optical immersion method, the ***a***- and ,!?-values are very useful.

Summary

The capillary melting point of mesaconic acid was found to be 204.5". The ethyl ester boiled at 93–95' at 10 mm. The melting point of the hydrazide is 217–218°, and of the p-nitrobenzyl ester, 134". Both the hydrazide and the p-nitrobenzyl ester were found to be satisfactory derivatives for the purpose of identification, but the hydrazide is the more easily prepared, if the ester is available. Optical crystallographic data for the acid and two of the derivatives are given.

WASHINGTON, D. C.

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[4] E. E. Reid, THIS JOURNAL, 39,124 (1917)

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS. V. REVERSIBILITY OF THE BENZOIN CONDENSATION AND THE PREPARATION OF MIXED FROM SIMPLE BENZOINS

BY JOHANNES S. BUCK AND WALTER S. IDE

RECEIVED APRIL 9, 1931 PUBLISHED JUNE 8, 1931

Much work has been done on the benzoin condensation and various suggestions have been advanced as to its mechanism, but it can scarcely be said that the reversibility of the reaction has been demonstrated in an unexceptionable manner. Much of the work is irrelevant as it was carried out under conditions far different from those ordinarily used. For example, the heating of the dry reagents to high temperatures can scarcely be called a benzoin reaction. In most cases where the conditions were comparable, benzaldehyde was estimated by difference, or detected by the odor, a risky procedure where many side-products may be formed. Another factor apparently not recognized by earlier workers is what may be called the eccentricity of the reaction, that is, the occasional rapid and unusually favorable progress of the reaction. An instance is remarked by Adams[1] and the present authors have frequently encountered similar cases. No explanation for this phenomenon can be offered at present.

The best yields recorded for benzoin itself are about 90%, the other 10% being accounted for as unchanged benzaldehyde and side-products such as mandelic acid, benzoic acid, benzyl alcohol, toluylene hydrate, amarine, etc. In the equation $2C_6H_5CHO \longleftrightarrow C_6H_5CHOHCOC_6H_5$ it is evident that the equilibrium lies well over to the right. A means of removing benzaldehyde as generated would enable the right-to-left reaction to be demonstrated clearly. Such a means was found by adding a second aldehyde to the solution of benzoin in aqueous alcoholic potassium cyanide, whereby a mixed benzoin was formed. In a number of cases this mixed benzoin could be isolated and identified.[2] The equation is

$$C_6H_5CHOHCOC_6H_5 + 2XC_6H_4CHO = 2C_6H_5CHOHCOC_6H_4X$$

Specifically, benzoin and *p*-dimethylaminobenzaldehyde, refluxed in aqueous-alcoholic solution, in the presence of potassium cyanide, gave an excellent yield of *p*-dimethylaminobenzoin, proving beyond doubt that the benzoin had broken up into benzaldehyde. Piperoin and furoin were found to behave similarly. In the case of anisoin, no mixed benzoin was

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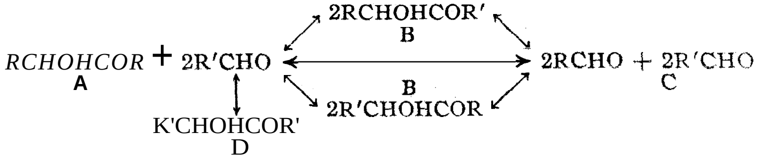
[1] Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 34.

[2] Hörbye, "Dissertation," Dresden, 1917, seems to have had a similar idea in mind. He heated benzoin with anisaldehyde and anisoin with benzaldehyde (no cyanide was used) and obtained only negative results.

obtained, but a portion of the anisoin was recovered, even after ample refluxing.

Having proved that a benzoin may give rise to the corresponding aldehyde, the scheme shown for the formation and equilibrium of a mixed benzoin follows logically



In previous work, the authors have obtained the mixed benzoin B by going from C to B. In the present work, the benzoin B is obtained by the route A to B. It would be of interest to compare these two routes from a strictly quantitative point of view, but the practical difficulties in the way are formidable.

The above scheme carries several interesting implications. A mixed benzoin, in the presence of aqueous-alcoholic potassium cyanide, should give rise to a mixture containing the two corresponding simple benzoins. In the presence of added aldehydes, further mixed benzoins would be formed. Similarly, a mixture of two simple benzoins should be capable of giving rise to mixed benzoins. There is also a possibility that a given mixed benzoin, in aqueous-alcoholic potassium cyanide solution, might change into its isomer, but this would only be expected in the sense of the less stable isomer changing into the more stable isomer. Work is in progress on some of these possibilities, but it is not to be expected that more than a few instances of each type will be found, on account of experimental difficulties. It is evident that unless one particular product is uncommonly favored by conditions such as yield, solubility, crystallizing tendency, etc., its isolation from a complex reaction mixture would be impossible—at least, provided that it contained no special groups such as $-NMe_2$. The same considerations make it evident why comparatively few mixed benzoins are isolable from the usual condensation mixtures.

Ideally, the same point should be reached (using appropriate molecular proportions) by starting with (a) two aldehydes X and Y, (b) aldehyde X with the benzoin from Y, (c) aldehyde Y with the benzoin from X, (d) the benzoin from X with the benzoin from Y, (e) either of the isomeric mixed benzoins from X and Y. It is improbable that this can be demonstrated for several reasons, such as the formation of side products, the instability of certain aldehydes (*e.* g., furfural), the inability of an aldehyde to form a simple benzoin (*e.* g., *p*-dimethylaminobenzaldehyde) or the impossibility of isolating the simple benzoin (*e.* g., veratroin), and the difference in stability of any two isomeric mixed benzoins.

The method under discussion (the preparation of a mixed from a simple benzoin) does not appear to offer any marked advantages over the older method, starting with two aldehydes. It is also limited by the non-existence of many simple benzoins.

The authors have refrained from discussing the various hypotheses of benzoin formation given in the literature. Lachman[3] gives a review of this field.

Experimental

The experimental conditions were chosen so that the reactions took place under conditions approximating those of the usual benzoin condensation. One mole of the benzoin and two moles of the aldehyde were dissolved hot in the given volume of alcohol and the potassium cyanide added in saturated aqueous solution. The mixture was then boiled under a reflux condenser on the steam-bath, **5** cc. of water being added as soon as boiling commenced. After the elapse of the stated time, the flask was removed and cooled, alcohol or water added as required, and the mixture kept in a cold place. With manipulation and attention, the product crystallizes out in time. A second or third crop may sometimes be obtained by diluting the liquors or by adding further potassium cyanide and again refluxing. The yields are given for unrecrystallized but washed material of good grade. For identification, this was recrystallized and compared with an authentic specimen. Mixed melting point determinations also were made. Experiments carried out with anisoin and different aldehydes resulted in the recovery of part of the anisoin. Mixed benzoins, which were doubtless formed, were not isolated. **A** peculiar product was obtained from anisoin and piperoin. This appears to be a double compound of anisoin and piperoin, since it can be obtained by simply crystallizing anisoin with piperoin from alcohol. Analysis so far has not given concordant results, but the crystalline form, melting point, etc., of the product are distinct from those of the components.

p-Dimethylaminobenzpiperoin, not previously described, may be obtained as given in the table, or, more conveniently, by refluxing for two hours, **6.00** *g*. of piperonal and 5.96 g. of p-dimethylaminobenzaldehyde, dissolved together in **30** cc. alcohol, with **4.0** g. of potassium cyanide (added in saturated aqueous solution). The crystalline mass which separates is filtered off after three days and recrystallized from alcohol. The compound forms a dull-white mass of tiny fern-like crystals. It is moderately soluble in alcohol, soluble in cold acetic acid, cold dilute (1:1) hydrochloric acid, cold acetone and cold chloroform; readily soluble in warm benzene, and soluble in cold concd. sulfuric acid to an intense blackish-crimson solution. The benzoin melts at 132° to a turbid liquid, clear at **136°**.

Anal. Calcd. for $C_{17}H_{17}O_4N$: **C, 68.19; H, 5.73; N, 4.68.** Found: **C, 68.47; H, 5.92; N, 4.77.**

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[3] **Lachman, This** Journal, 46, **708 (1924).**

TABLE I

PREPARATIONAL DATA

Benzoin	Taken, g	Aldehyde	Taken, g.	Product	Yield, g.	KCN, g.	Hours heating	Cc of alcohol
Benzoin	4.24	Dimethylaminobenz-	5 96	Dimethylaminobenzoin[4]	9 18	3 0	3 0	20
Benzoin	4 24	Anis-	5 44	Benzanisoin[5]	7.36	4 0	2 0	20
Benzoin	4 24	Furfural	3 84	Benzfuroin[5]	398	3.0	1 5	20
Benzoin	4.24	Piperonal	6.00	Benzpiperoin[2]	2 16	2.0	0 5	30
Piperoin	3 00	Dimethylaminobenz-	2 98	Dimethylaminobenzpiperoin	2 12	2 0	3.0	15
Piperoin	3 00	o-Chlorobenz-	2 82	o-Chlorobenzpiperoin[5]	205	2.0	3 0	15
Piperoin	6 00	Benz-	4 24	Benzpiperoin[2]	1.29	4.0	2.0	30
Furoin	3 84	Dimethylaminobenz-	5 96	Dimethylaminobenzfuroin[6]	5 77	3 0	1	20
Furoin	3 84	Benz-	4 24	Benzfuroin[5]	4 06	2 0	0.16	20

[4] Staudinger, Ber., 46, 3535 (1913).

[5] Fischer, *Ann.*, 211, 214 (1882).

[6] Buck and Ide, THIS JOURNAL, 52,220 (1930).

Summary

A general method for demonstrating the reversibility of the benzoin condensation is described, involving the preparation of mixed benzoins from simple benzoins. Some of the consequences of the reversibility are discussed. A new mixed benzoin is described.

TUCKAHOE, NEW YORK

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

STEREOCHEMISTRY OF N,N′-DIPYRRYLS. RESOLUTION OF N,N′,2,5,2′,5′-TETRAMETHYL-3,3′-DICARBOXYDIPYRRYL. XVI[1]

BY CHIN CHANG[2] AND ROGER ADAMS

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The resolution of N,2-carboxyphenyl-2,5-dimethyl-3-carboxypyrrole[1b] (I) demonstrated that optical isomerism which was possible in properly substituted diphenyls, due presumably to restricted rotation of the rings, may also occur in substituted N-phenylpyrroles. This indicates the probability of optical isomerism in other dicyclic compounds such as in properly substituted dipyrryls. The more important general types of this class of compounds which from analogy to the diphenyls might exhibit isomerism may be represented by the Formulas II, III, IV.

The investigation described in this communication has involved the

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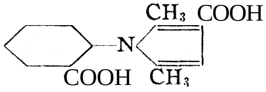
[1] For the previous papers in this series see (a) Shildneck and Adams, THIS JOURNAL, 53, 343 (1931); (b) Bock and Adams, *ibid.*, 53,374 (1931)

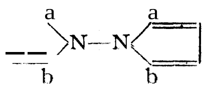
[2] This communication is an abstract of a portion of a thesis submitted by Chin Chang in partial fulfilment of the requirements for the degree of Doctor of Philosophy in chemistry.

preparation and resolution of a N,N′-dipyrryl of type III, namely, N,N′-2,5,2′,5′-tetramethyl-3,3′-dicarboxydipyrryl, the two enantiomorphs of which might be represented by Formulas V and VI.

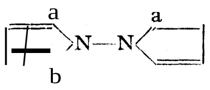
These are written as if the three valences of each nitrogen were in a single plane, upon which assumption the compounds would resemble diphenyl in structure. It is probable, also, that under such conditions restricted rotation in the dipyrryl molecules would conform more or less closely to that of the diphenyl series.



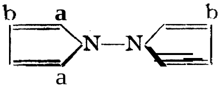
I



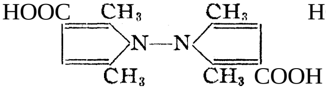
II



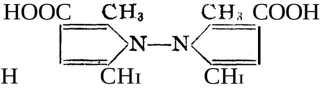
III



IV



V



VI

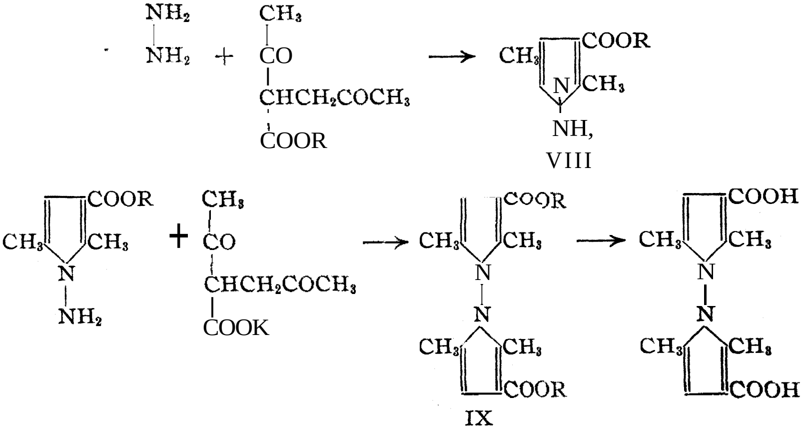
On the other hand, on the assumption of a tetrahedral structure for nitrogen, the geometric structures of the phenylpyrroles and the N,N′-dipyrryls will be quite different from the diphenyls. In the latter compounds there is a single axis for the two rings, but in the phenylpyrroles and the dipyrryls this would not be true. The formula for phenylpyrrole is illustrated by (VII) and a dipyrryl would be of a similar character excepting that the angle between the two pyrrole rings in the molecule would be considerably different from the angle between the benzene and the pyrrole rings in phenylpyrrole. It might well be expected in molecules of these types that other conditions of substitution would affect restricted rotation between the rings. In fact, upon the assumption of a regular tetrahedral structure for the nitrogen atom, it is difficult to see how *ortho* substituted groups in the pyrrole rings of a dipyrryl would interfere with each other at all.

VII

Other possibilities for isomerism may occur in these molecules that do not have a single axis for the two rings. If one ring is unable to rotate on the C–N or the N–N axis to the other side of the second ring, conditions exist which are not possible in the diphenyl series. Whereas in diphenyls the molecules must have restricted rotation between the rings and in addition each ring must be asymmetrically substituted in itself to allow the possibility of mirror images, in a phenylpyrrole or dipyrryl restricted rotation and asymmetry in only one of the rings would be necessary in order to make possible optical activity. Such molecules may readily be produced and some light should thus be thrown on the structures of the phenylpyrroles and dipyrryls from the results of the investigation now under way.

The racemic N,N',2,5,2',5'-tetramethyl-3,3'-dicarboxydipyrryl was readily resolved through the brucine salt arid the two optically active forms (V and VI) obtained in a pure state. They proved to be very resistant to racemization under ordinary conditions. After twenty-four hours of boiling in pyridine no change in rotation occurred. Even after boiling for eighty-four hours in 0.1 *N* sodium hydroxide the racemization was only partial. Insolubility in all ordinary solvents except pyridine limited the study of the ease of racemization.

The compound N,N',2,5,2',5'-tetramethyl-3,3'-dicarboxydipyrryl has already been described by Korschun,[3] who obtained it as a by-product in the condensation of hydrazine with 3-carboxy-2,5-dimethylhexadione in alcohol solution. It was found, however, that it could be produced in quantity more readily by using a slightly different procedure. Hydrazine was first condensed with 3-carboethoxy-2,5-dimethylhexadione in alcohol and acetic acid with the formation of N-amino-2,5-dimethyl-3-carboethoxypyrrole (VIII). This latter substance was then condensed again with 3-carboethoxy-2,5-dimethylhexadione with the formation of the substituted dipyrryl (IX).



Outside of the fact that the dibrucine salt tended to hydrolyze readily in the presence of solvents containing any water, there was nothing unusual to mention in connection with the resolution of this compound into its active forms.

The results of this investigation offer additional evidence that optical isomerism due to restricted rotation between rings may be expected in many, if not in all, heterocyclic and alicyclic types that are semi-aromatic in character where the proper number and kind of groups are substituted in the ortho positions to the linkage between the rings.

[3] Korschun, *Ber.*, **37**, **2183** (1904)

Experimental

N,N′,2,5,2′,5′-Tetramethyl-3,3′-dicarboethoxydipyrryl.—A solution of 15 g. of N-amino-2,5-dimethyl 3-carboethoxypyrrole (Korschun)[3] in 200 cc. of absolute methyl alcohol was heated with 15 g. of 3-carboethoxy-2,5-dimethylhexadione in a 500-cc. flask fitted with a reflux condenser for four hours on a steam-bath. The solvent was then evaporated from the reaction mixture. A thick oily substance was obtained; yield 26 g. (94% of the theoretical).

N,N′,2,5,2′,5′-Tetramethyl-3,3′dicarboxydipyrryl.—A mixture of 26 g. of N,N′,2,5,2′,5′-tetramethyl-3,3′-dicarboethoxydipyrryl with 70 cc. of 10% alcoholic potassium hydroxide was heated for two hours on a steam-bath. Upon acidifying the resulting solution with a little hydrochloric acid, a brownish precipitate was obtained. The product was filtered and washed with water. This was then dissolved in about 400 cc. of absolute methyl alcohol and refluxed for half an hour with 6 g. of decolorizing charcoal. After filtration, sufficient water was added until a precipitate just appeared. Upon standing the dipyrryl separated as a white precipitate which upon drying amounted to 18 g. (84% of the theoretical). It was purified by crystallizing from absolute methyl alcohol until it had a constant melting point of 278–280°.

It is slightly soluble in ethyl acetate, ethyl alcohol, benzene and chloroform and somewhat more soluble in absolute methyl alcohol and acetone.

Anal. Calcd. for $C_{14}H_{16}O_4N_2$: mol. wt., 276; N, 10.11. Found: mol. wt., 279; N, 9.96.

Resolution of **N,N′,2,5,2′,5′-Tetramethyl-3,3′-dicarboxydipyrryl.**—A solution of 20 g. of brucine in 400 cc. of absolute methyl alcohol was heated to its boiling point and 7 g. of powdered N,N′,2,5,2′,5′-tetramethyl-3,3′-dicarboxydipyrryl was added slowly with stirring. After standing for several hours at 0°, the salt which separated was filtered. The first fraction thus obtained which amounted to 12.7 g. was crystallized from absolute methyl alcohol three times until a constant rotation was obtained; melting point 153–157°.

Rotation. d-Salt, 0.1024 g. made up to 25 cc. with pyridine at 20° gave or, —0.60; $l = 2$; $[\alpha]^{20}_{D}$ —73.2.

Anal. Calcd. for $C_{60}H_{68}N_6O_{12}$: N, 7.87. Found: N, 7.76.

The more soluble fraction obtained in solution as a filtrate from the less soluble salt was evaporated part way to dryness and again allowed to cool. Any crystalline material which separated was filtered and consisted of a mixture of the two salts, though primarily of the less soluble. It was necessary to concentrate to dryness before the more soluble salt was obtained. It then separated from the methyl alcohol as a gum which on long standing in a desiccator solidified. It was found impossible to recrystallize this material so that in the crude form a sample was weighed out and a rotation taken. The rotation undoubtedly is not the maximum one for the salt.

Rotation. I-Salt, 0.1550 g. made up to 50 cc. with pyridine at 20° gave a, —0.51; $l = 2$; $[\alpha]^{20}_{D}$ —82.3'.

The I-salt in this crude form melted at 293–304°. It turned dark at 241°.

***d*- and l-N,N′,2,5,2′,5-Tetramethyl-3,3′-dicarboxydipyrryl.**—The active acids were liberated from the individual salts by suspending in water and treating with hydrochloric acid. A suspension of 4 g. of the less soluble salt in 100 cc. of water was treated with 4 cc. of concentrated hydrochloric acid and thoroughly stirred. The solid acid which precipitated was filtered and recrystallized to a constant melting point from absolute methyl alcohol. Melting point, 218–219°.

Rotation. *d*-Acid, 0.1817 g. made up to 25 cc. with pyridine at 20° gave or, +0.40; $l = 2$; $[\alpha]^{20}_{D}$ +27.5.

Anal. Calcd. for $C_{14}H_{16}O_4H_2$: C, 60.87; H, 5.85. Found: C, 61.03; H, 6.10.

The I-acid was obtained in a similar manner from the crude soluble salt. The free acid was recrystallized from absolute methyl alcohol; melting point 220–221°.

Rotation. Z-Acid, 0.1544 g. made up to 25 cc. with pyridine a t 20° gave or, −0.31; $l = 2$; $[\alpha]^{20}_{D}$ −25.1.

Racemization Experiments.—A solution of 0.1817 g. of d-acid made up to 25 cc. with pyridine at 20°, α_D +0.40, $l = 2$, $[\alpha]^{20}_{D}$ +27.5, was refluxed for twenty-four hours. No change in initial rotation was observed.

A solution of 0.1990 g. of d-acid in 50 cc. of 0.1 N sodium hydroxide gave an initial rotation of α_D +0.19; $l = 2$; $[\alpha]^{20}_{D}$ +23.9; upon boiling for eighty-four hours the rotations were as follows: nine hours, α_D +0.14, $l = 2$, $[\alpha]^{20}_{D}$ \$17 6; forty-eight hours, or, +0.12, $l = 2$, $[a]^{20}_{D}$ +15.1; seventy-two hours, a +0.07, $l = 2$, $[\alpha]^{20}_{D}$ +8.8; eighty-four hours, α_D +0.06, $l = 2$, $[\alpha]^{20}_{D}$ +7.5.

Summary

1. N,N′,2,5,2′,5′-Tetramethyl-3,3′-dicarboxydipyrryl has been prepared by condensing N-amino-2,5-dimethyldicarboethoxypyrrole with 3-carboethoxy-2,5-dimethylhexadione.

2. The product was resolved through the brucine salt and the active forms were found to be unusually resistant to racemization.

URBANA, ILLINOIS

[CONTRIBUTION PROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

THE REDUCTION OF AROMATIC NITRO AND NITROSO COMPOUNDS WITH SODIUM ALCOHOLATES. II.

BY F. B. DAINS AND W. O. KENYON

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The reduction of aromatic nitro compounds with sodium or potassium hydroxide in alcohol solution or with sodium alcoholates has been studied by a number of investigators from the time of Mitscherlich to the present.' Under various conditions there have been obtained amines, azoxybenzene, azobenzene and in the case of *p*-nitrotoluene stilbene derivatives.' In addition, Suter and Dains have found that the reduction of o-halogen nitrobenzenes with sodium propylate or butylate gave an unexpected product, a substituted amino acid.[2]

$$o\text{-ClC}_6\text{H}_4\text{NO}_2 + n\text{-C}_3\text{H}_7\text{ONa} \longrightarrow o\text{-ClC}_6\text{H}_4\text{NHCH(CH}_3\text{)COONa} + \text{H}_2\text{O}$$

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[1] E. Mitscherlich, *Ann.*, 12, 311 (1834); Kasenack, *Ber.*, 5, 364 (1872); Zinin, J. prakt. Chem., *[I]* 36, 98 (1845); Klinger, Ber., 15, 865 (1882); Schultz and Smith, Ann., 207, 328 (1881); Holleman, Rec. trav. *chim.*, 35, I (1915); Blom, *Helv. Chim. Acta*, 4,297 (1921) ; Pry and Cameron, THIS JOURNAL, 49,864 (1927); Heumann, *Ber.*, 5, 911 (1872); Brand, J. prakt. *Chem.*, *[11]*68, 208 (1903); Richardson, *J.* Chem. *Soc.*, 522 (1926); McMasters and Magill, THIS JOURNAL, 50, 3038 (1928); Perkin, J. Chem. *Soc.*, 37, 546 (1880); Goldschmidt, Ber., 11, 1624 (1878); Buchka and Schachtebeck, ibid., 22, 834 (1889); Schmidt, *ibid.*, 32, 2919 (1899); Green, Davies and Horsfall, *J.* Chem. *Soc.*, 91, 2076 (1907); Brühl, Ber., 37, 2066 (1904); Lyons and Pleasant, *ibid.*, 62,1723 (1929).

[2] Suter and Dains, THIS JOURNAL, 50,2733 (1928).

The present paper is a continuation of their investigation and was undertaken with the following purposes: (1) to study the reducing action in benzene solution of polyhydric alcohols and of ketones which are capable of forming sodium derivatives; (2) to ascertain whether ortho groups other than halogen atoms will cause the formation of amino acids; (3) to compare the action of nitroso compounds as oxidizing agents; (4) to ascertain the amount of halogen removed from the ring.

Experimental

The method outlined by Dains and Suter was used in most cases. When the reduction was complete the separation of products was carried out as outlined in their paper. The benzene layer of the distillate contained the unchanged nitro compounds.

The amine formed was estimated by the method of Francis and Hill.[3] The brominated amine thus formed was used for identification wherever possible.

After separation of azo or azoxy derivatives, acidification with sulfuric acid precipitated the amino acids, organic acids, or phenolic products. These were removed, the filtrate diluted to a definite volume and the halogen removed was estimated by a Volhard titration of an aliquot portion. When soluble organic acids were present which would affect the titration, they were removed by making the solution alkaline, evaporating to dryness and fusing the residue until all carbon was removed. The melt was then dissolved and the halogen estimated.[4]

Table I gives a résumé of the laboratory results and in the later discussion references are made to the particular experiments involved. All melting points are uncorrected.

Discussion

The Effect of Added Amines upon Reduction.—The work of Fry and Cameron and of Fry and Bowman[5] has shown that when pyridine or other organic bases such as aniline are present in the reaction mixture, they increase the reduction of nitrobenzene by sodium methylate.

In benzene solution it was found that nitrobenzene is reduced to only a slight extent (Ia) and the presence of an equimolar amount of aniline has only slight effect on the amount of reduction (Ib).

In the case of *p*-chloronitrobenzene and sodium propylate, Suter has shown that 33% of the nitro compound goes to the *p*,*p*'-dichloroazoxybenzene. A series of reductions (IIIa, b, c, d) in the presence of organic bases gives yields almost twice as great as when no base is added. In

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[3] Francis and Hill, THIS JOURNAL, 46, 2488 (1924).

[4] All products with chlorine in the ring had been removed before fusion.

[5] Fry and Bowman, THIS JOURNAL, 52, 1531 (1930)

TABLE I

EXPERIMENTAL RESULTS

300 Cc. of Benzene in Each Experiment

No.	Nitro compd., moles	Alcohol, moles	Sodium, moles	Amine formed, %	Azoxy formed, %	Nitro recovered, %	Acids and other products	Halogen removed, %
Ia	0.1 $C_6H_5NO_2$	0.6 C_2H_5OH	0.2	6.24	Tar	73.17		
b	.1 $C_6H_5NO_2$ .1 $C_6H_5NH_2$	.6 C_2H_5OH	.2	8.25		82.93		
c and d	.1 $C_6H_5NO_2$	.6 $(CH_3)_2CO$	.2	36.13 36.2	Tar			
e	.1 $C_6H_5NO_2$	.6 $C_3H_5(OH)_3$	.2 NaOH	1.06	Azobz. 22.0		0.0044 mole oxalic, 0.0487 mole formic, 0.0153 mole acetic, 0.0004 mole oxalic	
f	.5 $C_6H_5NO_2$	.3 $C_3H_5(OH)_3$	.1	39.83		49.0		
g	.1 $C_6H_5NO_2$	.6 $C_2H_4(OH)_2$	.2 NaOH	17.46	Azobz. 43.50		0.0024 mole oxalic, 0.006 mole vol. acids	
h	.1 $C_6H_5NO_2$	.6 $C_2H_4(OH)_2$	.2	9.00	Azobz. 28.10	3.20	0.0017 mole oxalic, 0.0054 mole vol. acid	
IIa	0.1 o-$ClC_6H_4NO_2$	0.6 C_2H_5OH	0.2	20.40	29.85	6.33	Tar	7.25
b	.1 o-$ClC_6H_4NO_2$	.2 $C_2H_5OC_2H_4OH$	.2	4.35		0.6	Tar	
c	.1 o-$ClC_6H_4NO_2$	.2 $CH_3COCH_2COOC_2H_4$	.2	16.34[b]			CO_2	20.48
d	.1 o-$ClC_6H_4NO_2$	.2 $CH_2(CO_2C_2H_5)_2$	.2	7.5	Tar		CO_2	5.33
IIIa[a]	0.1 p-$ClC_6H_4NO_2$	0.6 n-C_3H_7OH	.2	18.70	60.00	10.76	Tar	12.72
b	.1 p-$ClC_6H_4NO_2$ .1 $C_6H_5NH_2$	.6 n-C_3H_7OH	.2	30.00	67.10			
c	.1 p-$ClC_6H_4NO_2$ .1 p-$ClC_6H_4NH_2$	.6 n-C_3H_7OH	.2	12.00 Lost	74.63	12.66		
d	.1 p-$BrC_6H_4NH_2$ .1 p-$ClC_6H_4NH_2$	.6 n-C_3H_7OH	.2	9.67	69.50			
e	.1 p-$ClC_6H_4NO_2$	50 cc. $C_2H_4(OH)_2$	.2 NaOH		82.20			
f	.1 p-$ClC_6H_4NO_2$	0.6 $(CH_3)_2CO$	.2	44.50				
g	.05 p-$ClC_6H_4NO_2$	.1 $C_6H_5COCH_2C_6H_5$	.1	3.68	Trace	6.33	Benzoic trace, Benzilic 18.75	

Table I (*Continued*)

No.	Nitro compd., moles	Alcohol, moles	Sodium, moles	Amine formed, %	Azoxy formed, %	Nitro recovered, %	Acids and other products	Halogen removed, %
h	0.1 p-$ClC_6H_4NO_2$	0.2 $CH_3COCH_2CO_2C_2H_5$	0.2	14.48[b]	16.42	61.40	CO_2 acetone, oxalic acid, 0.397 mole	12.61
i	.1 p-$ClC_6H_4NO_2$	.08 $C_6H_5COCH_2CO_2C_2H_5$	.08	7.71	Tar			3.78
j	.1 p-$ClC_6H_4NO_2$	.2 $CH_2(CO_2C_2H_5)_2$	.2	7.13	26.27	47.50		2.52
IVa	20 g. 3,4-Dichloro-1-nitrobenzene	200 cc. C_2H_5OH	40 g. KOH		90.48			Trace
b	10 g. "	100 cc. 95% C_2H_5OH	4.6 Na		43.45			7.68
c and				5.45	55.95			21.60
d	0.1 "	0.6 C_2H_5OH	0.2	25.70	61.90			Trace
e	0.1 "	0.6 n-C_3H_7OH	0.2	3.78	61.90		Tar	17.64
f	0.1 "	100 cc. n-C_3H_7OH	4.6 g.		41.66		CO_2	Trace
g[c]	20 g. "	50 cc. $C_6H_5CH_2OH$	40 g. NaOH	3.04	49.50		0.0594 mole benzoic acid	
h	0.1 "	0.6 $C_6H_5CH_2OH$	0.2	2.80	67.50		0.166 mole benzoic acid	11.59
Va	0.1 2,5-Dichloro-1-nitrobenzene	0.6 C_2H_5OH	.2	13.43	26.70	26.56	Tar, trace of phenols	
VIIa	0.1 o-nitrotoluene	0.6 n-C_3H_7OH	.2	48.00		18.26	Tar	
VIIIa	0.1 p-nitrotoluene	0.6 CH_3OH	.2	32.70		13.87	0.0194 mole formic acid	Stilbene, 61.60
b	.1 p-nitrotoluene	0.6 C_2H_5OH	.2	36.21	46.02		0.009 mole formic, 0.013 mole acetic	Stilbene, 3.00
c	.1 p-nitrotoluene	0.6 $C_2H_5OC_2H_4OH$	.2	7.95		1.46		Stilbene, 85.30
d	.1 p-nitrotoluene	0.3 $CH_3COC_6H_5$	.1	83.03	Trace	14.60	0.025 mole benzoic acid	
IXa	0.1 2-chloro-6-nitrotoluene	0.6 n-C_3H_7OH	.2	29.70	Tar	8.15		

TABLE I (*Concluded*)

No.	Nitro compd., moles	Alcohol, moles	Sodium, moles	Amine formed, %	Azoxy formed, %	Nitro recovered, %	Acids and other products	Halogen removed, %
Xa	0.4 4-chloro-2-nitrotoluene	0.6 C_2H_5OH	0.2	15.00	13.50	2.3	Tar	8.36
XIa	.1 2-chloro4-nitrotoluene	.6 C_2H_5OH	.2	7.70		3.5		Stilbene, 58.70
b	.1 "	.6 n-C_3H_7OH	.2	9.33		4.70		Stilbene, 61.80
XIIIa	.1 *o*-nitroanisol	.6 n-C_3H_7OH	.2	3.01	Tar		Tar	
XIVa	.1 *o*-nitrodiphenyl ether	.6 n-C_3H_7OH	.2	12.85		4.18	Tar	
XVa	.1 *o*-nitrodiphenyl	.6 n-C_3H_7OH	.2	21.00	34.10		Tar	
XVIa	.1 *p*-nitrodiphenyl	.6 n-C_3H_7OH	.2	2.17	93.72	5.00		
XVIIa	.05 *m*-Nitrobenzylidine aniline	.3 n-C_3H_7OH	.1	63[b]			Tar	
XIXa	.1 *m*-nitrobenzaldehyde	.6 n-C_3H_7OH	.2				97 *m*-Nitrobenzoic acid	
XXa	.1 *o*-Nitrobenzaldehyde	.6 n-C_3H_7OH	.2				Tar	
XXIa	.1 *p*-Nitroethyl benzoate	.6 n-C_3H_7OH	.2		86.5 Azoxybenzoic acid			
XXIIa	.1 *o*-Nitroacetanilide	.6 n-C_3H_7OH	.2	13.13[e]	Resins			
XXIIIa	.1 Nitrosobenzene	.6 n-C_3H_7OH	.2	10.00	Tar			
XXIVa[d]	.05 *p*-Nitrosotoluene	200 cc. C_2H_5OH	10 g. NaOH		95.2			
b	.05 "	0.3 n-C_3H_5OH	0.1	8.07	83.00			
XXVa	.5 *p*-Nitrosodimethylaniline	.3 n-C_4H_9OH	.1	44.00	46.5			

[a] 0.1 Mole of pyridine added to solvent benzene. [b] Aniline. [c] 25 cc. of water as solvent. [d] 40 cc. of water as solvent. [e] Diamine.

(IIIc), 0.1 mole of amine was added to the reaction mixture but only 88% of this could be recovered.

The Action of Glycol and Glycerol.—The reductions using glycerol and sodium in benzene were very slow due to the formation of two layers in the reaction medium. In the case of sodium or sodium hydroxide with glycol and glycerol in an excess of the alcohol (Ie, g, h), the formation of azobenzene is unique and rather surprising. In contrast to this, *p*-chloronitrobenzene with glycol and alkali yields mainly *p,p'*-dichloroazoxybenzene (IIIe). The formation of oxalic and volatile acids is also to be noted.

The Oxidation of Ketones and Ketone Acids.—The sodium salt of acetone is a powerful reducing agent (Ie, d, IIIf) and gives from 36 to 44% amines, but otherwise thick tars. Acetophenone behaves in an analogous manner (VIIId).

With phenyl benzyl ketone (IIIg) there was observed the interesting formation of benzilic as well as benzoic acid. This is due to oxidation of the ketone to benzil, which in part is oxidized to benzoic acid but mainly undergoes rearrangement in the alkaline solution during the steam distillation[6] to benzilic acid.

Ethyl acetoacetate (IIc, IIIh) was not only oxidized by o- and P-chloronitrobenzenes, but was able to replace the chlorine in the ring by hydrogen, since the amine recovered was practically all aniline, which was not the case with benzoylacetic ester (IIIi) or malonic ester (IId, IIIj).

Reactions with 3,4-Dichloronitrobenzene.—The series IVa-h deals with the reduction of the 3,4-dichloronitrobenzene. Three different alcohols were used, the reactions being carried out in various ways and the product, aside from small amounts of the corresponding amine, was tetrachloroazoxybenzene. A typical experiment is as follows.

Preparation of **3,4,3',4'-Tetrachloroazoxybenzene.**—Sodium (4.6 g.) was dissolved in a mixture of benzene (300 cc.) and n-propyl alcohol (45 cc.). To this was added 3,4-dichloronitrobenzene (19.2 g.) dissolved in a little benzene. The mixture was refluxed for two hours.

After distillation, the distillate showed 3.78% of 3,4-dichloroaniline. The residue in the flask gave 10.4 g. of brown material. This was extracted with ether alcohol and recrystallized from carbon disulfide and benzene. The melting point is 137–138°; 61.9% yield.

Anal. Calcd. for $C_{12}H_6ON_2Cl_4$: Cl, 42.2. Pound: Cl, 42.02, 42.08.

The molecular weight in benzene by the freezing point method gives 372; calculated. 336. In no case under the conditions employed was any evidence obtained for the formation of ethers of 4-nitro-3-chlorophenol such as were described by McMaster and McGill[7] as resulting from the interaction of sodium alcoholates on this dichloronitrobenzene.

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[6] Klinger, Ber., 19, 1867 (1886).

[7] McMaster and McGill, THIS JOURNAL, 50, 3041 (1928).

The Nitrobenzaldehydes, Acids and Phenols.—*o*-Nitrobenzaldehyde and sodium propylate (XXa) gave only tars, while the *m*-nitrobenzaldehyde (XIXa) was changed almost quantitatively to m-nitrobenzoic acid. Evidently in the alkaline solution it undergoes the Cannizzaro reaction and then the nitrobenzyl alcohol, in turn, with dilute alkali is oxidized to the acid. o-, m- and *p*-nitrobenzoic acids (XVIIIa) gave no reduction products, though the ethyl ester of *p*-nitrobenzoic acid (XXIa) was reduced (86%) to the *p,p'*-azoxybenzoic acid, identified by its properties and analysis of its silver salt. a-Nitrophenol was not reduced but went over into the red sodium salt of the acid form.

Formation of Amino Acids.—Suter and Dains[2] showed that such amino acids resulted from the reduction of o-halogen nitro compounds. Thus far this seems to be an essential condition since no amino acids have been isolated with the following ortho substituents: CH_3, OH, OCH_3, OC_6H_5, C_6H_5, CHO and $NHCOCH_3$ (in IXa, Xa, XIIIa, XIVa, XVa, XXIIa).

Since ethyl alcohol failed to give an amino acid with dichloronitrobenzene, while propyl did, it is evident that a 3-carbon alcohol at least is necessary for this synthesis. The following illustrates, however, the synthesis of such acids.

α-2,5-Dibromoanilinopropionic Acid, $CH_3CH(NHC_6H_3Br_2)COOH$.—Sodium (4.6 g.) is dissolved in a mixture of benzene (250 cc.) and n-propyl alcohol (45 cc.) and 2,5-dibromonitrobenzene (28.1 g.) in 50 cc. of benzene is slowly added. When the violent reaction subsides, the mixture is refluxed on the water-bath for two hours. The amine present (21.65%) is removed by steam distillation and the residue filtered. Acidification precipitated the acid as an oil which later solidified. This crude material was dissolved in alcohol, boiled with norite and the product precipitated by dilution of the hot filtered solution with water. It forms colorless crystals, m. p. 156°, which became brown on contact with air.

Anal. Calcd. for $C_9H_9O_2NBr_2$: Br, 49.49. Found: Br. 49.59, 49.37.

Its constitution was further proved by its synthesis from dibromoaniline and a-bromopropionic acid on refluxing in water solution until the mixture was homogeneous. A mixed melting point showed identity.

In connection with the method of determining the amount of 2,5-dibromoaniline formed (method of Francis and Hill) in the preceding reduction, it was found necessary to synthesize the possible product. When bromine water is added to a dilute sulfuric acid solution of 2,5-dibromoaniline, the 2,4,5,6-tetrabromoaniline is found. The crystals from alcohol melt at 118°.

Anal. Calcd. for $C_6H_3NBr_4$: Br, 78.21. Found: Br, 78.08.

α-2-Chloro-5-methylanilinopropionic Acid.—This was formed in 49.18% yield together with 8.43% of amine from the chloronitrotoluene and sodium propylate in benzene solution. The white crystals from hot water melt at 158°.

Anal. Calcd. for $C_{10}H_{12}O_2NCl$: Cl, 16.57. Found: Cl, 16.64, 16.72.

The same acid was synthesized from a-bromopropionic acid and 3-amino-4-chloro-

In a previous paper[8] it was suggested that the formation of these amino acids may be due to an increased ability of the *o*-nitroso group to add an aldehyde complex and then rearrange. This does not seem to be true of the *p*-nitroso derivatives (XXIIIa, XXIVa, XXVa), since they exhibit strong oxidizing properties, yielding amines and azoxy compounds.

Halogen Removal.—While varying amounts of halogen were removed in many cases, no definite phenols were isolated. This is probably due to the interaction of the intermediate nitroso compounds with such phenols, yielding tarry products.

Summary

1. A study has been made of the action of sodium alcoholates (or tautomeric substances) on nitrobenzene, substituted nitrobenzenes and nitrosobenzenes in anhydrous benzene solution.
2. The products are normally amines or the corresponding azoxy derivatives, though polyhydric alcohols tend to form azo compounds.
3. Sodium derivatives of tautomeric substances are often good reducing agents, being oxidized usually at the inethylene bond.
4. When p-nitrotoluene or its substitution products are used, stilbenes may be formed.
5. No substituting groups other than halogen form a-amino acids.

LAWRENCE, KANSAS

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

STEREOCHEMISTRY OF DIPHENYLS. PREPARATION AND PROPERTIES OF 4,4'-DICARBOXY-1,1'-DIANTHRAQUINOYL. XVII[1]

BY W. M. STANLEY AND ROGER ADAMS

RECEIVED APRIL 17, 1931 PUBLISHED JUNE 8, 1931

It was pointed out in a previous paper[2] that it should be possible to resolve a 2,2'-disubstituted diphenyl derivative into optical antipodes, provided the two substituting groups are sufficiently large and assuming that a hydrogen atom may serve as a blocking group. Diphenyl-2,2'-disulfonic acid[3] was investigated but it could not be resolved. In the present investigation 4,4'-dicarboxy-1,1'-dianthraquinoyl (I) and its di-*l*-menthyl ester were synthesized in order to determine whether the CO group in a quinone ring would be a sufficiently large 2-substituted group to cause inter-

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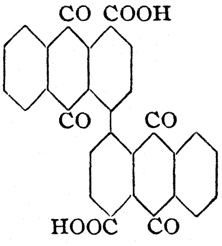
[8] Ref. 2, p. 2738.

[1] For the two previous papers in this series see Shildneck and Adams, THIS JOURNAL, 53, 2203 (1931); Chang and Adams, ibid., 53, 2353 (1931).

[2] Stanley and Adams, ibid., 52, 1200 (1930).

[3] Stanley and Adams, *ibid.*, 52, 4471 (1930).

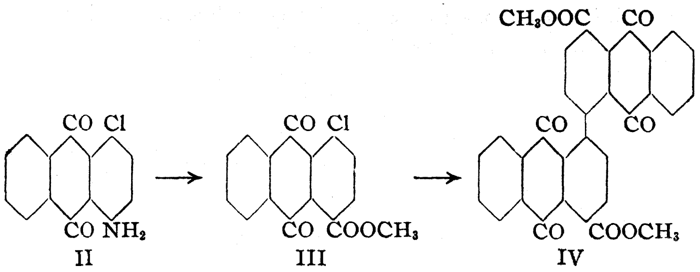
ference with the 2'-hydrogen atom and thus allow resolution into optical isomers. It could not, however, be resolved.



I

If the interference of the C—CO is calculated as an additive value of the C—C and C=O distances (2.45 Å.), an assumption which is hardly warranted, the compound should be resolvable: C—CO, 2.45 Å. + C—H, 0.94 Å. $\longrightarrow$ 3.39 Å. − 2.90 Å. (distance between 2,2′ carbons) $\longrightarrow$ 0.49 Å. On such a basis, the x-ray values do not agree with the facts. However, there are factors in the structure of such a compound as has been described in this investigation which make it somewhat different from the simple diphenyls. The positions of the carbon atoms in the quinone rings are fixed in such a way that the effective interference diameter of each of the C—C and of the C=O groups would probably be modified from that in an ordinary diphenyl. Certainly the values would not be additive. The forces of the C=O group extend probably in a vertical direction from the quinone ring and, therefore, with the fixed position of the carbon atom, a set of conditions is introduced which necessitates a modification of the simple assumption for interfering values which has been used so successfully for the diphenyls with no condensed nuclei.

The 4,4′-dicarboxy-1,1′-dianthraquinoyl was prepared from 1-chloro-4-benzoylaminoanthraquinone by removal of the benzoyl group, diazotization and replacement of the amino group by a cyano group, hydrolysis and esterification of this derivative to give 1-chloro-4-carbomethoxyanthraquinone, condensation of this to 4,4′-dicarbomethoxy-1,1′-dianthraquinoyl and saponification of this to the acid. Due to its extreme insolubility the dimethyl ester was not isolated from the condensation reaction mixture, the uncoupled 1-chloro-4-carbomethoxyanthraquinone being removed by extraction with chloroform and the residual mixture being saponified directly to give 4,4′-dicarboxy-1,1′-dianthraquinoyl. It was impossible to purify the free acid by crystallization due to its slight solubility. Purification was accomplished by crystallization of the disodium salt, repeated treatment with charcoal in alkaline solution, and repeated precipitation of the acid from solutions of the salt by means of dilute mineral acid.



It was found impossible to fractionate the alkaloid salts of 4,4′-dicarboxy-1,1′-dianthraquinoyl due to their insolubility. In one experiment the monoquinine salt of the acid was extracted with three liters of hot *p*-cymene with no indication of resolution. It was also found impossible to render the acid soluble by forming the monoquinine-monosodium salt of the acid since this derivative rearranged to a mixture consisting mainly of the disodium salt and the diquinine salt. The di-*l*-menthyl ester was prepared and fractionated from three different solvents without giving any change in the rotation or melting point.

The authors wish to thank The Jackson Laboratory of E. I. du Pont de Nemours and Co. through Mr. Clark for the 1-chloro-4-benzoylamino-anthraquinone used in this investigation.

Experimental Part

1-Chloro-4-aminoanthraquinone (II).—A solution of 250 g. of technical 1-chloro-4-benzoylaminoanthraquinone in 400 cc. of concentrated sulfuric acid was heated to 80–90° for four hours. The solution was then cooled to 0" and poured slowly onto ice with continual stirring. The red precipitate was removed by filtration, warmed with strong ammonium hydroxide, filtered and washed with dilute ammonium hydroxide until the filtrate gave no precipitate upon acidification. After a final washing with 250 cc. of water, the red precipitate was dried under vacuum at 100°. The yield was 175 g.

1-Chloro-4-cyanoanthraquinone.—A solution of 55 g. of sodium nitrite in 500 cc. of concentrated sulfuric acid was prepared by dusting small portions of thoroughly dried sodium nitrite powder into concentrated sulfuric acid at 0° with continual stirring. The addition required about forty minutes, after which the sulfuric acid was heated to 50–60° to effect complete solution of the sodium nitrite. The solution was then cooled to 0°, and to it was added an ice-cold solution of 175 g. of 1-chloro-4-aminoanthraquinone in 850 cc. of concentrated sulfuric acid. After standing at 0° for fourteen hours, the solution was poured slowly with stirring onto cracked ice. The bright yellow precipitate which formed was quickly removed by filtration with suction, washed with 100 cc. of ice water and immediately taken up in 3 liters of ice water. This mixture was added slowly to a cold solution of 325 g. of cupric sulfate pentahydrate and 365 g. of potassium cyanide in 2 liters of water. This solution was previously prepared by adding a saturated aqueous solution of potassium cyanide to a boiling aqueous solution of cupric sulfate. After the addition of the diazonium salt, the mixture was heated to boiling during three hours and filtered hot. The precipitate was washed with hot 10% aqueous potassium cyanide solution and finally with 8 liters of boiling water. After drying, the precipitate weighed 250 g., so it was heated to boiling with 2 liters of 5% aqueous potassium cyanide, filtered hot, washed with 2 liters of hot 5% aqueous potassium cyanide, then with 4 liters of boiling water and dried. The yield was 155 g. (85%) of a product melting at 265–268°. The melting point after two crystallizations from glacial acetic acid was 271–272°.

Anal. Calcd. for $C_{15}H_6O_2NCl$: Cl, 13.25. Found: Cl, 12.97.

1-Chloro-4-carboxyanthraquinone.—A mixture of 150 g. of 1-chloro-4-cyanoanthraquinone, 300 cc. of water and 900 cc. of concentrated sulfuric acid was heated to boiling (190°), cooled and diluted with 2 liters of water. The precipitate so obtained was removed by filtration, washed with water and then digested and washed with a total of five liters of dilute ammonium hydroxide. The ammoniacal filtrate was acidified and the brown colored acid so obtained was removed and dried. The yield was 135 g. (82%) of a product melting at 220–224° without recrystallization. Heller and Schulke[4] give the melting point of 1-chloro-4-carboxy anthraquinone obtained by the oxidation of I-chloro-4-methylanthraquinone as 228–229° after two crystallizations.

1-Chloro-4-carbomethoxyanthraquinone (ID).—A mixture of 66 g. of 1-chloro-4-carboxyanthraquinone and 2 liters of absolute methyl alcohol was saturated with dry hydrogen chloride (required 580 g.). After refluxing for twenty-four hours, 600 cc. of alcohol was removed by distillation, and the residual mixture was cooled to 0° and filtered. The precipitate was washed with water, then with dilute sodium carbonate solution until acidification of the filtrate gave no precipitate and finally with water. The yield was 60 g. (87.5%) of a product melting at 183–185°. The run was repeated using 34 g. of 1-chloro-4-carboxyanthraquinone and 500 g. of absolute methyl alcohol. The yield was 30 g. (85%). The ester was recrystallized twice from chloroform and gave large rhombic crystals having a melting point of 187.5–188.5°.

Anal. Calcd. for $C_{16}H_9O_4Cl$: Cl, 11.80. Found: Cl, 11.90.

4,4′-Dicarboxy-1,1′-dianthraquinoyl (I).—A mixture of 30 g. of 1-chloro-4-carbomethoxyanthraquinone and 30 g. of copper powder (Kahlbaum's Naturkupfer C) in a Pyrex tube was heated by means of a metal bath slowly to 265° during ten minutes and then at 265° for twenty minutes with occasional stirring. A noticeable reaction took place at about 250° during which the temperature of the mixture went to 300°. The run was repeated using 54 g. of 1-chloro-4-carbomethoxyanthraquinone and 75 g. of copper powder. The two runs were combined, cooled, pulverized and extracted with 500 cc. of hot chloroform, the evaporation of which gave 30 g. of solid material. The reaction mixture was again extracted successively with 300 cc. and with 200 cc. of chloroform, the evaporation of which gave 2.0 g. and 0.5 g., respectively, of solid material, thus indicating the removal of the uncoupled material. The remaining mixture, consisting of copper powder, copper chloride, and 4,4′-dicarbomethoxy-1,1′-dianthraquinoyl, was refluxed with a mixture of 32 g. of potassium hydroxide and 800 cc. of ethyl alcohol for twelve hours. The alcohol was removed by distillation, the residue was heated to boiling with 750 cc. of water and filtered hot. The residue was extracted twice with 500 cc. of hot water, and the combined filtrates acidified with hydrochloric acid. The light brown precipitate of 4,4′-dicarboxy-1,1′-dianthraquinoyl was removed by filtration and dried. The yield was 44 g. of a product melting unsharply from 350–360°. The disodium salt of the acid was crystallized from water and then dissolved in water, boiled with charcoal, filtered and precipitated with hydrochloric acid six successive times. The light cream colored acid so obtained weighed 25 g. and melted sharply at 448° (corr.) on the block. The acid is slightly soluble in pyridine (0.06 g. in 100 g.) and insoluble in all other common solvents.

Anal. Calcd. for $C_{30}H_{14}O_8$: C, 71.69; H, 2.81. Found: C, 71.31; H, 2.81.

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[4] Heller and Schulke, *Ber.*, 41,3636 (1908)

Di-*l*-menthyl Ester of **4,4′-Dicarboxy-1,1′-dianthraquinoyl.**—A mixture of 5 g. of 4,4′-dicarboxy-1,1′-dianthraquinoyl and 175 g. of thionyl chloride was refluxed for six hours, the acid going slowly into solution. The excess thionyl chloride was carefully removed under vacuum and the yellow residue dried until the odor of thionyl chloride was very faint. A 10-g. portion of Lmenthol was then added and the mixture heated to 150° for six hours, after which 150 cc. of dry benzene was added and the mixture refluxed for six hours. The benzene was removed under vacuum, and the residue steam distilled to remove the excess 1-menthol. The residue was recrystallized from chloroform, giving 6.5 g. (85%) of light yellow product melting at 298–299°. The di-1-menthyl ester is soluble in chloroform, slightly soluble in ether, ethyl acetate and acetone and insoluble in petroleum ether and ethyl alcohol.

Rotation. 0.2206 g. made up to 12 cc. with chloroform at 20° gave a, 0.28; $l = 1$; $[\alpha]_{\mathrm{D}}^{20}$ −15.2°.

Anal. Subs., 3.974 mg.; CO_2, 11.19 mg..; H_2O, 2.27 mg. Calcd. for $C_{50}H_{50}O_8$: C, 77.08; H, 6.47. Found: C, 76.79; H, 6.39.

Fractionation of the ester from chloroform, ether and ethyl acetate did not change the rotation or the melting point.

Attempt to Resolve **4,4′-Dicarboxy-1,1′-dianthraquinoyl with** Quinine.—A mixture of 5.02 g. (0.01 mole) of 4,4′-dicarboxy-1,1′-dianthraquinoyl, 3.24 g. (0.01 mole) of quinine and 200 cc. of chloroform was refluxed for sixty hours. The mixture was then cooled and the insoluble material was removed by filtration. This material consisted of the quinine salt, since the weight was 8.26 g. It had an unsharp melting point starting at 210°. The salt is insoluble in benzene, p-cymene, acetone, gasoline, chloroform, alcohol, nitrobenzene, ethyl acetate and ether. The extraction of 3 g. of salt with 2 liters of hot p-cymene gave about 0.1 g. of salt, the acid from which gave no rotation in 0.1 N sodium hydroxide. Pyridine was found to decompose the salt. An attempt was then made to solubilize the salt by forming the mono-quinine mono-sodium salt. To a suspension of 4 g. of the mono-quinine salt of 4,4′-dicarboxyl-1,1′-dianthraquinoyl in 400 cc. of water was added slowly 47 cc. of 0.108 *N* sodium hydroxide solution (1 equiv.). The mixture was warmed for six hours at 80° and filtered from 2.6 g. of insoluble material. The insoluble material was again combined with the filtrate and warmed for twelve hours at 80°. The amount of insoluble material was again 2.6 g. The material was found to be the diquinine salt, for upon hydrolysis one equivalent of acid and two equivalents of quinine were obtained. The soluble portion was found to consist chiefly of the disodium salt. It gave no rotation in aqueous or pyridine solution.

Summary

1. 4,4′-Dicarboxy-1,1′-dianthraquinoyl and its di-*l*-menthyl ester have been prepared. Only one di-*l*-menthyl ester was obtained.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

DEGUELIN. II. RELATIONSHIPS BETWEEN DEGUELIN AND ROTENONE

BY E. P. CLARK

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Recently[1] attention has been directed to a relationship between deguelin and rotenone in ,which the following facts were involved. Upon mild oxidation rotenone is converted to dehydrorotenone, $C_{23}H_{20}O_6$, which when boiled with alcoholic potassium hydroxide and zinc dust yields an hydroxp acid, $C_{23}H_{24}O_8$.[2] When this acid is oxidized in alkaline solution with hydrogen peroxide, the molecule is ruptured, and derric acid, $C_{12}H_{14}O_7$,[3] is obtained. Derric acid contains the two methoxyl groups originally in rotenone and represents one-half of the rotenone molecule.

In an analogous manner deguelin is oxidized with potassium ferricyanide to dehydrodeguelin, $C_{23}H_{20}O_6$,[4] which upon boiling with alcoholic potassium hydroxide yields a phenolic monocarboxylic acid, $C_{23}H_{24}O_8$, known as deguelic acid. When this acid is oxidized with hydrogen peroxide, as was the acid from dehydrorotenone, it also yields derric acid.

It thus follows that in deguelin as in rotenone derric acid constitutes one-half of the molecule, and hence the structural differences between deguelin and rotenone must be sought either in the second half of the molecule or in the linkages between the two parts.

Another set of experiments showing the same relationship has been performed more recently. Takei, Miyajima and Ono[5] described an acid, $C_{11}H_{12}O_7$, which they called risic acid (Rissaure). The compound was obtained by permanganate oxidation of the hydroxy acid, $C_{23}H_{24}O_8$, derived from dehydrorotenone through the action of alcoholic alkali. LaForge and Smith[6] originally obtained this acid by permanganate oxidation of derric acid, and as derric acid is a part of the deguelin molecule, risic acid should be expected as an oxidation product of deguelic acid. This experiment was performed, and risic acid was obtained, having the properties recorded for it by the Japanese investigators.

The purpose of the present report is to record the experimental data obtained in establishing the relationship mentioned above and also to describe some experiments the results of which show that these two insecticides are even more closely related than was demonstrated in the first instance.

Dehydrodeguelin was catalytically reduced with hydrogen to dihydro-

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[1] Clark, *Science*, 73, 17 (1931).

[2] Butenandt, *Ann.*, 464,272 (1928).

[3] LaForge and Smith, THIS JOURNAL, 52, 1091 (1930).

[4] Clark, *ibid.*, 53, 313 (1931).

[5] Takei, Miyajima and Ono, Ber., 64, 248 (1931).

[6] LaForge and Smith, THIS JOURNAL, 52,2878 (1930).

dehydrodeguelin, $C_{23}H_{22}O_6$. This material was found to be identical with the compound recently described by Haller[7] as dehydro-β-dihydrorotenone. Mild oxidation of dihydrodehydrodeguelin with chromic acid under the conditions described in the experimental part yielded oxydehydrodeguelin, $C_{23}H_{20}O_8$. Dihydrodehydrodeguelin when treated with alcoholic alkali in the manner by which deguelic acid was obtained from dehydrodeguelin yielded dihydrodeguelic acid, $C_{23}H_{26}O_8$. The same substance was also prepared by catalytically reducing deguelic acid. This reduced deguelic acid was found to be identical with the compound described by Haller as dehydrodihydroxy-β-dihydrorotenoic acid.[7]

When dihydrodeguelic acid was subjected to alkaline oxidation with hydrogen peroxide, the yield of derric acid was essentially the same as that given by deguelic acid.

In the first communication of this series[4] it was shown that deguelic acid reverts to dehydrodeguelin when an attempt is made to acetylate the phenolic hydroxyl group in the acid with acetic anhydride and sodium acetate. However, it has been found that if the acid is treated with a large excess of acetic anhydride in pyridine, a monoacetyldeguelic acid is formed which no longer gives a phenolic reaction with ferric chloride.

The reactions under discussion are summarized diagrammatically in Chart I.

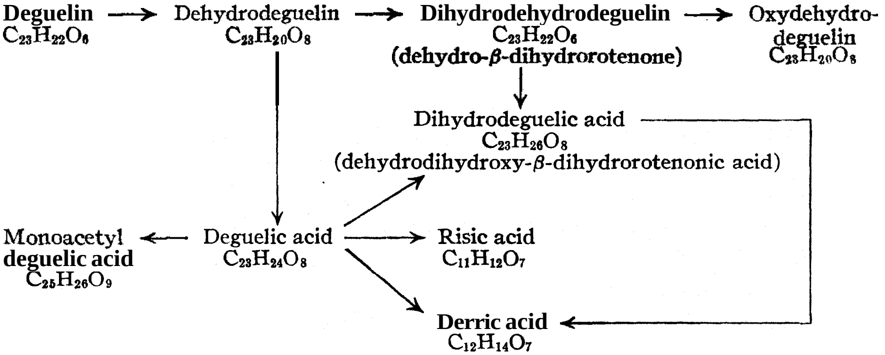

CHART I—DERIVATIVES OF DEGUELIN

The observations just recorded show that there exist structural relationships common to the entire molecule of both rotenone and deguelin. However, the information now available is so fragmentary that it seems best to present the facts now at hand and await further developments before attempts at correlation are made.

Experimental

Derric Acid from Deguelic Acid.—An aqueous solution of 2 g. of deguelic acid in 25 cc. of 5% potassium hydroxide solution, warmed to 60°, was treated portionwise with

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[7] Haller, THIS JOURNAL, 53, 733 (1931).

6 cc. of 30% hydrogen peroxide. After the reagent was added the mixture was gently boiled until foaming ceased The liquid was then cooled, acidified with sulfuric acid and thoroughly extracted with ether. The extract was dried with sodium sulfate, concentrated to 20 cc. and allowed to crystallize. After several hours 0.5 g. of derric acid separated. This was removed from the mother liquor, washed with a small quantity of ether and dried. Its melting point was 167–168°.

The acid was recrystallized from boiling n-butyl ether, from which it separated as colorless rods and needles that melted at 168° (corr.).

The crystals had both straight and inclined extinction and positive elongation: η_α, 1.525 (on rods crosswise showing straight extinction); η_β, 1.565 (common on fragments not extinguishing sharply); and η_γ, 1.640 (usually on irregular-shaped fragments).[8]

These properties are the same as those possessed by derric acid prepared according to the directions of LaForge and Smith[3] from rotenone and recrystallized from n-butyl ether.

Risic Acid from Deguelic Acid.—Two grams of deguelic acid, dissolved in 40 cc. of 1% potassium hydroxide was treated portionwise with a warm aqueous solution of 15 g. of potassium permanganate. After the reaction was completed, the liquid was filtered from the manganese dioxide and concentrated to 15 cc. The solution was then acidified with sulfuric acid and allowed to crystallize. The yield was 0.25 g. or 21%. Recrystallization of the acid from boiling n-butyl alcohol yielded colorless sheathes of fine needles and rods which melted at 256° with decomposition. A sample of the acid which Dr. LaForge obtained by the oxidation of derric acid had the same melting point upon recrystallization from n-butyl alcohol, and a mixture of the two acids showed no melting point depression.

Dihydrodeguelic Acid from Deguelic Acid.—A solution of 2 g. of deguelic acid in 100 cc. of alcohol was reduced at atmospheric pressure with hydrogen and the platinum catalyst of Voorhees and Adams.[9] After the reaction was completed the solution was filtered and heated to boiling. An equal volume of hot matcr was then added. As the solution cooled long colorless needles separated. These began to soften at 70° and melted at 80°, apparently with the loss of vapor. Upon further heating the melt solidified and then remelted at 144°. When the acid was recrystallized from boiling n-butyl ether, it separated as colorless rods showing inclined extinction and having a melting point of 147° (corr.); η_α, 1.490; η_β, indeterminate and η_γ, higher than 1.740. It also possesses two intermediate indices, η_ι, 1.605, and η_ι' 1.740, which are useful diagnostic values.

Anal. Calcd. for $C_{23}H_{26}O_8$: C, 64.17; H, 6.09; OCH_3 (2), 14.4. Found (material recryst. from butyl ether): C, 64.13; H, 6.24; OCH_3, 14.6.

Dihydrodeguelic acid and the compound described by Haller[7] as dehydrodihydroxy-β-dihydrorotenonic acid were shown to be identical when it was found that both materials possess the same optical properties and melting point and that when the two substances were mixed no melting point depression occurred.

Derric Acid from Dihydrodeguelic Acid.—Two grams of dihydrodeguelic acid was treated with alkali and hydrogen peroxide according to the directions given before for the preparation of derric acid from deguelic acid. The yield of crystalline product was 0.55 g. This material, recrystallized from n-butyl ether, had a melting point of 167–168° and it showed no depression of the melting point when mixed with derric acid. It also had the optical properties that are characteristic of derric acid.

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[8] The optical data recorded in this communication were determined by George L. Keenan of the Food and Drug Administration of the U. S. Department of Agriculture. Appreciation is gratefully acknowledged for this coöperation.

[9] Voorhees and Adams, THIS JOURNAL, 44, 1397 (1922).

Monoacetyldeguelic Acid.—Two grams of deguelic acid was dissolved in 12 cc. of pyridine, and the solution was treated with 16 cc. of acetic anhydride. The mixture was allowed to stand at room temperature for three hours, and then one volume of acetic acid and four volumes of water were added. The liquid was made acid to Congo red with 10% sulfuric acid and set aside to crystallize. The yield was 1.85 g. The material was recrystallized by dissolving it in acetic acid and adding hot water until a slight turbidity was produced. Upon standing the acetyl derivative separated as colorless crystals which melted at 128–129°. It gave no color reaction with ferric chloride as did the free acid.

For analysis it was necessary to heat the material to its melting point in a high vacuum to remove an indefinite quantity of solvent which could not be completely eliminated otherwise.

Anal. Calcd. for $C_{25}H_{26}O_9$: C, 63.82; H, 5.57; OCH_3 (2), 13.2. Found: C, 63.85; H, 5.6; OCH_3, 13.1.

Dihydrodehydrodeguelin.—Five grams of dehydrodeguelin dissolved in 200 cc. of hot acetic acid was reduced at atmospheric pressure and approximately 75° with hydrogen and the platinum catalyst of Voorhees and Adams.[9] After the reaction was completed and the solution cooled to room temperature, a product crystallized from the acetic acid. This was removed by filtration, and dissolved in 40 cc. of chloroform. The solution was filtered through norit, again heated to boiling, and five volumes of boiling ethanol was then added. Crystallization began at once, yielding 1.9 g. of long yellow rods and needles which melted at 267". Their extinction was inclined and in convergent polarized light (crossed nicols) biaxial interference figures were common. 2E was small and the double refraction was very strong. The only index of refraction determinable was the minimum value η_α, 1.498; η_γ is greater than 1.74

A comparison of dihydrodehydrodeguelin and the compound **dehydro-β-dihydro**rotenone described by Haller showed the two substances to be identical, as their melting points and optical properties were the same, and when the two substances were mixed the melting point was not depressed.

Anal. Calcd. for $C_{23}H_{22}O_6$: C, 70.03; H, 5.63; OCH_3 (2), 15.7. Found: C, 69.86; H, 5.79; OCH_3, 15.5.

Oxydehydrodeguelin.—Two grams of dihydrodehydrodeguelin dissolved in the minimum quantity of boiling acetic acid was oxidized with 15 cc. of a 10% acetic acid solution of crystalline sodium dichromate. The mixture was allowed to stand until the next day. The oxydehydrodeguelin was then removed by filtration. The yield was 0.36 g. It was recrystallized by dissolving 0.3 g. of the crystals in 20 cc. of boiling chloroform and adding to the solution 60 cc. of boiling ethanol. The substance melted at 303°, and the yield was almost quantitative. It consisted of small yellow needles and rods with square ends. The extinction was straight, and the elongation was negative. Only faint partial biaxial interference figures were shown in convergent polarized light (crossed nicols); η_α, 1.490 (frequently shown lengthwise on rods), η_β, 1.595 (crosswise), and η_γ, >1.740.

Anal. Calcd. for $C_{23}H_{20}O_8$: C, 65.08; H, 4.75; OCH_3 *(2)* 14.6. Found: C, 64.81; H, 4.85; OCH_3, 14.2.

Dihydrodeguelic Acid from **Dihydrodehydrodeguelin.**—A mixture of 0.5 g. of dihydrodehydrodeguelin, 1 g. of zinc dust, 12 cc. of ethanol and 3 cc. of a 50% aqueous potassium hydroxide solution was refluxed for thirty minutes. The reaction mixture was cooled by the addition of crushed ice and diluted with water to a volume of 75 cc. The zinc was removed by decantation, and the alkaline solution was made acid to Congo red with sulfuric acid. The acid solution was extracted with ether, The ethereal extract was dried over sodium sulfate and evaporated to dryness. The residue was dissolved in hot n-butyl ether. Upon cooling 0.36 g. of dihydrodeguelic acid separated which had the properties recorded for the acid obtained by catalytically reducing deguelic acid.

Summary

1. Derric and risic acids have been obtained from deguelic acid by methods analogous to those used in preparing these acids from derivatives of rotenone. This shows that in degueiin as in rotenone, derric acid constitutes one-half of the molecule.
2. Reduction of dehydrodeguelin yields dihydrodehydrodeguelin, which is identical with dehydro-β-dihydrorotenone.
3. Upon treatment with alcoholic alkali, dihydrodehydrodeguelin gives dihydrodeguelic acid. This acid is also obtained by catalytically reducing deguelic acid.
4. Dihydrodeguelic acid has been found to be identical with dehydrodihydroxy-β-dihydrorotenonic acid described by Haller.
5. These facts show that there exist structural relationships common to the entire molecule of both rotenone and deguelin.

WASHINGTON, D. C.

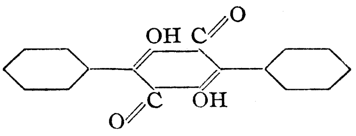
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SYNTHESIS OF POLYPORIC ACID AND ATROMENTIN DIMETHYL ETHER

BY P. R. SHILDNECK[1] AND ROGER ADAMS

RECEIVED APRIL 21, 1931 PUBLISHED JUNE 8, 1931

Two of the important coloring matters found in fungi are polyporic acid (I) obtained from *Polyporous nidulans* and atromentin (II) from *Paxillus atrotomentosus*. Kogl[2] determined the structures of these two compounds to be derivatives of diphenylquinone.



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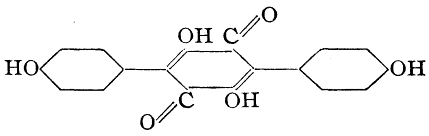

II

Moreover, he synthesized each of these compounds in two ways. The first method was that devised by Fichter.[3] For the polyporic acid, ethyl phenylacetate and ethyl oxalate[2] were condensed together with sodium;

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[1] This communication is an abstract of a portion of a thesis submitted by P. R. Shildneck in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Kogl, Ann., 447, 78 (1926).

[3] Fichter, *ibid.*, 361, 363 (1908).

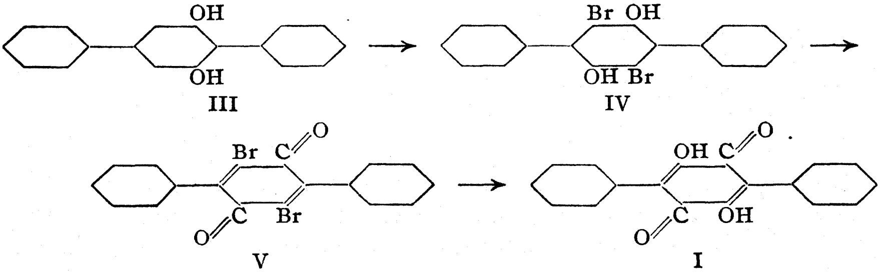
for the atromentin, ethyl *p*-methoxyphenylacetate and ethyl oxalate.[4] Although sufficient product in each case was obtained to characterize the compounds and to form one or two derivatives, the yields were extremely poor, as they amounted only to about one per cent. of the theoretical.

Kogl used a second method of synthesis also which consisted in preparing diphenylquinone or p-hydroxyphenylquinone by the method of Pummerer[5] and then in introducing methoxyls adjacent to the carbonyl groups of the quinone by heating with zinc chloride in methyl alcohol. Upon demethylation of the ethers the two natural coloring matters were obtained Even by this procedure, however, the introduction of the methoxyl groups resulted in such low yields that these syntheses may be considered valuable only so far as the identification of structure is concerned.

During recent work on substituted diphenylquinones in connection with the stereochemistry of diphenylbenzenes, it was noticed that diaryldibromoquinones were easily hydrolyzed to the corresponding hydroxy derivatives. This procedure has now been applied to the synthesis of polyporic acid and atromentin dimethyl ether with the result that the compounds were prepared with ease in excellent yields.

Diphenylhydroquinone (III) was prepared by the general procedure of Pummerer but with such changes in detail as to increase the yield seven-fold to about 65%. This was then brominated to diphenyldibromohydroquinone (IV) and the latter oxidized to diphenyldibromoquinone (V). Upon hydrolysis of this product, the corresponding dihydroxyquinone was obtained which was polyporic acid (I). Each of the steps involved in the process just mentioned resulted in yields of 90% or better.

Acetylation of the diphenyldihydroxyquinone gave an acetyl derivative which analyzed correctly for the diacetate and agreed as to melting point with the diacetylpolyporic acid prepared by Kögl.[3] The corresponding diacetylhydroquinone and tetraacetate were also prepared.



III → IV → V → I

In a similar manner anisole was condensed with quinone to dianisylhydroquinone (VI). Upon treatment with bromine in glacial acetic

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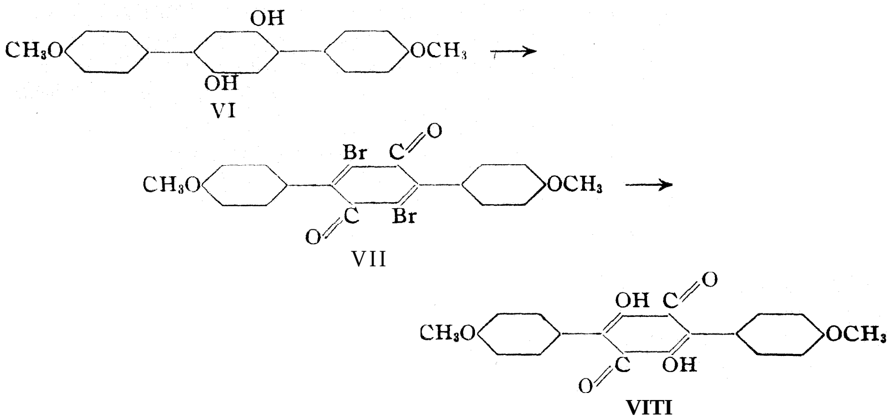
[4] Kogl and Becker, Ann., 465, 251 (1928).

[5] Pummerer and Prell, *Ber.*, 55, 3108 (1922).

acid, bromination and oxidation took place simultaneously and di-(p-methoxyphenyl)-dibromoquinone (VII) was produced. This in turn was hydrolyzed with aqueous sodium hydroxide to the dimethyl ether of atromentin (VIII).



Experimental

2,5-Diphenylquinone.—To a suspension of 300 g. of finely powdered anhydrous aluminum chloride in 500 cc. of dry benzene in a 2-liter three-necked flask equipped with a mechanical stirrer, 500-cc. separatory funnel, thermometer and reflux condenser was slowly added with stirring a solution of 100 g. of pure benzoquinone in 1000 cc. of dry benzene. Heat was evolved and the rate of addition was regulated to maintain the reaction mixture at a temperature of 35–40°. The addition required two to three hours. Stirring was continued for five hours thereafter and the temperature allowed to drop to that of the room.

The reaction product was decomposed by pouring it slowly onto a mechanically-stirred mixture of 2 kg. of ice and 250 cc. of concentrated hydrochloric acid. Stirring was continued until a light brown emulsion was formed and no lumps of undecomposed material remained. The benzene was removed by steam distillation. The residual light brown solid was definitely granular and was readily separated by filtration. It was washed with hot water and air-dried. The yield of dry material was 140 g., green in color and obviously a mixture of quinones, hydroquinones and quinhydrones.

To obtain the yellow crystalline diphenylquinone, the crude reaction product was oxidized carefully in a hot glacial acetic acid solution with chromic acid, but since any excess chromic acid over that required to oxidize hydroquinones and quinhydrones in the crude product to the quinone state will rapidly oxidize the terphenyl molecule to benzoic acid, it was necessary to determine beforehand the amount of chromic acid to be used per unit weight of the crude material. This was carried out as follows.

Three 1-g. samples of the crude product were accurately weighed out and placed in 50-cc. Erlenmeyer flasks. To the first flask was added 0.100 g. of chromic acid; to the second 0.133 g. and to the third 0.150 g. To each flask was then added 25 cc. of glacial acetic acid. Each was heated to boiling for two to three minutes and filtered hot. The first filtrate was a definite mixture of yellow quinone plates and dark green quinhydrone needles; the second showed only yellow plates of the quinone at first but the dark colored quinhydrone crystallized later as a fringe around the upper edge of the solution, and the third filtrate exhibited only the yellow plates of the quinone even on long standing.

The remaining 137 g. of crude product was placed in a 5-liter round-bottomed flask with 3 liters of glacial acetic acid and 21 g. of chromic acid and rapidly heated to boiling. The solution was immediately filtered through a large fluted filter, the filtrate cooled for two to three hours under the tap and then filtered through a Büchner funnel. The mat of yellow flakes was washed first with water, then with 150 cc. of 50% ethyl alcohol. The yield of air-dried material amounted to 51 g. and it melted at 210–212° (corr.). It was pure enough to be used for further preparations. A single recrystallization from either benzene or glacial acetic acid yielded the pure substance melting constantly at 214° (corr.). An additional 7 g. of pure material was obtainable from the mother liquors, bringing the total yield up to 58 g. (72%).

2,5-Diphenylhydroquinone (II).—In a 1-liter round-bottomed flask was placed a mixture of 500 cc. of glacial acetic acid, 25 g. of diphenylquinone and 50 g. of powdered zinc. The mixture was stirred for one hour without external heating and then refluxed for thirty minutes. The solution was filtered hot and the solid material on the filter washed with two 50-cc. portions of warm glacial acetic acid, the washings being added to the filtrate. The filtrate was transferred to a 3-liter round-bottomed flask equipped with a reflux condenser and heated to boiling. Hot water was added slowly through the condenser until the white hydroquinone crystallized from the boiling solution. A few hundred cc. more of water may be slowly added if desired to complete the precipitation of the product and the filtrate then cooled. It was filtered and the product washed with hot water. The pale straw-colored air-dried material amounted to 23 g. and was sufficiently pure to be used for the next step. A single recrystallization from either chloroform or dilute ethyl alcohol yielded white needles melting constantly at 225° (corr.).

2,5-Diphenyl-3,6-dibromohydroquinone (IV).—To a 1-liter three-necked flask, equipped with a mechanical stirrer, thermometer, 125-cc separatory funnel and outlet tube, was added 400 cc. of chloroform and 20 g. of diphenylhydroquinone. The stirrer was started and the contents of the flask cooled to 10° by external cooling. Through the separatory funnel was then added rapidly a solution of 39 g. of bromine in 50 cc. of chloroform. At first a heavy dark crystalline precipitate, presumably the quinhydrone, appeared which later dissolved to a clear orange solution. The solution was stirred for eight hours at room temperature.

The solvent was removed under reduced pressure, avoiding a temperature above 30°. The light yellow solid remaining was refluxed with 1500 cc. of 95% ethyl alcohol and 20 g. of stannous chloride until a clear pale yellow solution was obtained. Dilute hydrochloric acid (6 N) was added slowly to the boiling solution until needles of the white hydroquinone appeared. The solution was chilled to 0° and filtered. The mat of white needles was washed with 6 N hydrochloric acid, followed by hot water and then air-dried; yield, 29 g. (90%).

The product as obtained was quite pure. A single recrystallization from 95% ethyl alcohol yielded long, slender white needles melting constantly at 237° (corr.).

Anal. (Parr bomb). Calcd. for $C_{18}H_{12}O_2Br_2$: Br, 38.10. Found: Br, 38.44.

2,5-Diphenyl-3,6-dibromoquinone (V).—A mixture of 25 g. of the diphenyldibromohydroquinone, 1 liter of 95% ethyl alcohol and 15 g. of benzoquinone was refluxed for one-half hour. The mixture was cooled and filtered. The orange crystalline quinone was washed free of benzoquinone on the filter with cold alcohol and air-dried; yield, 21 g. The product crystallized from *n*-butyl alcohol in slender orange needles melting constantly at 224°.

Anal. (Parr bomb). Calcd. for $C_{18}H_{10}O_2Br_2$: Br, 38.23. Found: Br, 38.03.

2,5-Diphenyl-3,6-dihydroxyquinone (I).—A mixture of 20 g. of the diphenyldibromoquinone, 1 liter of methyl alcohol and 1 liter of 10% sodium hydroxide solution was stirred mechanically for two hours at 40–50°. The purple solution was filtered and acidified with concentrated hydrochloric acid. One liter of water was added and the volume of solution reduced to one-half by evaporation on a hot-plate. This boiling and concentrating served to coagulate the brown precipitate material and to remove a considerable amount of alcohol, all of which aided subsequent filtration. The filtered product after washing and drying amounted to 13 g. (92%).

The product may be crystallized from toluene––1.4 g. in 630 cc. of boiling toluene yielded 1.1 g. of bronze-colored plates melting with sublimation at 305° (obs.)—or purified through the diacetate as described below.

Anal. (Crystallized from toluene.) Calcd. for $C_{18}H_{12}O_4$: C, 73.85; H, 4.14 Found: C, 73.61, 73.50; H, 4.11, 4.19.

2,5-Diphenyl-3,6-diacetoxyquinone.—A mixture of 10 g. of the dihydroxyquinone, 150 cc. of pyridine and 150 cc. of acetic anhydride was refluxed for two minutes and then poured with stirring into a mixture of 1500 cc. of water and 250 cc. of concentrated hydrochloric acid. The light yellow solid was filtered, washed and dried; yield, 11.5 g. (quantitative). A single recrystallization from benzene yielded yellow needles melting constantly at 215° (corr.).

Anal. Calcd. for $C_{22}H_{16}O_6$; C, 70.18; H, 4.29. Found: C, 70.09; H, 4.30.

Hydrolysis of the **Diacetoxyquinone.**—A solution of 5 g. of the diacetoxy derivative in 150 cc. of glacial acetic acid was heated to boiling under a reflux condenser. Through the condenser was added 40 cc. of 6 N hydrochloric acid and refluxing continued for thirty minutes. The hydroxyquinone crystallized from the boiling solution in bronze-colored flakes. If the mixture was cooled before filtering, the recovery of material was nearly quantitative — 4.2 g. The product melted at 305° (obs.) with sublimation and was otherwise identical with that obtained by crystallization from toluene.

2,5-Diphenyl-3,6-diacetoxyhydroquinone.—A solution of 3.35 g. of the diacetoxyquinone and 7 g. of stannous chloride in 200 cc. of acetone was gently refluxed for ten to fifteen minutes. The original yellow solution was almost completely decolorized. Through the condenser was added 25 cc. of 6 N hydrochloric acid and heating continued for two to three minutes. The flask was removed, 200 cc. of 3 *N* hydrochloric acid added at once and the solution immediately cooled to 15–20°; yield of slender white needles, 3.2 g. Two crystallizations from n-butyl alcohol gave a white product consisting of minute needles and melting constantly at 246° (corr.).

Anal. Calcd. for $C_{22}H_{18}O_6$: C, 69.81; H, 4.80. Found: C, 70.10; H, 4.95.

2,5-Diphenyl-1,3,4,6-tetraacetoxybenzene.—Acetylation of 2 g. of the diacetoxyhydroquinone with pyridine and acetic anhydride in the usual manner gave a quantitative yield of the crude material (2.45 g.). Two crystallizations from n-butyl alcohol yielded minute white needles melting constantly at 267–268° (corr.).

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.50; H, 4.80. Found: C, 67.33; H, 4.79.

2,5-Di(*p*-methoxyphenyl)-hydroquinone, VI.—The corresponding quinone was prepared from benzoquinone and anisole according to the directions of Pummerer and Prell.[5] The hydroquinone was obtained by reduction with stannous chloride and hydrochloric acid in acetone solution.

A mixture of 20 g. of the dianisylquinone, 40 g. of stannous chloride and 600 cc. of acetone was stirred for one hour at room temperature. Heat developed, the red quinone disappeared and the resulting bluish-green solution deposited small lustrous white plates of the hydroquinone. If cooled to 0° and allowed to stand for two to three hours, the yield of practically pure product was 16–17 g. A single recrystallization from acetone containing a trace of stannous chloride and hydrochloric acid yielded a pure white product melting constantly at 210° (corr.).

2,5-Di-(*p*-methoxyphenyl)-3,6-dibromoquinone, VII.—A solution of 8.5 g. of dianisylhydroquinone in 4.5 liters of glacial acetic acid was prepared by gentle heating and stirring on the steam-bath. The warm solution was cooled to 25". To this was added with stirring a solution of 17 g. of bromine in 100 cc. of glacial acetic over a period of one hour. The red solution was slowly stirred for forty-eight hours during which time a small crop of dark reddish-brown needles separated. (The dianisylquinone, produced by oxidation with bromine of the hydroquinone in cold glacial acetic acid solution, separates in bright red silky needles easily distinguished from the darker colored brominated product.) Stirring was then discontinued and the solution allowed to stand at 15" or a few degrees lower for three to four days. The needles were filtered off and washed with cold methyl alcohol; yield 5.7 g. Three crystallizations from glacial acetic acid, using 125 cc. per gram of substance, gave a reddish-brown product melting with decomposition constantly at 282–283° (corr.).

Anal. Calcd. for $C_{20}H_{14}O_4Br_2$: Br, 33.44; C, 50.21; H, 2.95. Found: Br, 33.75; C, 50.66; H, 3.12.

This substance crystallized unchanged in m. p. or appearance from acetic anhydfide, pyridine, or a mixture of the two.

2,5-Di-(*p*-methoxyphenyl)-3,6-dihydroxyquinone (Atromentin Dimethyl Ether), VIII.—A mixture of 1.7 g. of the dibromodianisylquinone in a solution consisting of 170 cc. of methyl alcohol and 170 g. of 10% sodium hydroxide was stirred at room temperature for forty-eight hours. The dibromoquinone was nearly completely replaced by the purple sodium salt of the corresponding dihydroxyquinone. The mixture was filtered and the filtrate, being nearly colorless, was set aside. The sodium salt was separated from the unreacted starting material on the filter by pouring repeatedly over it 500 cc. of cold water. The permanganate-colored filtrate was acidified with acetic acid and heated to boiling. The brown flocculent precipitate was filtered with gentle suction and washed with hot water. It was redissolved on the filter with 500 cc. of cold 2% sodium hydroxide, reprecipitated with acetic acid, filtered, washed and dried as before; yield of air-dried material 1.0 g. (80%). Two crystallizations from toluene, using 500 cc. of toluene per gram of substance, gave minute, glistening, bronze-colored plates melting with decomposition constantly at 297–298° (corr.) and free of halogen.

Anal. Calcd. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 67.65, 67.72; H, 4.66, 4.60.

2,5-Di-(*p*-(*n*)-butoxyphenyl)-quinone.—To a solution of 10.8 g. of benzoquinone and 15 g. of n-butyl phenyl ether in 150 cc. of dry carbon disulfide maintained at 0–5° with an ice-bath, 27 g. of anhydrous aluminum chloride was slowly added with vigorous stirring. The addition required about thirty minutes and the mixture was stirred for four hours longer. The reaction mixture was decomposed by pouring onto ice and dilute hydrochloric acid. The carbon disulfide was steam distilled out and the residual black solid material crystallized from 1 liter of n-butyl alcohol to which was previously added 2 g. of norite and 3 g. of benzoquinone; yield of yellow flakes, 4 g. Recrystallization from 50 cc. of toluene gave 3.2 g. of similar crystals melting constantly at 173° (corr.).

Anal. Calcd. for $C_{26}H_{28}O_4$: C, 77.18; H, 6.98. Found: C. 77.02; H, 6.99.

Summary

1. Polyporic acid and atromentin dimethyl ether have been prepared by new procedures in excellent yields.

2. Diphenylquinone from the condensation of benzene and quinone was reduced to diphenylhydroquinone. This was in turn brominated to diphenyldibromohydroquinone and the latter, after oxidation to the

corresponding quinone, was hydrolyzed to diphenyldihydroxyquinone (polyporic acid).

3. In a similar manner atromentin dimethyl ether was produced from dianisylquinone, the condensation product of anisole and quinone.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. VII. CONDENSATION OF BENZYL ALCOHOL WXTH PARA-CRESOL

BY R. C. HUSTON AND W. C. LEWIS

RECEIVED APRIL 22, 1931 PUBLISHED JUNE 8, 1931

Para-cresol and benzyl alcohol in the molecular ratio of 2 to 1 dissolved in petroleum ether and treated with **0.5** mole of aluminum chloride gave a condensation product which upon fractional distillation yielded *35%* of crude mono and 36% of crude dibenzylated p-cresol. When the reactants were used in the ratio of **3** to 1, with the same amount of aluminum chloride. the yields were **53** and 30%, respectively. Crystallization of the monobenzylated *p*-cresol from petroleum ether in the cold gave transparent needles melting at 35–36°. The dibenzylated p-cresol did not crystallize.

These compounds were found to agree in properties with those prepared by Claisen[1] by the action of benzyl chloride on the sodium salt of p-cresol in toluene, except that he did not obtain the monobenzyl derivative in crystal form.

The 2-benzyl-4-methylphenol was easily soluble in dilute potassium hydroxide and when treated with the calculated amount of benzoyl chloride gave the ester. **As** was anticipated, the 2,6-dibenzyl-4-methylphenol was not soluble, even in strong potassium hydroxide, but formed a solid. This, however, treated with benzoyl chloride reacted to produce the ester.

Bromination of 2-benzyl-4-methylphenol in chloroform gave 2-benzyl-4-methyl-6-bromophenol. This configuration **was** proved by preparing the **same** compound by benzylating 4-methyl-6-bromophenol by the Claisen reaction. In addition a small amount of 4-methyl-6-bromophenyl benzyl ether was obtained,

The monobenzylated p-cresol **was** further characterized by preparing benzene sulfonic and toluene sulfonic esters by the pyridine method.

Experimental

Benzyl Alcohol and *p*-Cresol with Aluminum Chloride.—A mixture of 108 g. of p-cresol, 54 g. of benzyl alcohol and 75 g. of petroleum ether (40–60°) was placed in a tall cylinder and stirred mechanically while adding 33 g. of anhydrous aluminum chloride in small portions over a period of one hour. The temperature was kept below 30".

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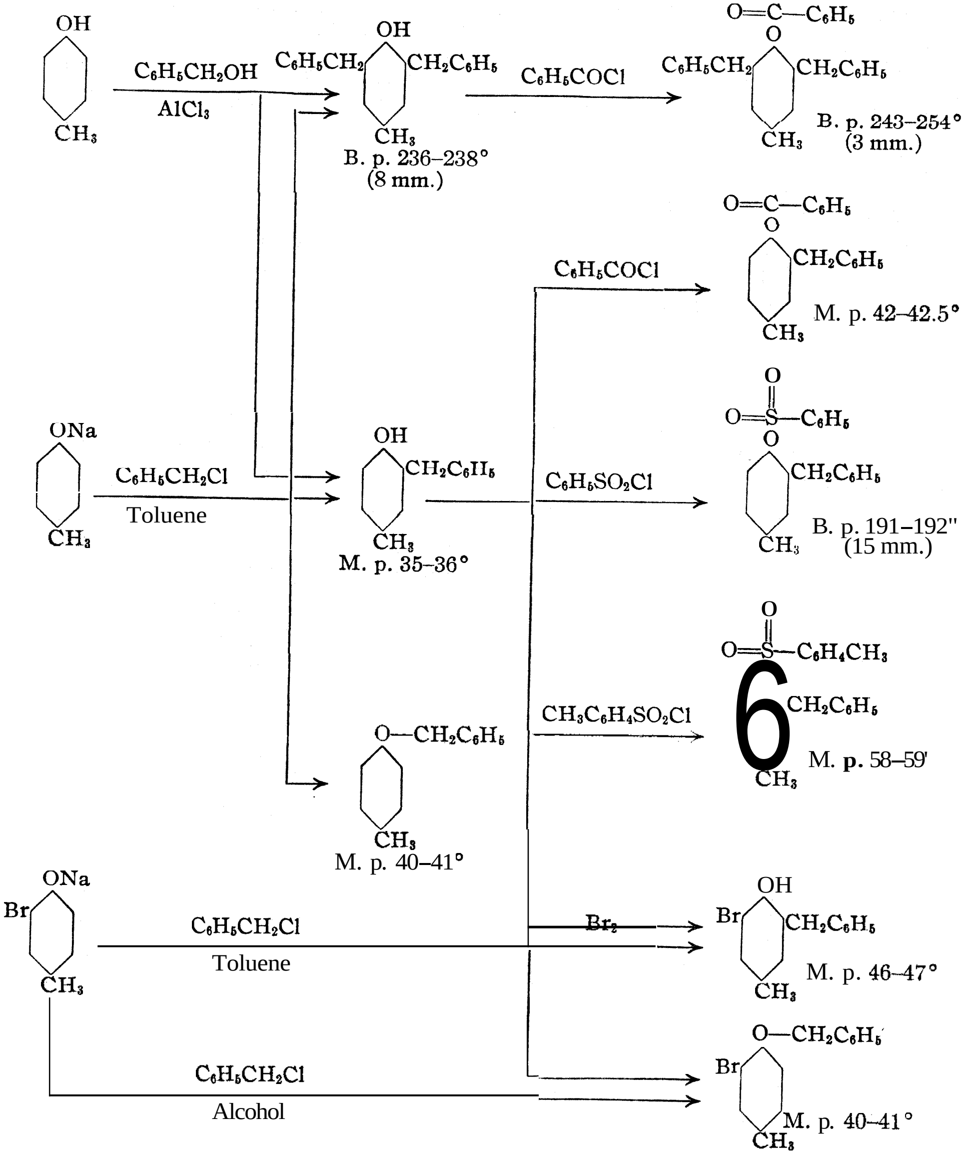
[1] Claisen, *Ann.*, 442,210 (1925).



Hydrogen chloride gas was freely evolved. The mixture was allowed to stand overnight and then decomposed with ice and a little hydrochloric acid. The white oily product was extracted with ether. After distilling off the ether the residue was fractionated at 10 mm. The third fractionation gave:

Up to 100°	61.5 g. (*p*-cresol)
165–185°	34.0 g.
185–250°	25.5 g.

The 165–185° fraction crystallized when seeded and placed in the cold. Recrystallization from petroleum ether gave transparent, prismatic crystals that melted at 35–36°.

Anal. Subs., 0.1508: CO_2, 0.4695; H_2O, 0.0980. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.12. Found: C, 84.93; H, 7.27.

From the 185–250° fraction there was isolated a portion which boiled at 236–238° (8 mm). This was a viscous liquid that did not crystallize, and was assumed to be 2,6-dibenzyl-4-methylphenol.

Anal. Subs., 0.1732: CO_2, 0.5553; H_2O, 0.1068. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 6.99. Found: C, 87.41; H, 6.63.

Preparation of **2-Benzyl-4-methylphenol, 2,6-Dibenzyl-4-methylphenol** and **4-Methylphenyl Benzyl** Ether by the Claisen Method.—Using half molar quantities of p-cresol, sodium and benzyl chloride in three runs gave an average of 40 g. of 2-benzyl-4-methylphenol, m. p. 35–36°, and 11.8 g. of 2,6-dibenzyl-4-methylphenol, b. p. 236–238° (8 mm.). The petroleum ether extract from the above condensations gave an average of 6 g. of 4-methylphenyl benzyl ether, recrystallized from alcohol, m. p. 40–41°.

Preparation of Benzoyl Esters.—Employing the Schotten–Baumann reaction, 21 g. of 2-benzyl-4-methylphenol, 6.97 g. of potassium hydroxide in 20 cc. of water and 14.82 g. of benzoyl chloride gave a white oil which boiled at 205–206° (5 mm.). After long standing, it crystallized. Recrystallization from alcohol gave transparent plates, m. p. 42–42.5°.

Anal. Subs., 0.1008: CO_2, 0.3056; H_2O, 0.0541. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.33; H, 6.03.

The 2,6-dibenzyl-4-methylphenol was treated with strong (50%) potassium hydroxide. The resulting solid was filtered off and treated with the calculated amount of benzoyl chloride. Heat was evolved and a yellowish oil was formed which was washed with dilute alkali and water, b. p. 243–245 (6 mm.).

Anal. Subs., 0.2300: CO_2, 0.7200; H_2O, 0.1342. Calcd. for $C_{28}H_{24}O_2$: C, 85.67; H, 6.168. Found: C, 85.35; H, 6.43.

Preparation of Sulfonyl Esters.—By the pyridine method, 5 g. of 2-benzyl-4-methylphenol, 12.5 g. of pyridine and 4.5 g. of benzene sulfonyl chloride gave a viscous yellowish-red liquid, that boiled at 190–192° (2 mm.) and did not solidify.

Anal. Subs., 0.1029: $BaSO_4$, 0.0739. Calcd. for $C_{20}H_{18}SO_3$: S, 9.47. Found: S, 9.86.

By the same method, 5 g. of 2-benzyl-4-methylphenol, 12.5 g. of pyridine and 4.8 g. of toluene sulfonyl chloride gave a crystalline product. Recrystallization from petroleum ether gave transparent rhombohedra, m. p. 58–59°.

Anal. Subs., 0.1000 g.: $BaSO_4$, 0.0676. Calcd. for $C_{21}H_{20}SO_3$: S, 9.1. Found: S, 9.28.

Preparation of the Monobromo Derivative.—Addition of the calculated weight of bromine to 15 g. of 2-benzyl-4-methylphenol dissolved in chloroform produced 2-benzyl-4-methyl-6-bromophenol. Crystallization from about 85% alcohol gave a white silky felt-like product melting at 46–47°.

Anal. Subs., 0.1000: cc. of 0.1 N $AgNO_3$, 3.6. Calcd. for $C_{14}H_{13}OBr$: Br, 28.84. Found: 28.771.

One-half mole of 6-bromo-p-cresol dissolved in toluene and treated with sodium and benzyl chloride by the Claisen method gave a product identical in crystal form and melting point with that obtained by brominating 2-benzyl-4-methylphenol.

From the petroleum ether extract in the above condensation there was isolated a small amount of 4-methyl-6-bromophenyl benzyl ether. Crystallization from strong alcohol gave transparent rhombohedra, m. p. 40–41°.

Anal. Subs., 0.1015: cc. of 0.1 *N* $AgNO_3$, 3.68. Calcd. for $C_{14}H_{13}OBr$: Br, 28.84. Found: Br, 29.03.

Summary

Para-cresol was benzylated by both the Claisen and the aluminum chloride methods and the yields were compared.

Bromination of 2-benzyl-4-methylphenol gave 6-bromo-2-benzyl-4-methylphenol, which was also prepared from 6-bromo-4-methylphenol by the Claisen reaction.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES. V. THE STRUCTURE OF CHLOROPHYLL A

BY J. B. CONANT, EMMA M. DIETZ, C. F. BAILEY AND S. E. KAMERLING

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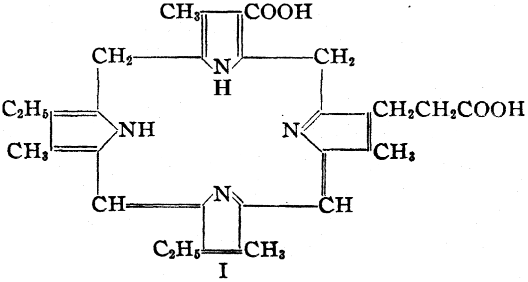
The experiments reported in the fourth paper of this series[1] indicated that chlorophyll a and the closely related compound phaeophorbide a contained the grouping $-\mathrm{CHOH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-$. In allomerization or "phase test saponification," we supposed that this structure was transformed into the a-ketonic acid grouping which was subsequently easily removed as potassium oxalate by boiling the compounds with alkali. The resulting simple chlorin, chlorin *f*, was thus to be regarded as a partially hydrogenated rhodoporphyrin. It was uncertain whether the two hydrogen atoms which were removed from the secondary alcohol group were transferred to some other molecule or intra-molecularly to a pyrrole ring. A further study[2] has shown that the first alternative is correct and that the dehydrogenating agent is oxygen of the air. The structure of chlorin f is therefore that of a dihydrorhodoporphyrin (I); this formula replaces



I

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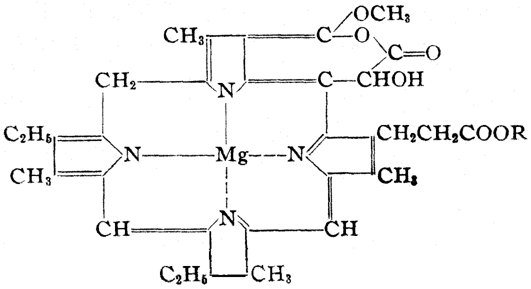
[1] THIS JOURNAL, 53, 359 (1931). For other papers of this series see *ibid.*, 51, 3668 (1929); 52, 1233, 3013 (1930).

[2] A brief statement of these results was given in a letter to the editor, THIS JOURNAL, 53, 1615 (1931). The corresponding experiments are recorded in this present paper except for the study of the phase test, which will form a separate paper by Miss C. C. Steele.

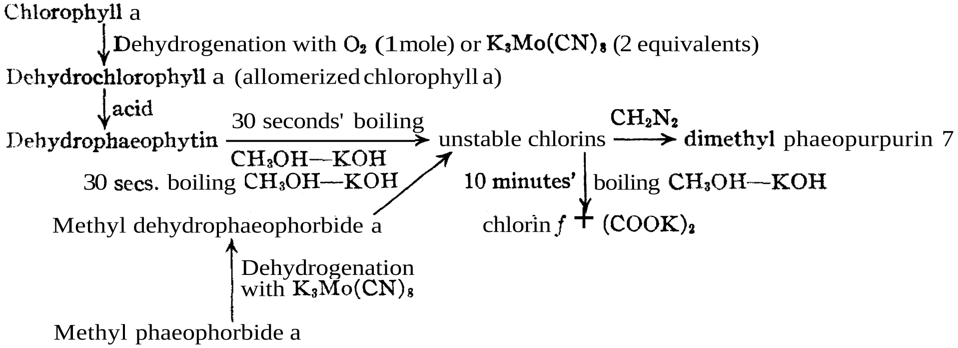
the one given in our previous paper. The position of the double linkages is arbitrary and many tautomeric modifications of Formula I may be written. The quantitative dehydrogenation of this simple chlorin is now being studied in order to throw more light on such problems.

We are now in a position to write a structural formula for chlorophyll *a* with some assurance. Such a formula is given below (II) R = phytyl, and the recent evidence is summarized in the accompanying diagram.



II

The corresponding formulas for methyl phaeophorbide *a* and phaeophorbide *a* are obtained by letting R = CH_3 and H, respectively, and substituting two hydrogen atoms for the magnesium atom.[3]



We may briefly review the arguments for Formula II for chlorophyll *a* and related compounds. The skeleton structure of chlorin *f* follows from its easy conversion to rhodoporphyrin (paper IV) whose structure has been established by Fischer by synthesis. From the above diagram it is clear that the nucleus of dehydrochlorophyll *a* is chlorin *f* plus the oxalic acid grouping; this agrees in the number of carbon atoms with the analyses of methyl phaeophorbide, etc. (paper III, p. 3016). Two mole-

[3] The distinction indicated by the heavy and dotted lines from the magnesium is only useful in showing that two hydrogen atoms are replaced by the metal; there is no reason, of course, to believe that there is a real difference between any of the four coordinate links.

cules of potassium molybdicyanide (a powerful oxidizing agent) are involved in the dehydrogenation of chlorophyll *a* (or methyl phaeophorbide *a*). This fact, together with the formation of potassium oxalate on alkaline decomposition of the dehydro compounds, shows the presence of an esterified or otherwise masked a-hydroxy acid group in the original molecule. The methoxyl group of chlorophyll *a* is attached to the β-position of a pyrrole ring because the transformations described in the fourth paper yielded a monomethyl ester of chlorin f which, unlike chlorin f itself (a dibasic acid), does not readily lose carbon dioxide on heating. The well-known relationship of chlorophyll *a* to phaeophorbide *a* shows that the phytyl group is attached to the acid group which is free in the latter compound. This is the propionic acid residue since on pyrolysis of phaeophorbide *a* this acid group is not eliminated as carbon dioxide (paper I).

The position of the $-\mathrm{CHOH}-\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup\mathrm{O}}{\diagdown\mathrm{OH}}$ group and the masking of its acidic hydrogen remain to be considered. The latter necessity arises from the fact that phaeophytin *a* and methyl phaeophorbide *a* are only di-esters although they contain three potential carboxyl groups The analyses of methyl phaeophorbide *a* indicate six oxygen atoms; the masking of one carboxyl group as a lactam (but not as a lactone) or as an anhydride (as shown in Formula II) is consistent with these analyses. The second alternative seems preferable to us because on pyrolysis phaeophorbide *a* loses carbon dioxide and methyl alcohol, the methoxyl group being destroyed (see experimental portion of this paper). This points to a close interconnection of the masked carboxyl group and the carboxyl group in the β-position of the pyrrole ring, the propionic acid group being free. We therefore write Formula II, placing the CH_2 link arbitrarily, there being at present no direct evidence in regard to this portion of the molecule.[4]

The analyses of chlorin e correspond to Formula III, as do its transformations into pyrochlorin e described in the last paper. It is rapidly oxidized by potassium molybdicyanide (two equivalents are involved)

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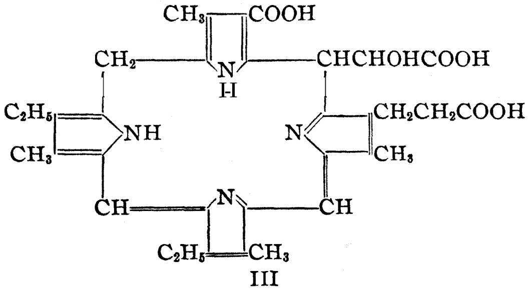
[4] Since this paper was sent to the editor, an article by Fischer, Moldenhauer and Süs [*Ann.*, 486, 107 (1931)] has appeared on the same subject. These authors write a structural formula for chlorophyll *a* (largely based on their investigation of phylloerythyrin) which is very different from the one proposed in the present paper. The chief differences are as follows: they consider the chlorophyll nucleus to be an oxidized porphyrin ring instead of a partially reduced porphyrin as we have postulated; they write a five-membered carbon ring joining one pyrrole ring to the bridge, a tertiary hydroxyl (instead of a secondary in our formula) and the phytyl and methyl groups in different positions. Without going into a long discussion of this new paper, we can only say that we do not believe that the formula for chlorophyll *a* there proposed is capable of explaining the dehydrogenation reactions and certain other transformations described in this and our previous papers.

and like all a-hydroxy acids loses carbon dioxide during the oxidation.[6] The resulting chlorin (designated hereafter as chlorin *k*) gives a monomethyl ester on treatment with diazomethane. Presumably the aldehydic group formed by the oxidation has closed a lactone ring with a carboxyl group. The further transformations of chlorin k will be reported in detail in a later paper. The trimethyl ester of chlorin e (formed by the action of diazomethane) unlike the parent compound is not oxidized by potassium molybdicyanide. This fact together with the analyses, which show a loss of water during the esterification, indicate a lactone formation between a carboxyl and the hydroxyl of the $—CHOHCOOCH_3$ group; enolization would account for the ability to form a trimethoxyl derivative.



III

The unstable chlorins appear to be a tribasic acid and its monomethyl ester corresponding to the removal of the two hydrogen atoms of the CHOH group of chlorin *e*. (They are chlorin f + $—\overset{O}{\overset{\|}{C}}—COOH$.) The nature of their transformation into the phaeopurpurins has not yet been established with certainty and a discussion of the structure of the latter will be postponed. Although they are important as a method of characterizing the dehydro series, the details of their structure are not involved in the evidence which leads to Formula II for chlorophyll a. As would be expected, the phaeopurpurins and methyl dehydrophaeophorbide are not oxidized by potassium molybdicyanide. It may be mentioned that methyl phaeophorbide b is more rapidly oxidized than the corresponding *a* compound. A study of the b series from the point of view presented in this paper is now in progress.

Methyl dehydrophaeophorbide *a* is a crystalline compound which can be purified and studied in the usual way; it differs only slightly in its visible absorption spectrum from the unoxidized compound. However, in the near ultraviolet there is considerable difference (Fig. 1). In studying chlorophyll a itself we have been forced to use spectroscopic methods and chemical transformations since the amount of material at

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[6] It may be noted that phaeophorbide *a* (a free acid) on oxidation does not lose carbon dioxide but behaves exactly like its methyl ester. This is additional proof that the phytyl group is not on the bridge carboxyl.

our disposal was small and the compounds containing the phytyl group crystallize with difficulty. The absorption spectra in the near ultraviolet of the compounds are given in Fig. 2. It will be seen that the dehydrochlorophylls prepared with oxygen (allomerization) or with molybdicyanide are identical (curve B) and differ from chlorophyll a (curve A) as methyl dehydrophaeophorbide differs from methyl phaeophorbide. However, there is a difference in the absorption spectrum of dehydrochlorophyll *a* in the visible according to whether oxygen or molybdicyanide is used in the preparation. This difference amounts to some 40 Å. in the position of the band at 662 mμ and the same amount of shift at 530 mμ is found in the corresponding dehydrophaeophytins. The com-

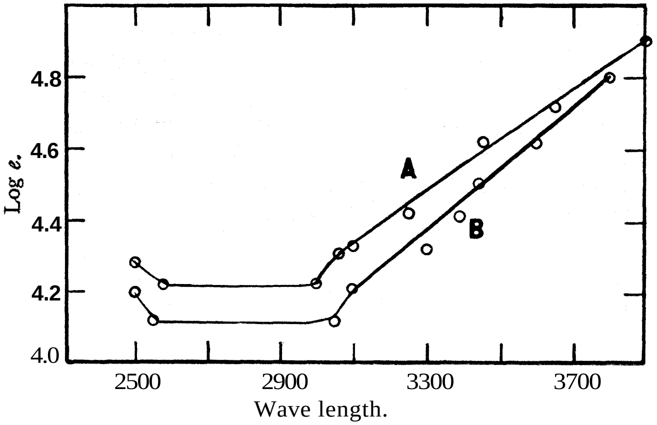

Fig. 1.—Log extinction coefficient–wave length curves for: A, methyl phaeophorbide *a*; B, methyl dehydrophaeophorbide *a*.

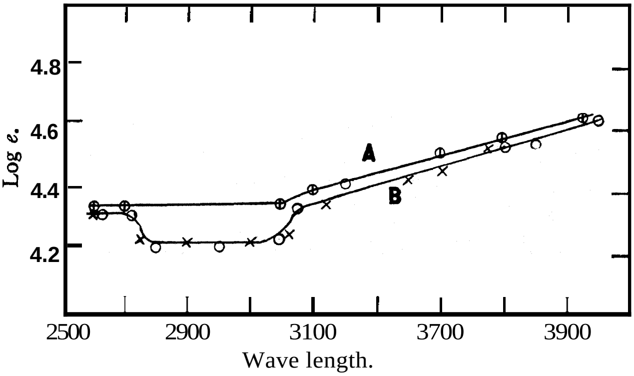

Fig. 2.—Log extinction coefficient–wavelength curves for: A, chlorophyll a; B, X X X, allomerized chlorophyll a; ○○⊖, dehydrochlorophyll a.

pound prepared with oxygen is the one which resembles dehydrophaeophorbide in regard to the position of this one band which represents a shift from phaeophorbide *a* itself. Since the chemical transformations of the two dehydrochlorophylls are the same, and they are both formed by the removal of two hydrogen atoms, any difference between them must he slight. We cannot be certain at present whether we are dealing with a subtle isomeric shift or the presence of an impurity in the material made with molybdicyanide.

The possible significance of the easily oxidized group $-\mathrm{CHOHC}\overset{\mathrm{O}}{/\!\!/}-$ in chlorophyll from the point of view of photosynthesis has been discussed in a brief note[6] and will be considered in more detail in a later paper of this series.

We are indebted to Miss Helen F. Hawes for carrying out the microanalyses reported in this paper.

Experimental

Quantitative Dehydrogenation Experiments with Potassium Molybdicyanide.—The molybdicyanide reagent was freshly prepared before each set of experiments as follows:[7] 5 cc. of 0.06 M $K_4Mo(CN)_8$ and 0.7 cc. of glacial acetic acid were mixed and approximately 0.1 *N* potassium permanganate added drop by drop until present in very slight excess; the mixture was then made up to a total volume of 10 cc. In each experiment approximately 10^{-5} mole of compound (accurately weighed) was dissolved in 5 cc. of acetone containing enough anhydrous pyridine to be molar with respect to this base. One cc. of the molybdicyanide reagent was then added, the time noted and the mixture made up to 10 cc. with more molar pyridine in acetone. Definite samples (1 cc. or 0.7 cc.) were withdrawn from the reaction mixture from time to time, diluted with 5-fold aqueous acetate buffer solution and the molybdicyanide content determined by electrometric titration with 0.001 M $K_4Fe(CN)_6$ using a micro-buret and a very small titration vessel. The end-point is very sharp even at these high dilutions and the accuracy is determined by the error in sampling (about ±5%). With each set of experiments a "control experiment" was carried out, by introducing 1 cc. of the same reagent into the pyridine–acetone solution, making the volume exactly 10 cc. and withdrawing a sample at the same time as the samples were withdrawn from the various reaction mixtures. There was very little change in the control titration even after twenty-four hours but it was deemed best to correct for this change by taking the extent of reduction of the molybdicyanide as being the difference between the "control titration" and the titration of the reaction mixture. A typical experiment was as follows: 4.97 mg. of methyl phaeophorbide a plus 1 cc. of molybdicyanide reagent (prepared as described above, approximately 0.03 M) in molar pyridine in acetone with a total volume of 10 cc.; the control was exactly like the experiment but the methyl phaeophorbide *a* was omitted. The titrations of 0.7-cc. samples with 0.001 M $K_4Fe(CN)_6$ were as follows: 20 min. control 1.65 cc., reaction 1.42, diff. 0.23; 90 min. control 1.65 cc., reaction 1.30, diff. 0.35; 390 min. control 1.65 cc., reaction 0.75, diff. 0.90; 1400 min. control 1.49 cc., reaction 0.50, diff. 1.04; since the 4.97 mg. of methyl phaeophorbide a is 8×10^{-6}

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[6] Conant, Dietz and Kamerling, Science, 73, 1888 (1931).

[7] For the use of molybdicyanide in organic reactions, see Conant and Pratt, THIS JOURNAL, 48, 3229 (1926).

mole, two equivalents of oxidizing agent is 16×10^{-6} mole for the whole sample or 1.12 cc. for a 0.7-cc. sample. The extent of the reaction is thus 93% based on two equivalents after 1400 min., with an increase of only 13% in the last 1000 min.; the limit is clearly two equivalents per mole within the experimental error. To save space the other quantitative experiments may be summarized by giving the extent of the reaction based on two equivalents at each time: ***chlorophyll a:*** 12 min. 67%; 60 min. 87%; 400 min. 110%; ***chlorin e:*** 30 min., 90%; 90 min., 96%; 390 min., 95%; 600 min., 99%; ***methyl phaeophorbide b:*** 30 min., 35%; 90 min., 66%; 390 min., 102%; 1400 min., 125%; ***dimethyl phaeopurpurin 7*:** none in 390 minutes; ***trimethyl ester chlorin e:*** none in 1400 minutes. In all these experiments at least three moles of reagent per mole of substance was employed. The rates are roughly reproducible if all the conditions are kept rigidly constant. The potassium molybdocyanide crystallizes on the sides of the container during the reaction since it is much less soluble than the molybdicyanide in acetone. This separation of the reduced reagent probably helps to keep the reaction proceeding at a definite pace as the oxidation potential of the solution is thus kept high throughout the experiment.

The Dehydrogenation of Chlorophyll a

(a) With Molybdicyanide.—Twenty-five milligrams of pure chlorophyll *a* were dehydrogenated as follows: 5 cc. of approximately 0.03 M $K_3Mo(CN)_8$ (prepared freshly as described above) was diluted with a molar pyridine solution in acetone to exactly 50 cc. Five cc. of this mixture was kept as the control and the 25 mg. of chlorophyll *a* added to the remainder (45 cc.); 0.7-cc. samples of the mixture and the control were titrated for oxidizing power with 0.001 M $K_4Fe(CN)_6$ as described above; after 400 minutes the titration corresponded to slightly more than 100%, compared with about 90% at the end of one hour. The mixture was then poured into water, extracted with ether and the ether layer repeatedly washed with water to remove pyridine and inorganic salts. The ether layer was finally dried over sodium sulfate and evaporated to dryness in *vacuo* leaving the dehydrochlorophyll as an amorphous wax. A solution of this in alcohol showed the following spectrum in the visible: principal absorption 678.5–653.0; weak absorption centers 615,568,531; E.A. 444. The ultraviolet extinction coefficient curve is given as B (circles) in Fig. 2. On removal of the magnesium by shaking an ethereal solution of this dehydrochlorophyll with dilute hydrochloric acid, a solution of dehydrophaeophytin was obtained which showed the following spectrum in the visible: I, 681.7–653.1; II, 615–604; III, 538.9–529.5; IV, 509.0–490.0; E.A., 439; Order I, IV, III, II. The hot rapid saponification of this dehydrophaeophytin by the usual Willstatter procedure (30 sec. with 35% methyl alcoholic potassium hydroxide) yielded no chlorin *e* but gave the unstable chlorins which were identified by conversion to dimethyl phaeopurpurin 7 with diazomethane (ether and acid spectrum identification). In another experiment, 7 mg. of pure chlorophyll *a* was dehydrogenated in the same manner as just described and the magnesium removed with acid. The resulting dehydrophaeophytin (as an amorphous wax) was treated with boiling methyl alcoholic potassium hydroxide (35%) and boiled for three minutes under a reflux. The reaction mixture was worked up in the usual way, being first methylated with diazomethane and then carefully acid fractionated. No chlorin e ester was obtained; the major product was identified spectroscopically in acid and ether as chlorin *f* ester. This was judged to be about 50% of the total; the other product was a porphyrin of acid number lower than 10. (The acid number of dimethyl chlorin *f* is 13.)

(b) With Oxygen (Allomerization).—The oxygen absorption during allomerization was demonstrated by using a modified Warburg apparatus.[8] A number of experiments

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[8] Hyde and Scherp, THIS JOURNAL, 52,3359 (1930).

were carried out, of which the following is typical. Pure chlorophyll ***a*** (9.03 mg., 0.01 millimole) was dissolved in 10 cc. of absolute ethyl alcohol (prepared by distillation from magnesium ethylate) and the solution immediately placed in one of the bottles of the absorption apparatus; the other bottle contained the corresponding amount of pure solvent. The apparatus was placed in a water-bath at 25° and shaken continuously; pressure readings were taken from time to time and the number of moles of gas absorbed calculated from a previously determined factor (1 cm. of manometer liquid = 0.0017 millimole of gas). The course of the reaction is indicated by the following figures, which give the millimoles of gas absorbed at different times: 1 hr., 0.0017; **3.3** hrs., 0.0037, 7.5 hrs., 0.0053; 31 hrs., 0.0088; 46 hrs., 0.0099. The reaction clearly proceeds at a progressively diminishing rate as illustrated by the fact that the rate in 10^{-6} mole per hr. is 1.7 for the first hour, 0.4 for the 3.3–7.5-hr. period and 0.075 for the period between the last readings. The limit is clearly one mole of oxygen per mole of chlorophyll, corresponding to the reaction chlorophyll ***a*** $+ O_2 \longrightarrow$ dehydrochlorophyll a $+ H_2O_2$.

As Willstatter emphasized, the rate of the process of allomerization is very sensitive to impurities. Since we now know that allomerization is a kind of autoxidation, this sensitivity to positive and negative catalysts is not surprising. We are planning a thorough study of this interesting problem. For the present, we may note that among the variables are the water content and the alkalinity. By using an amount of barium hydroxide corresponding to a 0.01 M solution, the rate of oxygen absorption was greatly accelerated. As would be expected dehydrochlorophyll prepared by the use of potassium molybdicyanide did not absorb any oxygen even after twenty hours of shaking.

The absorption spectrum in the visible of dehydrochlorophyll *a* prepared by the use of oxygen was as follows: principal absorption, 672.8–641; weak absorption centers, 608, 568, 528; E. A., 442. The corresponding dehydrophaeophytin spectrum **was** as follows: (identical with methyl dehydrophaeophorbide): I, 683.7–653.5; II, 6.16–604.5; 111,535.6–526.5; IV, 508.6–488.9; E. A. 436; Order: I, IV, III, II.

The ultraviolet absorption curve is given as B (crosses) in Fig. 2. The transformation of dehydrochlorophyll prepared with oxygen (*i. e.*, allomerized chlorophyll) into the unstable chlorins was described in the fourth paper.

Preparation of Methyl Dehydrophaeophorbide a.—A typical preparation was as follows. A solution of 2 g. of potassium molybdocyanide in a mixture of 120 cc. of water and 12 cc. of glacial acetic acid was oxidized with 0.1 M potassium permanganate solution, and the excess of oxidizing agent destroyed with a few milligrams of the reduced salt. The resulting yellow solution was mixed with 600 cc. of acetone and 80 cc. of dry pyridine, and the amorphous brown precipitate which formed was filtered out. Acetone was added to bring the total volume to 900 cc. and 25 cc. was removed at this point as a control for subsequent titration. Six hundred milligrams of methyl phaeophorbide ***a*** was then added and the solution shaken for several minutes. Titration of samples showed the reduction of 50% of two equivalents of oxidizing agent after one hour and 20% more than two equivalents after nineteen hours.

The solution was then filtered and one-third of the solvent was removed with a water pump at room temperature. The remaining solution was added to 3 liters of ether and the resulting olive-green ether solution was washed thoroughly with a total of ***3*** liters of water. The washings were a dark olive-brown in color and were thick with scum. This was filtered off and dissolved in a chloroform–acetone mixture, poured into ether and fractionated separately. Usually, the aqueous washings contained considerable material in colloidal form, which settled out only after standing several hours, preferably in the presence of sodium chloride or hydrochloric acid. Before acid fractionation, the alkali–soluble material was removed with 0.05 M potassium hydroxide. The fractionation **was** carried out with 500-cc. extracts of cooled acid, each being washed with two

500-cc. portions of ether. Five extracts of 14% hydrochloric acid removed some phaeopurpurin 7 and olive-brown material, which on standing for several days changed somewhat further, but not completely, into phaeopurpurin 7. The remaining solution was extracted exhaustively with eight 500-cc. portions of 17% acid, then with one of 18% acid,

The 16–17% fraction was estimated to contain 155 mg. by comparison with a standard solution in a Zeiss comparison spectroscope. After washing with alkali and concentrating the solution, 95 mg. crystallized. The homogeneity of the product was shown by its spectrum and by hot rapid saponification which yielded only the unstable chlorins, which were identified by conversion into dimethyl phaeopurpurin 7 with diazomethane.

Approximately 150 mg. of scum was obtained per gram of methyl phaeophorbide a used. This could not be avoided even by taking the solution to dryness in a vacuum desiccator and adding a pyridine solution of the residue to ether. The first 14% extracts were rose-brown in color and showed a marked phaeopurpurin 7 spectrum though they were alkali-insoluble. The material rendered alkali-soluble by acid hydrolysis during fractionation was converted by diazomethane to equal quantities of dimethyl phaeopurpurin 7 and methyl dehydrophaeophorbide a.

The purity of the various crops of crystals of methyl dehydrophaeophorbide a is best tested by examining the products of hot rapid saponification. As described by Willstatter, unchanged methyl phaeophorbide a goes mainly to chlorin e under these circumstances although some oxidation by the air seems unavoidable. However, dehydrophaeophorbide a, which is in the oxidized series, forms no chlorin e but goes to unstable chlorins, which on methylation with diazomethane yield dimethyl phaeopurpurin 7. The detection of chlorin lines in the spectrum of the 8% fraction of methylated saponification products probably indicates from 10–25% of methyl phaeophorbide a in the starting material. The absence of chlorin lines in the spectrum of the 8% fraction probably indicates that the fraction of unoxidized methyl phaeophorbide a is below 10%. The experimental conditions are as follows, and aim to exclude air oxidation of the sensitive methyl phaeophorbide a. Five milligrams of solid is warmed in a silver crucible with 0.1 cc. of dry pyridine, 7 cc. of boiling 35% potassium hydroxide in methyl alcohol is added and the boiling continued over a free flame for thirty seconds. The intensely green alkaline solution is washed into a separatory funnel and the product transferred by acidification to 75 cc. of ether. The aqueous layer is shaken with fresh ether to remove more completely the strongly basic chlorins. The combined ether solutions are washed, dried with sodium sulfate and treated with an ethereal solution of diazomethane.

An instantaneous change in color and spectrum occurs if unstable chlorins are present. Acid fractionation is carried out as usual. With unoxidized material, 8% hydrochloric acid extracts most of the product, namely, chlorin e ester. In the oxidized series, the main product, dimethyl phaeopurpurin 7, is removed by 11% acid, although there is always some chlorin *f* ester of slightly higher acid number, which results through further saponification of the unstable chlorins.

Methyl Dehydrophaeophorbide a.—This substance was recrystallized for analysis from acetone–methyl alcohol. Black iridescent plates with irregular corners formed slowly. In thin layers they appear red-brown by transmitted light. The acid number is 16.5 and the color in acid solution is the same green-blue as that of methyl phaeophorbide a. The ether solution, however, is a much brighter green than that of the unoxidized compound and the solubility is greater. A "mixed solubility" test proved more satisfactory than mixed melting points to show the difference between the two. This is carried out by preparing in small test-tubes thoroughly saturated solutions of each of the two substances in question and of their mixture. If the two samples are identical, the three solutions should show the same shade and intensity of color. If different substances are actually present, the solution containing the mixture will be as concentrated as the sum of the other two, and its color will be a blend of theirs. Such a comparison indicated methyl dehydrophaeophorbide *a* and the unoxidized compound to be distinct individuals. When a dilute ether solution of methyl dehydrophaeophorbide *a* is treated with concentrated methyl alcoholic potassium hydroxide (phase test), only an uncertain. fleeting, light yellow precedes the green color; under the same conditions methyl phaeophorbide *a* gives a strong yellow persisting for several seconds. The material sinters at 260–265°.

The spectrum in ether differs from that of methyl phaeophorbide *a* by a shift of about 40 Å. in the position of the narrow green band at 530: (1 mg. in 30 cc. of ether) I, 690.5–650; II, 618–603; III, 565---556; IV, 536–524.5; V, 512.4–485; E. A., 444. Order: I, V, IV, II, III. The spectrum in 19% acid: I, 690442; II, 615---603; III, 584.5–569; IV, 538–523; E. A., 454. Order: I, III, IV, II.

Anal. Calcd. for $C_{36}H_{36}O_6N_4$: C, 69.7; H, 5.8; N, 9.0; OCH_3, 10.0. Found: C, 68.65, 68.48, 68.30; H, 6.28, 6.28, 6.34; N, 8 88, 8.62; OCH_3, 8.65, 8.99; ash, 0.34, 0.40.

Hot Quick Saponification of Methyl Dehydrophaeophorbide a.—The identification of phaeopurpurin 7 and its decomposition product, chlorin *f*, and the complete absence of chlorin e among the products of this reaction offer strong chemical evidence for the homogeneity of the methyl dehydrophaeophorbide *a* employed and for its relation to the oxidized series. To 165 mg. of methyl dehydrophaeophorbide *a* warmed with one cc. of pyridine in a silver crucible, was added 20 cc. of boiling 35% potassium hydroxide in methyl alcohol. The boiling was continued over a free flame for thirty seconds and the intense green solution was diluted with water and transferred to two liters of ether. The olive-green ether solution was dried and methylated with diazomethane. It was acid-fractionated into an 8–11% fraction containing mainly dimethyl phaeopurpurin 7, and a 12–14% fraction which was mainly dimethyl chlorin f. Careful refractionation and concentration of the resulting solutions gave 30 mg. and 55 mg., respectively, of well-formed crystals of each of the two products. These were identified spectroscopically in acid and ether solutions and by mixed melting points with known samples.

In another experiment with 100 mg. of methyl dehydrophaeophorbide *a* the alkaline solution was boiled for ten minutes under reflux in order to achieve a more complete conversion to chlorin f and potassium oxalate. The yields were 45 mg. of chlorin f and 7 mg. of calcium oxalate isolated in the usual way. One hundred milligrams of methyl phaeophorbide *a* under similar treatment yielded 55 mg. of chlorin *e*, 5 mg. of chlorin *f*, and 1.7 mg. of calcium oxalate. The last two are degradation products of the oxidized series and their presence here must be due to unavoidable oxidation even during the rapid hot saponification or else to the presence of a small fraction of methyl dehydrophaeophorbide in the original methyl phaeophorbide a. A phase test saponification of methyl dehydrophaeophorbide *a* follows a parallel course to that of methyl phaeophorbide *a*, with the formation of the same unstable chlorins as intermediates and dimethyl phaeopurpurin 7 as the product of methylation. The yield of crystalline dimethyl phaeopurpurin 7 was 65 mg. from 137 mg. of methyl dehydrophaeophorbide *a*. The identity of the product was tested by acid and ether spectra and by a mixed melting point with an authentic sample.

Preparation of Chlorin f.—A more efficient and less laborious method of preparing this compound from methyl phaeophorbide *a* follows from our present knowledge of the chemical steps involved. By bubbling oxygen through a solution of methyl phaeophorbide *a* in concentrated methyl alcoholic potassium hydroxide at 0°, oxidation was accomplished before appreciable hydrolysis to chlorin e could take place. The same alkaline solution was then rapidly heated to boiling and refluxed for ten minutes in order to effect the decomposition to potassium oxalate and chlorin f. As a precaution against the usual oxidation of chlorin f to a porphyrin in the hot saponification, nitrogen was bubbled through the solution both before and during the heating. The details are as follows. To a solution of 2 g. of methyl phaeophorbide *a* in 10 cc. of pyridine was added 250 cc. of 25% potassium hydroxide in methyl alcohol which had previously been cooled to 0° and saturated with oxygen for fifteen minutes. The intense green solution was kept at 0° and stirred by an oxygen stream for thirty minutes. Nitrogen was then passed through for twenty-five minutes after which the solution was quickly brought to the boiling point with a free flame and boiled vigorously under reflux for ten minutes in the nitrogen atmosphere. The product was cooled rapidly and diluted with one liter of water. The green alkaline solution was acidified in the presence of 4.5 liters of ether and transferred (there was some formation of scum). The olive-green ether solution was extracted as described in paper IV, the only two products being a porphyrin with an acid number of 5–6 and chlorin *f*, which is removed by 11% acid. No chlorin e could be detected when the temperature was kept low. The yield of crystalline product (isolated as the dimethyl ester after treatment with diazomethane) was 970 mg.

Conversion of the Unstable Chlorins to Chlorin f and Potassium Oxalate.—The unstable chlorins cannot be isolated from an ether solution but are stable in concentrated alkali. They are readily prepared from methyl phaeophorbide *a* in methyl alcoholic potassium hydroxide as was described in the preparation of chlorin f. An experiment was performed to demonstrate that potassium oxalate was the other product of the reaction which forms chlorin f. The calcium oxalate was precipitated and titrated with standard permanganate solution as previously described (paper IV). The yield from 400 mg. of methyl phaeophorbide *a* was 150 mg. of chlorin f and 37 mg. of calcium oxalate.

Chlorin k.—A typical preparation of this compound by the oxidation of chlorin *e* with molybdicyanide was as follows: 500 mg. of chlorine was added to a filtered oxidizing mixture which was made from 1.66 g. of potassium molybdocyanide in 100 cc. of 10% acetic acid oxidized with a slight excess of permanganate and 500 cc. of molar pyridine in acetone, the total volume being brought to exactly 750 cc. by the addition of water. A sample was removed as a control before the addition of chlorin e. After five hours at room temperature the reaction mixture was worked up in the usual way with water and ether; titration had previously shown that about 85% of two equivalents of oxidizing agent had been reduced. A "colorimetric comparison" in a Zeiss comparison spectroscope with chlorin f as an assumed standard showed little or no destruction of the organic colored material. The ether solution after repeated washing with water was fractionated with 9 and 14% hydrochloric acid; the lower fraction, which was small, was discarded. The 14% portion was carefully refractionated; the 13 and 14% portions were combined, transferred to ether and the solution concentrated and a small amount of petroleum ether added. The product crystallized with a steel-blue luster. The yield was 109 mg. (24%). The acid number is between 11 and 12; the color in ether is olive-green and in acid, blue. The spectrum in ether: I, 685–644.5; II, 615---613.5–601; III, 561---553; IV, 535.3–522.5; V, 510.5–483; E. A., 437. Order: I, V, IV, II, III. The spectrum in 13% hydrochloric acid: I, 682–630; II, 611–602; III, 582–571; IV, 535–522; E. A. 447. Order: I, IV, III, II.

Anal. Calcd. for $C_{33}H_{34}O_4N_4$: C, 72.0; H, 6.2; N, 10.18. Calcd. for $C_{33}H_{36}O_5N_4$: C, 69.7; H, 6.3; N, 9.86. Found: C, 71.6, 71.4; H, 6.64, 6.55; N, 10.5, 9.7, 10.2.

Chlorin k Monomethyl Ester.—Chlorin k was esterified in ether solution with diazomethane. The ester was crystallized from ether–petroleum ether. The melting point was 145–147° with some decomposition. The spectrum in ether and acid was identical with that of free chlorin k. The acid number was 13.

Anal. Calcd. for $C_{34}H_{36}O_4N_4$: C, 72.3; H, 6.4; N, 9.93; OCH_3, 5.5. Found: C, 71.4, 71.6; H, 6.5, 6.8; N, 9.66, 9.46; OCH_3, 4.5, 5.0, 6.2.

Evolution of Carbon Dioxide from Chlorin e on Oxidation.—An experiment exactly similar to that described under the preparation of chlorin k was carried out in a flask connected with an inlet tube for purified nitrogen and an outlet tube passing through an empty bottle set in a freezing mixture and then into barium hydroxide solution. Nitrogen was passed through the apparatus with the oxidizing mixture in place for three hours before adding the chlorin *e*; there was no trace of barium carbonate visible. After adding the chlorin e the gas stream was continued and in seven minutes time a cloudiness was observed in the barium hydroxide solution. After five hours, the heavy precipitate of barium carbonate which had formed rapidly during the first hour, was filtered, dried at 110° and weighed. It weighed 90 mg. (56% of the theoreticai amount of one mole of carbon dioxide per mole of chlorin *e*).

Further Experiments on the Pyrolysis of Methyl Phaeophorbide *a*.—In our first report of the preparation of pyrophaeophorbide *a* and methyl pyrophaeophorbide *a* (paper I), the fact that a methoxyl group was involved in the decomposition was overlooked due to the failure to carry out a methoxyl determination on the pyro compounds. The complete analysis of the two pyro compounds reported in Table I of the third paper of this series (p. 3016) showed that not only was carbon dioxide eliminated but methyl alcohol or formaldehyde was split out of the molecule. To test for the presence of these substances the gases evolved in the pyrolysis of 300 mg. of methyl phaeophorbide *a* in boiling diphenyl were passed into 5 cc. of distilled water, a current of nitrogen being used to sweep through the products. The aqueous solution gave a definite aldehyde test with decolorized fuchsine solution (Schiff's reagent) and with Tollens' reagent. The presence of methyl alcohol was demonstrated by the usual procedure of repeatedly introducing a heated bright copper wire and subsequently applying the aldehyde test, which is greatly increased by this treatment. The possibility that the methoxyl group of phaeophorbide *a* might have been eliminated as methane during the pyrolysis was investigated by using carbon dioxide to sweep the volatile products into a buret filled with potassium hydroxide solution. Half a millimole of methyl phaeophorbide *a* yielded only 1.75 cc. of gas which was shown by combustion analysis to be 63% carbon monoxide, 13% inert (probably nitrogen from air) and 23% methane, corresponding to a total of 0.4 cc. = 0.02 of millimole (in a duplicate experiment the methane was found to be 0.5 cc.). The actual yield of crystalline pyro compound was five times this amount. The possibility of a shift of the methoxyl group from oxygen to nitrogen during pyrolysis was also considered and the pyro compounds were tested for N-methyl groups by Pregl's quantitative method; no such groups were found, however.

Summary

1. The process of allomerization has been shown to be a process of dehydrogenation by atmospheric oxygen.

2. Chlorophyll *a* and methyl phaeophorbide *a* may be dehydrogenated by potassium molybdicyanide, two equivalents of reagent being involved. The dehydro compounds on rapid saponification yield no chlorin e but only the unstable chlorins which on longer boiling with alkali yield chlorin *f* and potassium oxalate.

3 Chlorin e is oxidized by potassium molybdicyanide with loss of carbon dioxide.

4. A structural formula for chlorophyll *a* has been proposed based on the experiments reported in this and previous papers of this series.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE PARTITION PRINCIPLE AS APPLIED TO THE STRUCTURES OF ENOLIC SODIUM DERIVATIVES OF 1,3-DIKETONES AND BETA-KETO ESTERS

BY ARTHUR MICHAEL AND JOHN ROSS

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The partition principle of Thomsen[1] was based upon the distribution of an insufficient amount of base for complete neutralization between two acids. This principle was extended to the course of organic reactions,[2] and was verified experimentally with a number of typical organic reactions.[3] Accordingly, the distribution of the sodium in a compound capable of reacting in more than one enolic form would be expected to follow the partition law, and the ratio of the amounts of the sodium enolates should stand to one another in a definite relation to the avidities of the corresponding enolic structures.

Geuther[4] represented the structures of acetoacetic ester and the sodium derivative by $CH_3C(OH)=CHCOOEt$ and $CH_3C(ONa)=CHCOOEt$ and although this conception was accepted by Claisen, Nef and other chemists, the commonly accepted view was that of FranMand[6] and J. Wislicenus[6] who considered the formulas CH_3COCH_2COOEt and CH_3-$COCHNaCOOEt$, respectively, to represent these compounds. In 1888 it was shown,' theoretically and experimentally, that the chemical relations of these substances could be explained only from the keto structure CH_3CO-CH_2COOEt for the ester and the*enol structure $CH_3C(ONa)=CH$-$COOEt$ (I), for the sodium derivative. However, it was emphasized[8] that a solution of the sodium compound should also contain some of the isomeric derivative $CH_3COCH=C(ONa)OEt$ (11), since malonic ester yields an enolate, and the formula of acetoacetic ester may be derived from that of malonic ester by replacing one of the carbethoxy groups of the former by the more negative acetyl group; further, that the relative amount of (I) should largely exceed that of (11), since acetyl is a much more negative radical than carbethoxyl.

This view is supported by the fact that along with the main product

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[1] **Thomsen,** *Pogg. Ann.*, 135,497 (1869).

[2] **Michael,** J. *prakt. Chem.*, 60, 341 (1899); *Ber.*, 39, 2138 (1906); THIS JOURNAL, 32, 1005 (1910).

[3] **Michael,** *Ber.*, 39, 2133–2156, 2569, 2786–2795 (1906); 40, 140 (1907).

[4] **Geuther,** *Jahresb.*, 323 (1863); *Z. Chem.*, 652 (1868); *Ann.*, 219,123 (1883).

[5] **Frankland,** *ibid.*, 138,204,328(1866).

[6] **J. Wislicenus,** *ibid.*, 186, 163 (1877).

[7] **Michael,** *J. prakt. Chem.*, 37,473 (1888); *Am. Chem.* J., 10, 158 (1888); 14, 481 (1892).

[8] **Michael,** *J. prakt. Chem.*, 37,488 (1888).

of the action of chlorocarbonic ester upon the sodium enol acetoacetic ester, *viz.*, $CH_3C(OCOOEt){=}CHCOOEt$ (III),[9] some of the isomeric $CH_3COCH(COOEt)_2$ (IV) is formed.[10] Since it has not been possible to convert the O-carbethoxy ester (III) into the enolic sodium derivative of (IV),[12] it would appear that (III) and (IV) are formed from the corresponding sodium derivatives I and II.

A reagent that would react with equal velocity with each of the above sodium enol derivatives to give stable products derived from the structures of the corresponding enols could be used to demonstrate the existence of such sodium enolic compounds, and the relative amounts should be in direct relation to the avidities of the enol structures; but no reagent is known that entirely fulfils these ideal conditions. In certain reactions, such as the above example of the sodium enol derivatives of acetoacetic ester, chlorocarbonic ester is the best reagent available but the proportions even in this case can only be accepted qualitatively.

J. Wislicenus[13] showed that the time required for complete reaction in alcoholic solution with a series of alkyl iodides was greater for sodium enol acetoacetic ester than for the a-ethyl derivative, and much greater than for sodium enol malonic ester. A comparison of the rates of reaction at 25° of methyl iodide and ethyl bromide with sodium enol malonic ester and sodium enol acetoacetic ester is given in the curves, which very clearly show that the reaction velocity with both of these alkyl halides is much greater for sodium enol malonic ester than for sodium enol acetoacetic ester.

The alkyl halide was added to an alcoholic solution of the sodium enol malonic ester and sodium enol acetoacetic ester prepared by adding the esters to the alcoholic solution of sodium ethoxide. At certain intervals, samples of the reaction mixture were removed by a pipet, immediately added to an excess of cold dilute hydrochloric acid, and the excess of acid titrated with alkali. The error due to formation of neutral sodium salts of carboxylic acids was probably small under these conditions.

The above reactions were carried out with approximately 2 *N* solutions, this being the concentration usually employed for alkylation of sodium enol derivatives of this type. For comparison, the curve for the rate of reaction between the alkyl halides and sodium ethoxide in alcohol is placed alongside the curves for sodium enol acetoacetic and malonic esters. The reaction with methyl iodide in all cases proceeds very rapidly

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[9] Michael, *J. prakt. Chem.*, 37, 474 (1888); 45, 583 (1892).

[10] Nef [*Ann.*, 266, 105 (1891); 276, 213 (1893)] stated that it is formed in considerable proportion, but Michael [*Am. Chem. J.*, 14, 491 (1892)] showed that less than 10% is formed, which proportion was confirmed by Claisen.[11]

[11] Claisen, *Ber.*, 25, 1761, 1767 (1892).

[12] Michael, *ibid.*, 38, 2089 (1905).

[13] Wislicenus, *Ann.*, 212, 239 (1882).

with these concentrations, and it was impossible in the case of malonic ester to prevent a small rise of temperature. With ethyl bromide the reaction velocity could be examined more accurately. It should be noticed that half the sodium had reacted with ethyl bromide within thirty minutes in the case of sodium enol malonic ester, and within eighteen hours in the case of sodium enol acetoacetic ester. The curves for the reactions between the alkyl halides and sodium ethoxide are of interest. With methyl iodide the reaction velocity of sodium ethoxide is less than for sodium enol acetoacetic ester, but with ethyl bromide the reverse relation exists. It is apparent, therefore, that using an alcoholic solution of sodium enol acetoacetate, a larger percentage yield of alkyl derivative will be obtainable with methyl iodide than with ethyl bromide.

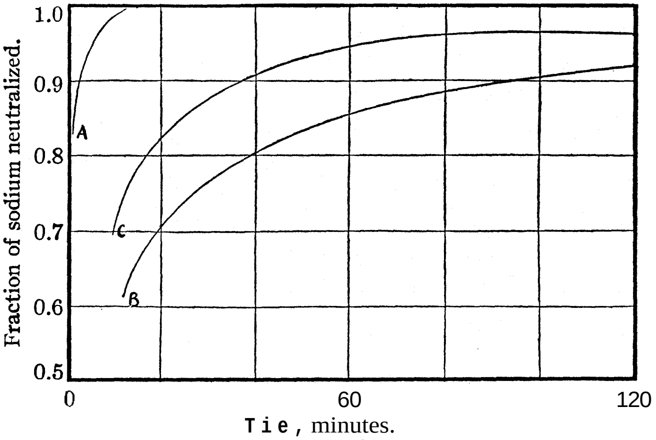

Fig. 1.—A, CH_3I + NaOEt + $CH_2(COOEt)_2$.
B, CH_3I + NaOEt + C_2H_5OH.
C, CH_3I + NaOEt + CH_3COCH_2COOEt.

When the reaction of methyl iodide (1 mole) with an alcoholic solution of equimolecular amounts of sodium ethoxide, acetoacetic and malonic esters was carried out at 0°, the product was found to consist of 6% methylmalonic ester and 70% methylacetoacetic ester. Under the same conditions using ethyl bromide, the product contained 30% ethylmalonic ester and only a trace of ethylacetoacetic ester. Therefore, using methyl iodide, the main reaction resulted in alkylation of acetoacetic ester, while with ethyl bromide, the main reaction was the alkylation of malonic ester.

These results and those of Wislicenus agree with the conclusion that the velocity relations in the action of alkyl halide upon the sodium derivatives of organic compounds depend upon the free positive chemical energy of the sodium in the respective compounds.[14] Thus, while methyl

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[14] *See* Michael, THIS JOURNAL, 32, 1003 (1910).

iodide replaces readily the sodium in sodium enol acetoacetic ester, by methyl, it does so with greater difficulty with sodium enol formylacetoacetic ester;[15] it can substitute the sodium of the sodium derivative of the more acidic enol oxalacetic ester only at a higher temperature (100°), and then with a poor yield;[16] and the well neutralized sodium of sodium enol nitromethane, or that of any neutral organic salt, cannot be replaced by methyl in this way.

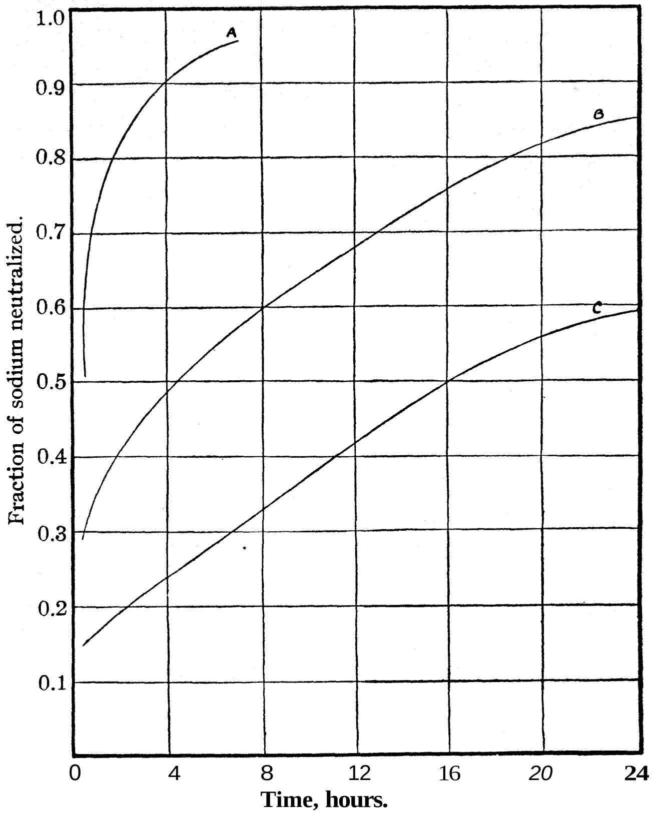

Fig. 2.—A, $C_2H_5Br + NaOEt + CH_2(COOEt)_2$.
B, $C_2H_5Br + NaOEt + C_2H_5OH$.
C, $C_2H_5Br + NaOEt + CH_3COCH_2COOEt$.

Since enol acetoacetic ester is decidedly more acidic than enol malonic ester, the distribution of the sodium in the above mixture must have been largely at the acetoacetic ester residue and, as there is a relatively small difference in the reaction velocity of methyl iodide toward the two sodium derivatives, the presence of the much larger mass of sodium enol aceto-

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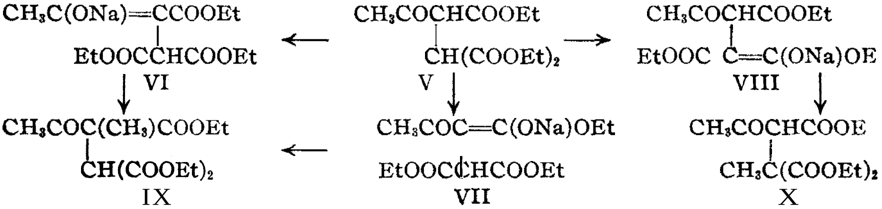
[15] Michael, Ber., 38, 2098 (1905).

[16] Wislicenus and Arnold, Ann., 246,336 (1888).

acetic ester mainly determined the proportions of the reaction products. It follows from the greater percentage of ethylation of the malonic than of the acetoacetic enolate with the use of the much less reactive ethyl bromide, that a transference of sodium from sodium enol acetoacetic ester to malonic ester must occur during the reaction. This conclusion evidently conforms with the partition principle.

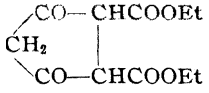
The methylation of a-acetyl-a'-carbethoxysuccinic ester (V) through its enolic sodium derivative was then examined to ascertain whether a partition of sodium among the possible enolic forms of this ester could be proved by use of methyl iodide as a reagent. The ester (V) should be capable of forming three structural sodium derivatives (VI), (VII) and (VIII). Upon alkylation (VI) and (VII) would give the same α-acetyl-a-methyl-a'-carbethoxysuccinic ester (IX), and the sodium derivative (VIII) would give the isomeric α-acetyl-α′-methyl-α′-carbethoxysuccinic ester (X).

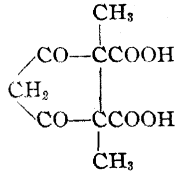


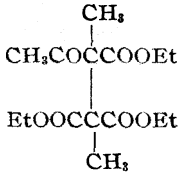
Treating the alcoholic solution of the sodium derivative of ester (V) with methyl iodide at 0° gave mainly α-acetyl-α′-methyl-α′-carbethoxysuccinic ester and no evidence of the formation of the isomeric ester (IX) could be obtained. Methylation therefore occurred at the malonic residue in preference to the acetoacetic residue, notwithstanding that there must have been a larger amount of sodium at the latter group in the original solution of sodium enolates. This result showed the much greater reactivity of the malonic enolate group compared with the acetoacetic enolate group.

In the original solution the sodium enol derivative (VI) should preponderate; there should also be a certain amount of the enolate (VII) together with a much smaller proportion of (VIII). In the structures (VI) and (VII) a greater neutralization of the sodium is realized, being directly derived from the enol forms of acetoacetic ester, as well as being indirectly under the influence of the negative malonic residue. In structure (VIII) the sodium is directly attached to the enolic malonic residue and is only under the indirect spatial influence of the enol acetoacetic residue. Evidently, the sodium atoms of Formulas (VI) and (VII) are relatively neutral compared with the sodium in (VIII). The experiment showed that the reaction occurred at the malonic enolate group, and that the enolates (VI) and (VII) are practically inert toward methyl iodide under the experimental conditions The entrance of the methyl group at the malonic residue proves that methyl iodide cannot be used to ascertain the position of the sodium in the sodium derivatives of esters of the mixed type (V).

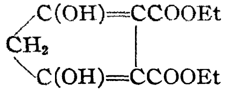
The structure of the methylated ester (X) was determined by saponification with barium hydroxide, when a mixture of α-methyl-α-carboxysuccinate was obtained together with α-methyl-α-carboxy levulinate There *was* also formed a small amount of the salt of 1,2-dimethylcyclopenta-3,5-dione-1,2-dicarboxylic acid (XII). It was shown that ester (V) readily forms the sodium derivative of cyclopenta-3,5-dione-1,2-dicarboxylic ester (XI) when treated with sodium ethoxide. It is not possible, therefore, to state whether this acid arose through methylation of the cyclic diketo ester (XI) or by cyclization of the dimethylated ester (XIII).

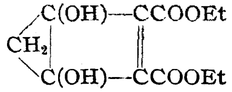

XI


XII


XIII

The formation of the pentacyclic keto ester (XI) from the open-chain keto ester (V) is analogous to the formation of 5-phenyldihydroresorcinol-4-carboxylic ester from the addition product of sodium enol acetoacetic ester to cinnamic ester[17] or from the addition product of sodium enol malonic ester to benzalacetone.[18] When ester (V) was treated in ether solution with alcoholic sodium ethoxide, two isomeric cyclic keto esters were obtained, a liquid and a solid, m. p. 86°. The liquid keto ester gave a deep blue color with alcoholic ferric chloride and was probably the mono enolic form of structure (XI). The solid isomer gave no coloration with ferric chloride, and may be derived by rearrangement of the di-enolic structure (XIV). This may be related to the phenomenon termed "intra-annular tautomerism," assumed in this type of compound by Farmer, Ingold and Thorpe,[19] in which case it would be represented by the structure (XV).


XIV


XV

The structure of benzoylacetone has been in the past the subject of many physical and chemical investigations, but the direction of enolization

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[17] Michael, *Am Chem. J.*, 9,117 (1887); *J. prakt. Chem.*, *35,353* (1887).

[18] **Vorlandrr,** *Ber* , **27,** 2053 (1 *894)*; Michael, *ibid.*, 27,2126 (1894).

[19] **Farmer, Ingold and Thorpe,** *J. Chem. Soc.*, 118,1362 (1920); 121,128 (1922).

has not yet been decisively established. Since the results of earlier investigations upon the constitution of enols have been summarized by Scheiber and Herold,[20] only brief references that are relevant to the structure of benzoylacetone need be made here.

The magnetic rotation,[21,22] and molecular refraction[22] indicate that benzoylacetone has the enol structure (XVI).

$C_6H_5C(OH){=}CHCOCH_3$ XVI

$C_6H_5COCH{=}C(OH)CH_3$ XVII

$C_6H_5C(OH){=}C{=}C(OH)CH_3$ XVIII

$C_6H_5COCH_2COCH_3$ XIX

The parachor of benzoylacetone[23] is very close in value to a calculation based upon an open-chain diketone structure (XIX) and this agrees with the results obtained from examination of the reaction with tertiary amines.[24]

The bromine titration method of K. H. Meyer[25] led him to conclude that benzoylacetone in alcohol solution exists as 94–98% of a mono-enol in reversible equilibrium with the diketone. The method evidently cannot decide between structures (XVI) and (XVII), but Meyer favored the structure (XVI) since he considered that the physical investigations as well as the results of the bromine titration of keto–enols in general showed that the benzoyl group has a greater enolizing capacity than the acetyl. Scheiber and Herold found that ozonization of benzoylacetone gave chiefly benzoic acid (97.5% of the theoretical) and carbon dioxide, and the formation of some methylglyoxal was proved through the osazone. These chemical results therefore also point to the structure (XVI) for benzoylacetone, although they do not exclude the presence of the isomeric enol (XVII) and of the di-enol (XVIII). The ozone addition is a slow process, and if one of the mono-enolic isomers adds much faster than the other, and the isomers are in a state of rapid reversible equilibrium, then the process may proceed mainly in one direction. The results obtained by the method would not then express correctly the quantitative relations between the mono-enolic forms.

On the other hand, Claisen[26] considered that the fission of benzoylacetone by the action of alkali into acetophenone and acetate, and the

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[20] Scheiber and Herold, *Ann.*, 405, 295 (1914).

[21] Perkin, *J. Chem. Soc.*, 61, 832 (1892).

[22] Smedley pointed out [Smedley, *ibid.*, 97, 1486 (1910); Auwers and Jacobsen, *Ann.*, 426, 161 (1922)] that when correction was made for exaltation in magnetic rotation common to cinnamyl derivatives, the value found agrees with the value calculated for hydroxybenzylideneacetone and it is unnecessary to postulate the presence of a dienol (XVIII) form, which Perkin had suggested.

[23] Sugden, *J. Chem. Soc.*, *321* (1929).

[24] Michael and Smith, *Ann* , **363,** 36 (1908)

[25] Meyer, *Ann.*, 380, 242 (1911); *Ber.*, 45, 2846 (1912).

[26] Claisen, *Ber.*, 59, 144 (1928).

reactions of benzoylacetone with ammonia, aniline or hydroxylamine to give, respectively, $C_6H_5COCH{=}C(NH_2)CH_3$, $C_6H_5COCH{=}C(NHC_6H_5)CH_3$ and 3,5-methylphenylisoxazole (XXII), indicated greater reactivity at the acetyl group, and consequently Claisen suggested structure (XVII) as possibly representing benzoylacetone.

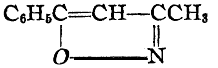
It would be expected from the partition principle that a solution of sodium enol benzoylacetone would contain sodium derivatives (XX and XXI), corresponding to the enolic structures (XVI and XVII).

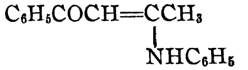
$C_6H_5C(ONa){=}CHCOCH_3$
XX

$C_6H_5COCH{=}C(ONa)CH_3$
XXI

In the hope of obtaining some information regarding the structure of the sodium derivative, the action of chlorocarbonic ester upon sodium enol benzoylacetone was studied.

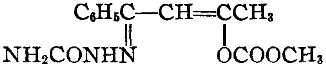
The sodium derivative was prepared by adding an ether solution of the benzoylacetone to an ether suspension of sodium ethoxide prepared by Brühl's method. Chlorocarbonic methyl ester was added gradually and the reaction allowed to proceed in the cold. Approximately 85% of a substitution product was obtained. This was found to consist of two isomeric O-carbomethoxy keto esters, one a crystalline solid, melting at 57°, and the other a liquid, boiling at 164° (2 mm.). The solid ester showed no sign of changing into the liquid isomer when heated slightly above its melting point for forty-eight hours; but, on fractionation of the liquid 0-ester, varying amounts of the solid 0-ester could be frozen out of the first and last fractions, although the liquid keto ester could be kept indefinitely at ordinary temperature without any indication of changing into the solid form. Each 0-ester gave benzoylacetone when treated with aqueous ammonia or aqueous hydroxylamine in the cold. With hydroxylamine acetate in the cold, each gave some 3-methyl-5-phenylisoxazole (XXII) and, with aniline, in ether solution, theoretical yields of the anilido derivative (XXIII).


XXII


$C_6H_5COCH{=}\underset{\displaystyle NHC_6H_5}{\underset{|}{C}}CH_3$
XXIII

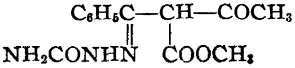
These reactions involving the elimination of the carbomethoxy group are of little value as evidence of the structures of the carbomethoxy compounds. It was found that benzoylacetone under like conditions gave the same products and there was no means of finding out whether condensation preceded or followed the elimination of the carbomethoxyl.

With semicarbazide acetate, the 0-esters showed a difference in behavior. The solid ester gave in the cold a semicarbazone derivative of benzoylacetoacetate (XXV) together with a semicarbazone derivative of the O-ester (XXIV). The latter could be converted into (XXV) by treatment with dilute acids when migration occurred of the —$COOCH_3$ group from the oxygen to the carbon atom



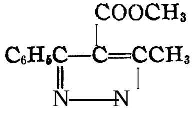
$$\begin{array}{lcl} & C_6H_5C{-}CH{=}CCH_3 & \\ & \| \qquad\quad | & \\ NH_2CONHN & & OCOOCH_3 \end{array}$$

XXIV



$$\begin{array}{lcl} & C_6H_5C{-}CH{-}COCH_3 & \\ & \| \qquad | & \\ NH_2CONHN & & COOCH_3 \end{array}$$

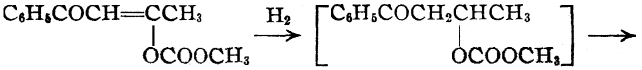
XXV



XXVI

The final product of the reaction in dilute acetic acid solution was the pyrazole derivative (XXVI). A definite product could not be isolated from the liquid 0-ester upon similar treatment with the semicarbazide acetate solution.

When the solid 0-ester was treated in methyl alcohol solution with hydrogen in the presence of platinum oxide catalyst,[27] it was found that two molecular equivalents of hydrogen were rapidly absorbed, producing *n*-propyl phenyl ketone. The addition must therefore proceed at the unsaturated carbon group and may be considered to take place as follows



$$\underset{\text{XXVII}}{\begin{array}{l} C_6H_5COCH{=}CCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad OCOOCH_3 \end{array}} \xrightarrow{H_2} \underset{\text{XXVIII}}{\left[\begin{array}{l} C_6H_5COCH_2CHCH_3 \\ \qquad\qquad\qquad | \\ \qquad\qquad OCOOCH_3 \end{array}\right]} \longrightarrow$$

$$\underset{\text{XXIX}}{C_6H_5COCH{=}CHCH_3} + HOCOCH_3 \xrightarrow{H_2} \underset{\text{XXX}}{C_6H_5COCH_2CH_2CH_3}$$

The rate of absorption did not show any marked decrease after the absorption of the first molecular equivalent of hydrogen, so that it may be supposed that the saturated carbonic ester derivative (XXVIII) was unstable and decomposed relatively rapidly to give phenyl propenyl ketone and acid carbonic methyl ester. The phenyl propenyl ketone (XXIX) would be reduced readily to the saturated ketone (XXX).

When treated with hydrogen under the same conditions, the liquid 0-ester gave as readily phenyl n-propyl ketone in almost quantitative yield.

Benzoylacetone similarly treated was reduced to give 1-phenylbutane-1,3-diol (XXXI).

$$\underset{\text{XXXI}}{C_6H_5CH(OH)CH_2CH(OH)CH_3}$$

This was obtained as a liquid distilling at 130° *(2* mm.) without decomposition. It gives a diacetate upon acetylation in pyridine. Franke and Kohn[28] obtained a 1-phenylbutane-1,3-diol melting at 73° by the action

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[27] **Adams.** "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

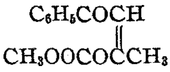
[28] Franke and Kohn, *Monatsh.*, **27, 1115** (1906).

of phenylmagnesium iodide upon acetaldol melting at 73°. Bauer[28a] by the action of sodium and alcohol. on benzoylacetone obtained some 1-phenylbutane-1,3-diol, a liquid of b. p. 168° (13 mm.), and Kubota and Hayashi[28b] by the action of hydrogen on benzoylacetone at 105° in the presence of copper catalyst, obtained, among other products, some of this diol. Whether our material is identical or stereomeric with the compounds obtained by these authors, can only be decided by further examination.

Since benzoylacetone is thus ruled out as a common intermediate in the reduction of the isomeric 0-esters, and since each of the 0-esters gives the same saturated ketone, it must be concluded that these two O-esters are related to one another as stereomers with configurations as follows

$$\begin{array}{l} C_6H_5COCH \\ \qquad\| \\ CH_3COCOOCH_3 \end{array}$$

XXXII



$$\begin{array}{r} C_6H_5COCH \\ \| \qquad \\ CH_3OOCOCCH_3 \end{array}$$

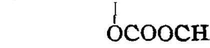
XXXIII

It also follows that in this reaction with the chlorocarbonic ester, the sodium enol benzoylacetone reacts (at least to 85%) as though it had the structure (XXI) and that the enolate consisted of a mixture of stereomeric sodium compounds. Such a result agrees with the partition principle since the sodium compounds would be derived from stereomeric enols of different acidity. The above results also raise the question of the stereochemical homogeneity of the corresponding free mono-en01 of benzoyl acetone.

In view of these results, it was of interest to examine the action of chlorocarbonic ester upon sodium enol dibenzoylmethane. When the sodium derivative was prepared, using an ether suspension of sodium methoxide as in the experiment with benzoylacetone, it was found that over 90% of the dibenzoylmethane was recovered unchanged after treatment with chlorocarbonic ester. Better results were obtained when the sodium derivative was prepared directly from pulverized sodium and dibenzoylmethane in ether solution. A yield of 7% of O-carbethoxy derivative (XXXV), together with some dibenzoylmethane, was obtained, but the main product was a thick sirup of undetermined composition that could not be distilled nor crystallized. It is possible that the method of preparing the sodium derivative resulted in a partial reduction of the dibenzoylmethane or produced some complex compound of high molecular weight.

$C_6H_5COCH{=}C(ONa)C_6H_5$

XXXIV



$$\begin{array}{l} C_6H_5COCH{=}CC_6H_5 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad OCOOCH_3 \end{array}$$

XXXV

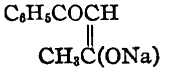
[28a] Bauer, *Compt. rend.*, 154, **1093 (1911).**

[28b] Kubota and Hayashi, Bull. *Chem. Soc. Japan*, **1,** 14 (1926).

In another experiment the sodium derivative was prepared using an ether solution of dibenzoylmethane and finely powdered sodamide. The solid sodium derivative was filtered off and washed free of ammonia with ether, before the addition of the chlorocarbonic ester; 50% of dibenzoylmethane was recovered, and 30% of the O-ester melting at 90° together with 20% of liquid material which possibly contained a stereomeric O-ester was obtained.

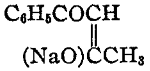
These experiments show the greater difficulty of replacing by carbomethoxyl the sodium of an enol group adjacent to a phenyl than to the methyl group.

Since benzoyl is a more negative radical than acetyl (the dissociation values, K, of acetic and benzoic acids are 0.0063 and 0.0018, respectively), it is evident that the sodium in the structure $C_6H_5C(ONa){=}CHCOCH_3$ should be better neutralized than in the structure $C_6H_5COCH{=}C(ONa)CH_3$. The isomeric enolic benzoylacetones are definitely acidic compounds, and the sodium in the first derivative should be considerably better neutralized and therefore less reactive than the sodium in the second structure, a conclusion supported by the relative difficulty of obtaining an O-carbethoxy derivative of dibenzoylmethane. The facile action of chlorocarbonic ester upon sodium enol benzoylacetone and upon sodium enol acetylacetone[29] has proved the greater reactivity of the sodium in the $C_6H_5COCH{=}C(ONa)CH_3$ than in the $C_6H_5C(ONa){=}CHCOCH_3$ structure. It has also shown that in the first structure the sodium is partitioned between the stereo structures (XXXVI) and (XXXVII), of which the latter enolate should preponderate.



$$\begin{array}{l} C_6H_5COCH \\ \qquad\;\; \| \\ \;\; CH_3C(ONa) \end{array}$$

XXXVI



$$\begin{array}{l} C_6H_5COCH \\ \qquad\;\; \| \\ (NaO)CCH_3 \end{array}$$

XXXVII

For comparison with the results of the experiments upon the action of semicarbazide acetate upon the keto esters above, the action of semicarbazide upon benzoylacetone was reexamined. Posner[30] stated that semicarbazide does not react with benzoylacetone in the cold, but with molecular amounts of semicarbazide hydrochloride at 60°, sodium acetate and benzoylacetone, he obtained 3,5-methylphenylpyrazole-1-carboxamide (XXXIX).

Using semicarbazide or semicarbazide acetate in alcoholic solution at 0°, it was found that pyrazole ring formation could be avoided. The monosemicarbazone (XXXVIII) is readily formed and with excess of semicarbazide a disemicarbazone is formed. Treatment of the monosemicarbazone in alcoholic solution with a small amount of acetic acid

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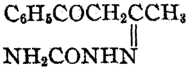
[29] Claisen, Ann., 277, 176 (1893).

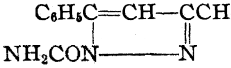
[30] Posner, Ber., 34, 3983 (1901).

or hydrochloric acid gave the 3,5-methylphenylpyrazole-1-carboxamide, which on warming or standing in acid solution readily hydrolyzed with loss of carbon dioxide to give the 3,5-methylphenylpyrazole (XL).

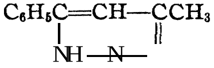


$C_6H_5COCH_2C(=NNHCONH_2)CH_3$

XXXVIII



XXXIX



XL

Accordingly, semicarbazide acetate in acid solution or semicarbazide hydrochloride with benzoylacetone gave directly mainly 3,5-methylphenylpyrazole together with some 3,5-methylphenylpyrazole-1-carboxamide.

The physical properties of benzoylacetone indicate that it exists mainly as $C_6H_5C(OH){=}CHCOCH_3$ (XVI). Since benzoyl is decidedly more negative than acetyl, the sodium derivative should consist largely of $C_6H_5C(ONa){=}CHCOCH_3$ (XX), yet the sodium derivative with chlorocarbonic methyl ester yields only stereomeric forms of $C_6H_5COCH{=}C(OCOOCH_3)CH_3$ which are formed from $C_6H_5COCH{=}C(ONa)CH_3$ (XXI), since benzoylacetone with alkali should give mainly a mixture containing much of (XX) and little of (XXI), and fluxing with it should result in a mixture of benzoate and acetone, with much less acetate and acetophenone. However, acetate and acetophenone are the sole or at least the main products of the decomposition. With typical carbonyl reagents, *e.* g., ammonia, hydroxylamine, phenylhydrazine and semicarbazide, benzoylacetone yields primarily derivatives by replacement of the 0-atoms of the carbonyl group of the acetyl radical,[31] and the introduced group then acts on the C-atoms of the —C(OH)=CH— group to form cyclic derivatives, or with a further quantity of the reagent yield products involving the enolic group. Physical investigation supports structure (XVI), while chemical investigation points unmistakably to $C_6H_5COCH{=}C(OH)CH_3$ (XVII). How may these opposing results be reconciled?

In sodium derivatives (XX) and (XXI), the metal in (XX) must be decidedly more neutralized than that in (XXI); sufficiently in the former that $ClCOOCH_3$ acted upon it slowly or not at all. The energetic reaction therefore extended only to (XXI), which is reformed progressively followed by introduction of the carbomethoxyl group. The course of alkali fission of (XX) and (XXI) depends upon the reaction mechanism of the

[31] This behavior led Claisen [Ber., 59, 146 (1926), footnote 10] to believe that the position of the enolic group in benzoylacetone is open to question, and Scheiber and Nerold [*Ann.*, 405, 318 (1914)] considered that the formation of acetophenone and acetate by alkali fission favors the structure $C_6H_5COCH{=}C(ONa)CH_3$ for the sodium derivative. The statement is not tenable that this view finds support in the easy synthesis of sodium enol benzoylacetate from acetophenone and ethyl acetate compared with the difficulty and poor yields encountered when it is attempted to prepare it from ethyl benzoate and acetone. The second reaction would depend upon the formation of sodium enol acetone, which appears in such small amount in the action of sodium upon acetone that its formation can hardly be considered as definitely established.

process. Carbonyl derivatives that do not form enolates with alkali react primarily by addition of the alkali to the carbonyl group to form the group —C(OM)OH—. The slightly neutralized energy of the alkali in this complex loosens the affinity of the C-atom to the directly attached C-atoms[32] and cleavage occurs between the C-atoms by hydrolysis. The rupture should take place at the carbon linkage which is most weakened by the positive influence of the alkali atom. In fluxing enolates (XX) and (XXI) with alkali, similar intermediate products should be formed by addition of water at the unsaturated carbon system and as the alkali atom in the addition product from (XXI) is decidedly less neutralized than in that from (XX), disruption of the carbon chain takes place with the (XXI) compound, thus

$$C_6H_5CO—CH{=}C(ONa)CH_3 + H_2O \rightarrow C_6H_5COCH_2C(ONa,OH)CH_3 \rightarrow C_6H_5COCH_3 + CH_3COONa$$

Finally, the course of the reaction of benzoylacetone with carbonyl reagents depends upon whether they add more facilely to the carbonyl or to the —C(OH)=C— group. This relationship may vary with the chemical character of the radicals in direct union with these groups. The course of the above reactions is therefore *prima facie* evidence that with the benzoylacetone structure (XVI) they act much more readily on the carbonyl than on the enolic group. Direct experimental confirmation of this is found in the action of hydroxylamine upon the isomeric keto ethers $C_6H_5COCH{=}C(OC_2H_5)CH_3$ and $C_6H_5C(OC_2H_5){=}CHCOCH_3$ since in each case the O of the carbonyl group is replaced by the hydroxylamine residue.[33]

There is no doubt that the principles developed in the examination of the above reactions can be applied to problems concerning compounds of this or similar types where the partition principle is involved.

Experimental

A. Reaction Velocity of Sodium Enolates with Methyl Iodide and Ethyl Bromide.—To a solution of 2–3 g. of sodium in 50 cc. of absolute alcohol 13 g. of acetoacetic ester was added; 14.5 g. of methyl iodide was added to the cold solution of the enolate and after mixing thoroughly was placed in a thermostat at 25°. At known intervals 10 cc. of this mixture was removed with a pipet and run into 50 cc. of 0.5 N hydrochloric acid cooled in ice. The excess acid was then titrated with standard caustic soda using phenolphthalein as indicator. Thus as the reaction proceeded, it was possible to measure the amount of sodium that had been neutralized by the alkyl halide.

Similar experiments were made using (a) malonic ester, (b) an equal volume of alcohol in the place of the acetoacetic ester. Also a series of experiments was carried out using ethyl bromide in the place of methyl iodide. The results are summarized in Curves I and II.

Reaction between Alkyl Halide and a Mixture of NaOEt, $CH_2(COOEt)_2$ and CH_3-

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[32] Michael, THIS JOURNAL, 32, 997 (1910); Michael and Ross, *ibid.*, 52, 4601 (1930).

[33] Claisen, *Ber.*, 59, 148 (1926).

$COCH_2COOEt$ in Alcohol Solution.—A mixture of 32.5 g. of acetoacetic ester with 40 g. of malonic ester was added to a solution of 5 75 g. of sodium in absolute alcohol. After standing for one hour, 36 g. of methyl iodide was added and the mixture stood in ice water for twelve hours. The product was then mixed with 500 cc. of water containing a small amount of acetic acid and the neutral esters extracted with ether, dried and the ether removed upon the water-bath.

The cold esters were then shaken with successive portions of 5% caustic potash (40 g. in 800 cc. of water). Toward the end of this extraction the amount of ester became so small that it was necessary to take it up in a small volume of ether. The ester that remained in ether solution was washed with water, dried, distilled and weighed as methyl malonic ester;[34] the yield was 2.5 g. or 6% of the possible yield calculated upon complete methylation of malonic ester.

The aqueous alcoholic extract was left overnight cooled in water in order to complete saponification. Using the procedure described by Michael and Wolgast,[35] the solution was acidified and after refluxing for two hours, the volatile ketones distilled off. The aqueous ketone distilled was saturated with salt and the ketones taken up in ether, separated, dried and distilled up an 8-inch Vigreux fractionating column. The fraction distilling at 76–77.5°, after separation from alcohol by the sodium bisulfite compound, was weighed as pure ethyl methyl ketone; yield, 12 g (70%) The semicarbazone gave large prisms, melting at 148° without recrystallization.[36]

A similar experiment was carried out using ethyl bromide in the place of ethyl iodide, allowing the reaction mixture to stand for seven days and using the same method as above for the separation of the products: 12 g. of ethylmalonic ester (30%) and 3 g. of methyl propyl ketone (16%), b. p. 101–102°, were obtained. The semicarbazone melted at 110°.[37] These results may be summarized as follows

	Yield of alkylacetoacetic ester, %	Yield of alkylmalonic ester, %
CH_3I	70	6
C_2H_5Br[38]	trace	30

B. Methylation of Sodium Enol α-Acetyl-α'-carbethoxysuccinic Ester.—a-Acetyl-*α'-carbethoxysuccinic* ester was prepared by the action of sodium enol acetoacetic ester on chloromalonic ester[38a]: 33 g. of acetoacetic ester was added to 5.75 g. of pulverized so-

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[34] Michael, J. *prakt.* Chem., 72, 537 (1905).

[35] Michael and Wolgast. Ber., 42,3176 (1909).

[36] Robinson, J. Chem. *Soc.*, 109,1044 (1916), gives m. p. 148°.

[37] Michael, THIS JOURNAL, 41,419 (1919)

[38] It is significant to note in comparison with this result that the products of complete reaction at *25* of 26 g. of acetoacetic ester, sodium ethoxide (from 4.6 g. of sodium in 100 cc. of alcohol), and 22 g. of ethyl bromide contain approximately 40% ethylacetoacetic ester and 10% di-ethylacetoacetic ester. It is apparent that when an alkyl halide acts upon a sodium enolate with equal or less velocity than it does upon alcoholic sodium ethoxide, it is evidently not advisable to carry out the reaction in alcoholic solution.

[38a] Gault and Klees [Bull. *soc.* chim , 39, 1000 (1926)] by the action of chloroacetoacetic ester upon sodium enol malonic ester obtained among other products a liquid of b. p. 170–175° (15 mm.), which they considered to be α-acetyl-α'-carbethoxy succinic ester. By the action of sodium enol acetoacetic ester upon chloromalonic ester they obtained a solid compound m p. 34" which they regard as the keto form of a-acetyl-a'-carbethoxysuccinic ester. However, the solid they describe is very close in its properties to α,α'-di-aceto-succinic ester (α_3 form, m p. 32") and we propose to examine this point in another communication

dium suspended in ether and the mixture allowed to stand overnight, when the formation of the sodium derivative was complete; 49 g. of chloromalonic ester was added and the mixture warmed gently on the water-bath for one hour. After cooling, the excess of alkali was neutralized by dilute acetic acid and the neutral product was washed with 10% sodium carbonate, dried and fractionated: 40 g. of material distilling at 60–120° (15 mm.) was apparently unchanged acetoacetic and chloromalonic esters; 20 g. distilling at 140–160° (5 mm.) consisted of a-acetyl-a-carbethoxysuccinic ester. A higher boiling fraction 160–200° (5 mm.) (10 g.) partially solidified; the solid was ethanetetracarboxylic ester.[39]

The a-acetyl-a'-carbethoxysuccinic ester was refractionated and obtained as a colorless oil, b. p. 147" (5 mm.), which gave a deep red color with alcoholic ferric chloride; yield, 25%.

Anal. Calcd. for $C_{13}H_{20}O_7$: C, 54.16; H, 6.94. Found: C, 53.95; H, 6.79.

It readily gave a semicarbazone, m. p. 76°.

Anal. Calcd. for $C_{14}H_{23}O_6N_3$: C, 48.70; H, 6.67. Found: C, 48.53; H, 6.90.

Methylation.—To a cold solution of 2.3 g. of sodium in 30 cc. of ethyl alcohol, 28.8 g. of a-acetyl-a'-carbethoxysuccinic ester was added. After the mixture had stood for two hours, 18 g of methyl iodide was added and the mixture left overnight cooled in ice water. The product was diluted with ether and washed with dilute acetic acid, then with aqueous sodium carbonate and dried and fractionated.

There was obtained 27 g. of ester, b. p. 144–152° (2 mm.), which gave a deep red color with alcoholic ferric chloride. Saponification with barium hydroxide showed that the product consisted almost entirely of **a-acetyl-a'-methyl-a'-carhoxysuccinic** ester.

Anal. Calcd. for $C_{14}H_{22}O_7$: C, 55.62; H, 7.28. Found: C, 55.03; H, 7.40.

Saponification with Barium Hydroxide.—Five grams of the above methylated ester, b. p. 144–152" (5 mm.), was boiled for four hours with a slight excess of 8% barium hydroxide solution. The product was cooled and the precipitate of barium salts filtered off, washed with ether, decomposed with hydrochloric acid in the cold and the organic acid extracted with ether. A sirupy acid was obtained which from chloroform-ligroin solution slowly deposited crystals (m. p. 158°). This solid acid (0.7 g.) on recrystallization melted at 166" with decomposition and analysis indicated that it had the composition $C_6H_8O_6$. The mixed melting point with a sample of a-methyl-a-carboxysuccinic acid (m. p. 170°) was not lowered. The latter acid was prepared from chloromalonic ester and sodium enol methylmalonic ester.[40] Moreover, upon heating a portion of this acid at 175° for fifteen minutes, methylsuccinic acid was obtained, melting at 111° after recrystallization, and shown to be identical, by mixed melting point, with methylsuccinic acid.

The remaining sirupy acid which could not be obtained in crystalline form was heated at 150° for fifteen minutes and a product obtained that distilled at 155° (5 mm.). This was then shown to be α-methyllevulinic acid by direct comparison and by a mixed melting point of the semicarbazone (m. p. 191°). No indication could be found of the presence of β-methyllevulinic acid in the decomposition product.

The filtrate from the insoluble barium salts was evaporated on the water-bath to a small bulk and the acid extracted with ether after acidifying. On concentration of the ether solution, the acid separated as glittering plates. It was recrystallized from ace-

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[39] It seems probable that in the alcoholic solution some chloromalonic ester was reduced to malonic ester, from which the necessary sodium enol malonic ester was formed that reacted with unchanged chloro ester to give the tetracarboxylic ester.

[40] Bischoff and Kuhlberg, *Ber.*, 23, 635 (1918); Blaise and Gault, Bull. *soc. chim.*, [4] 9,460 (1912).

tone and melted at 295–300° with sublimation It gave no color with alcoholic ferric chloride. Analysis agrees with the formula of 4,5-dimethylcyclopentane-1,3-dione-4,5-dicarboxylic acid; yield, 0.5 g.

Anal. Calcd. for $C_9H_{10}O_6$: C, 50.47; H, 4.67. Found: C, 50.29; H, 4.63.

α-Methyl-α-carboxylevulinic ester was prepared by the condensation of bromoacetone with sodium enol methylmalonic ester in alcohol solution. A yield of 50% was obtained and the keto ester distilled at 133° (5 mm.).

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.40; H. 7.83. Found: C, 57 15; H, 8.0.

This ester readily gave a sernicarbazone, m. p. 102°.

Anal. Calcd. for $C_{12}H_{21}O_5N_3$: C, 50.18; H, 7.32. Found: C, 49.95; H, 7.47.

α-Methyl-α-carboxylevulinic acid was obtained as a sirup through saponification of the above ester with barium hydroxide. Upon distillation, it gave a-methyllevulinic acid, b. p. 160° (5 mm.), which was characterized by the sernicarbazone, m. p. 191°.[41]

The Action of Sodium Ethoxide upon α-Acetyl-α-carbethoxysuccinic Ester.—To a suspension of sodium ethoxide prepared from 1.2 g. of pulverized sodium and **23** g. of ethyl alcohol in ether, 14 g. of the above ester was added and the mixture warmed for two hours upon the water-bath. The mixture was cooled and added to 40 cc. of water containing 4 g. of acetic acid, and extracted with ether. The ether solution was washed with sodium carbonate and a considerable amount of acid material removed. The acid fraction was acidified and the acid recovered as a thick sirup which, however, did not crystallize. The neutral ester was distilled and 9 g. of ester, b. p. 150–155° (2 mm.) was obtained which partially crystallized upon standing. The solid ester was filtered off and crystallized from ether–ligroin mixture. It melted at 86° and gave no coloration with alcoholic ferric chloride. It may have the bicyclic structure (XV).

Anal. Calcd. for $C_{11}H_{14}O_6$: C, 54.55; H, 5.79. Found: C, 54.91; H, 5.37.

The liquid ester, b. p. 149° (2 mm.), gave a deep blue color with alcoholic ferric chloride and because of this fact was tentatively ascribed the structure (XIV).

Anal. Calcd. for $C_{11}H_{14}O_6$: C, 54.55; H, 5.79. Found: C, 54.86; H, 5.60.

This liquid ester readily gave a di-semicarbazone melting at 220° and which crystallized in plates from dilute alcohol.

Anal. Calcd. for $C_{13}H_{20}O_6N_6$: C, 43.54; H, 5.62. Found: C, 43.84; H, 6.1.

With equimolecular quantities of semicarbazide acetate this ester gave a compound of m. p. 76°, crystallizing in large prisms from ether. From analysis it would appear to be a bicyclic pyrazole derivative

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: C, 52 39; H, 5.56. Found: C, 52.42; H, 6 10.

C. Action of Chlorocarbonic Methyl Ester upon Sodium Derivatievs of **Enol Benzoyl** Acetone.—Sodium methoxide was prepared by adding 8.0 g. of methyl alcohol to a suspension of 5.7 g. of pulverized sodium in ether, and standing for twelve hours at room temperature. An ether solution of 40.5 g. of berizoylacetone was added and to the sodium derivative thus obtained as a fine yellow suspension, 24 g. of methyl chlorocarbonate diluted with ether was gradually added to the cooled material. The mixture stood for twelve hours although most of the reaction was completed at the end of one hour. The ethereal mixture reacted slightly alkaline and was washed first with dilute acetic acid and then several times with 10% sodium carbonate, followed by water, and was dried with calcium chloride. The ether was removed on the water-bath and residue distilled up to 150° (3 mm.). A small quantity of unchanged benzoylacetone separated which had not been extracted by the sodium carbonate. On cooling 27 g. of solid keto ester, m. p. 57°, separated out as large needles, leaving 11.5 g. of a

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[41] *Cf* March, *Comfit. rend.*, 134,180; *Ann. chim* , [7]**26, 323** (1902).

liquid keto ester which on redistillation boiled at 164° (2 mm.). Approximately 5.7 g. of benzoylacetone was recovered, so that the 85% of benzoylacetone that had reacted gave a ratio of nine parts of solid to four parts of liquid keto ester.

Solid Keto Ester.—This crystallized in long, colorless needles from a mixture of ether and ligroin, m. p. 57°. It gave no coloration with alcoholic ferric chloride.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.46; H, 5.45. Found: C, 65.30; H, 5.63.

Liquid Keto Ester.—This was purified by two fractional distillations and freezing out of the solid isomer. It was noticed that after distillation the solid isomer always appeared in the first and last fractions, which made it probable that the liquid ester was converted into the solid isomer upon heating to the boiling point temperature. A sample after keeping for six months at ordinary temperature showed no sign of changing into the solid form. The ester is a slightly yellow, highly refractive liquid which gave a deep red color with alcoholic ferric chloride, and boils at 164" (2 mm.).

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.46; H, 5.45. Found: C, 65.60; H, 5.70.

Behavior Toward Semicarbazide and Salts

(a) Solid Keto Ester.—Using semicarbazide hydrochloride with an excess of sodium acetate in the cold gave the same results as free semicarbazide. An equivalent amount of the reagent in each case was added gradually to an alcoholic solution of the ester, cooling, and from 2.2 g. of the keto ester an immediate precipitation of 0.6 g. of a finely crystalline solid appeared, m. p. 166". After several hours, large crystals of a slightly yellow solid, m. p. 183° (1.5 g.), were deposited, and after several days, 0.3 g. of a white solid, m. p. 202°.

Semicarbazone, m. p. **166°.**—This recrystallized from aqueous alcohol as fine plates, which gave a deep blue color with alcoholic ferric chloride. This fact, with the analysis, suggests that it is a semicarbazone of benzoylacetoacetate of structure (XXV).

Anal. Calcd. for $C_{13}H_{15}O_4N_3$: C, 56.31; H, 5.54. Found: C, 56.35; H, 5.7.

Semicarbazone m. p. 183° crystallized in slightly yellow prisms from dilute alcohol It was the main product of the reaction, gave no color with alcoholic ferric chloride and was apparently the semicarbazone of the O-carbomethoxy keto ester. An alcoholic solution of this semicarbazone containing a small amount of acetic acid when warmed to 50° for a few minutes becomes colorless and upon cooling quantitatively deposits the semicarbazone of benzoylacetoacetate, m. p. 166". The small quantity of acetic acid apparently causes migration of the carbomethoxyl group from oxygen to the methylene carbon atom.

Anal. Calcd. for $C_{13}H_{15}O_4N_3$: C, 56.31; H, 5.54; Found: C, 56.42; H, 5.63.

Semicarbazone m. p. 202° crystallized in needles from dilute alcohol. The analysis pointed to a condensation product of keto ester with more than two molecules of semicarbazide.

Anal. Found: C, 34.7; H, 4.94.

Semicarbazide hydrochloride with an equivalent weight of sodium acetate in the cold reacted as follows: 2.2 g. of keto ester was mixed in the cold with an aqueous solution of 1.1 g. of semicarbazide hydrochloride and 1.3 g. of sodium acetate. There was an immediate precipitation of 0.6 g. of the solid semicarbazone of benzoylacetoacetate, m. p. 166°. None of the semicarbazone of the O-carbomethoxy keto ester, m. p. 183°, was formed. After seven days an oil separated which solidified on cooling. This crystallized from ligroin in large prisms, m. p. 62°. It gave no color with alcohclic ferric chloride. Analysis showed that it was 3,5-methylphenylpyrazole-4-carboxylic (methyl ester).

Anal. Calcd. for $C_{12}H_{12}O_2N_2$: C, 66 66; H, 5.55, N, 12.96. Found: C, 66.7; H, 5.28; N, 13.2.

(b) On Liquid Keto Ester.—No definite products could be isolated.

Action of Aqueous Ammonia.—This reagent added to an alcoholic solution of each of the isomeric O-esters caused decomposition in each case, benzoylacetone crystallizing out in about one hour.

Action of **Hydroxylamine.**—An aqueous solution of the free amine reacted on the solid keto ester in methyl alcohol solution in the same way as aqueous ammonia above. After half an hour, crystals of benzoylacetone were deposited. With hydroxylamine acetate, a 50% yield of 3-methyl-5-phenylisoxazole was obtained from the solid and also from the liquid carbomethoxy ester.

Action of Aniline.—To an ether solution of the solid ester, an equivalent quantity of freshly distilled aniline dissolved in ether was added. The anil of benzoylacetone $C_6H_5COCH{=}C(NHC_6H_5)CH_3$, m. p. 110°, crystallized out as deep yellow prisms after standing at room temperature for about three days. The isomeric esters gave the same product, the liquid 0-ester apparently showing slightly greater reaction velocity. Benzoylacetone with aniline in ether solution after standing several days at room temperature gives the same product.[42]

Action of Potassium Carbonate.—To a solution of 8.8 g. of solid keto ester in methyl acetate, 4.0 g. of dry potassium carbonate was added, and the mixture boiled on the water-bath for four hours. The solution was filtered from the solid potassium carbonate, washed with water and dried. Upon concentration 7.0 g. of unchanged solid ester crystallized out. There remained a small amount of material in the mother liquor which proved to be henzoylacetone. A small amount of benzoylacetone was also obtained upon acidifying the potassium carbonate residue; 80% of the solid ester was recovered unchanged and approximately 15% of benzoylacetone was obtained. No indication of benzoylacetoacetic ester was found.

Reduction.—The method described by Adams[43] was used. A solution of 8.8 g. of the solid keto ester (m. p. 57°) in methyl alcohol, to which 0.2 g. of the platinum oxide catalyst was added, was shaken in an atmosphere of pure hydrogen. A total volume of 1750 cc. of hydrogen (1.8 molecular equivalents) was rapidly taken up and then absorption ceased. The absorption curve showed no significant change in the rate of absorption at the point where one molecular equivalent of hydrogen was taken up, so that it was necessary to proceed until hydrogenation was complete under the conditions used.

The solution was filtered, shaken with activated charcoal and the reaction product distilled after removal of the methyl alcohol. It boiled at 117° (8 mm.) as a colorless liquid with a characteristic odor.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.07; H, 8.11. Found: C, 80.72; H, 8.30.

This ketone readily gave a semicarbazone with alcoholic sodium acetate solution of semicarbazide hydrochloride, which crystallized in fine needles, melting at 188°.

Anal. Calcd. for $C_{11}H_{15}ON_3$: C, 64.39; H, 7.32. Found: C, 64.62; H, 7.50.

A mixed melting point showed this semicarbazone to be identical with the semicarbazone of n-propyl phenyl ketone, which was prepared from butyryl chloride and benzene.[44]

When similarly treated with hydrogen, the liquid keto ester also gave n-propyl

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[42] Beyer, *Ber.*, 20, 1770, 2180 (1887).

[43] Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

[44] (a) Burckev, *Ann. chim.*, [5] 26,467 (188.2); (b) Sorge, *Ber.*, 35, 1073 (1902).

phenyl ketone. The rate of absorption of hydrogen was slightly more rapid than with the solid keto ester. The saturated ketone was identified through the semicarbazonc, m. p. 188°.[44b]

Catalytic Reduction of **Benzoylacetone.**—Benzoylacetone was carefully purified by recrystallization from methyl alcohol; 8.0 g. of benzoylacetone in 100 cc. of methyl alcohol was treated with hydrogen in the same manner as in preceding experiments; 1950 cc. of hydrogen was rapidly absorbed. The methyl alcohol was removed under reduced pressure and the product distilled. There was obtained 7.5 g. of **1-phenylbutane-1,3-diol,** b. p. 129–131" (2 mm.). It was a fragrant smelling oil which at this pressure distilled without decomposition, and gave no color with femc chloride immediately, but upon standing the solution developed a red coloration, possibly due to oxidation to benzoylacetone.

Anal. Calcd. for $C_{10}H_{14}O_2$: C. 72.25; H, 8.43. Found: C, 71.96; H, 8.13.

Addition of acetyl chloride to a pyridine solution of the above diol gave a diacetate, b. p. 140° (2 mm.), a colorless oil.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.20; H, 7.23. Found: C, 67.53; H, 7.6.

D. Action of Chlorocarbonic Methyl Ester upon Sodium **Enol Dibenzoylmethane.**—To a suspension of 3.3 g. of pulverized sodium in ether, 32 g. of dibenzoylmethane in ethereal solution was gradually added, and the mixture left overnight cooled in ice water. To the fine yellow mass of the anhydrous sodium derivative, 13.5 g. of chlorocarbonate methyl ester, diluted with ether was gradually added. The mixture did not rise in temperature and so was left at room temperature for twelve hours. The product was washed with water, then with sodium carbonate solution, dried and the ether distilled off on the water-bath. As the product decomposed on distillation *in vacuo,* it was therefore heated at 100° (10 mm.) to remove any lower boiling substance. The residual sirup was dissolved in a mixture of ether and ligroin and permitted to crystallize by slow evaporation in a desiccator over paraffin wax. After some unchanged dibenzoylmethane (12 g.) crystallized out, a crystalline solid of m. p. 90° separated. This was recrystallized from a mixture of ether and ligroin. This solid gave no color with alcoholic ferric chloride and is the O-carbomethoxy derivative of dibenzoylmethane; yield, 3 g.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.35; H, 4.85. Found C, 72.60; H, 5.04.

There remained 15 g. of sirup of undetermined composition. In another experiment the sodium derivative was prepared from powdered sodamide. The solid sodium enol dibenzoylmethane being filtered off and washed with dry ether, and treated as described above, a 30% yield of the O-carbomethoxy derivative, m. p. 90°, was obtained together with 20% of the sirupy liquid product.

E. Action of Semicarbazide and its Salts on Benzoylacetone

In the Presence of Excess Sodium Acetate.—An excess of semicarbazide hydrochloride (2.2 g.) was dissolved with 3.0 g. of sodium acetate in a minimum of cold water and the solution added to 3.2 g. of benzoylacetone dissolved in cold alcohol. After standing for an hour, at room temperature, large prisms were deposited but the reaction took about two days for completion. Upon recrystallization from dilute alcohol, the substance (3.8 g.) melted at 127–128° and was the monosemicarbazone of benzoylacetone. It gave a deep green color with alcoholic ferric chloride.

Anal. Calcd. for $C_{11}H_{13}O_2N_3$: C, 60.28; H, 6.12; N, 19.18. Found: C, 60.12; H, 6.04; N, 19.05.

Free **Semicarbazide.**—An equivalent quantity of 2.4 N caustic soda was added to a cold solution of semicarbazide hydrochloride, and this solution mixed in the cold with an alcoholic solution of benzoylacetone. The above monosemicarbazone was obtained in almost the theoretical yield.

Semicarbazide Hydrochloride.—Two and two-tenths grams of semicarbazide hydrochloride dissolved in a minimum of water was added in the cold to 3.2 g. of benzoylacetone in alcohol. After several minutes the solution became warm, a few bubbles of gas were evolved, and it was therefore cooled in water. Some long needle-shaped crystals were deposited (0.1 g., melting at 161°) which proved to be 3,5-methylphenylpyrazole-1-carboxamide. Later a flocculent mass (1.3 g.) separated. Upon dilution of the reaction liquid, some unchanged benzoylacetone was obtained. The flocculent material crystallized from a mixture of ethyl acetate and ligroin as large prisms, melting at 121–122°. Analysis and reactions showed this to be 3,5-methylphenylpyrazole. It was found to be identical with a sample prepared from hydrazine and benzoylacetone.[46]

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.95; H, 6.33; N, 17.72. Found: C, 75.72; H, 6.50; N, 18.0.

Action of Semicarbazide Acetate at 60°.—Two and two-tenths grams of semicarbazide hydrochloride was dissolved with 2.7 g. of sodium acetate in the minimum of water and the solution added to 3.2 g. of benzoylacetone in alcohol. The mixture was warmed in a water-bath at 60° for half an hour. The main product was 3,5-methylphenylpyrazole together with a small amount of 3,5-methylphenylpyrazole-1-carboxamide.

Action of Two Molecules of Semicarbazide on Benzoylacetone.—Two and two-tenths grams of semicarbazide hydrochloride was dissolved with 3.0 g of sodium acetate in a minimum of water and the solution added to 1.6 g. of benzoylacetone in alcohol. On standing for one hour in the cold, fine needle crystals of the disemicarbazone were deposited, melting at 242°.

Anal. Calcd. for $C_{12}H_{16}O_2N_6$: N, 30.43. Found: N, 30.80.

Action of Acids on Benzoylacetone Monosemicarbazone.—The pure monosemicarbazone, m. p. 128°, can be recrystallized from boiling aqueous alcohol without showing any signs of change or decomposition. However, when warmed to 60° in the presence of acetic or of hydrochloric acids (equivalent quantity), it readily undergoes ring formation to give a mixture of 3,5-methylphenylpyrazole-1-carboxamide and 3,5-methylphenylpyrazole of varying proportions. The substances are easily separated, the carboxamide crystallizes out as long needles before the pyrazole is deposited. The 3,5-methylphenylpyrazole-1-carboxamide must be carefully freed from traces of acid before recrystallization, as otherwise it readily undergoes hydrolysis, losing carbon dioxide to give the 3.5-methylphenylpyrazole.

Anal. Calcd. for $C_{11}H_{11}ON_3$: C, 65.67; H, 5.47; N, 20.9. Found: C, 65.42; H, 5.63; N, 21.0.

Summary

1. The reaction velocities of sodium enol acetoacetic ester, sodium enol malonic ester and sodium ethoxide in alcohol solution with methyl iodide and ethyl bromide are compared.

2. The products of the reactions in alcoholic solution between sodium ethoxide, acetoacetic ester and malonic ester and (a) methyl iodide and (b) ethyl bromide are determined quantitatively and the course of the reactions explained.

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[46] Sjollema, *Ann.*, 279, 268 (1894); Posner, *Ber.*, 34, 3983 (1901); and Moureu and Brachin, Hull. *soc. chim.*, [3] 31, 172 (1904), give m. p. 127°.

3. The results of the methylation of sodium enol α-acetyl-α'-carbethoxysuccinic ester is interpreted in the light of the above experiments.

4. The formation of carbomethoxy derivatives from chlorocarbonic methyl ester and sodium enol benzoylacetone in stereomeric forms is proved and its bearing upon the structure of sodium enol benzoylacetone discussed.

5. The products of the reaction between benzoylacetone and semicarbazide are described.

6. The structure of enol benzoylacetone is discussed and an explanation offered of the apparent discrepancy between the results of physical and chemical investigations.

7. The above experiments are interpreted in the light of the partition principle as applied to organic reactions, subject to the reaction velocities and reactivities of the groups involved.

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NOTES

Trichloromethylcyclopentanol-1.—The condensation of chloroform with ketones to give tertiary trichloro alcohols has been limited to acetone[1] and methyl ethyl ketone.[2] Other ketones have been tried but unsatisfactory results have been obtained in every case where a ketone of more than four carbon atoms was used.[3]

In view of the fact that this condensation reaction seemed to be limited to the two lowest members of the series of aliphatic ketones, it was decided to try two of the alicyclic type. Cyclopentanone and cyclohexanone were used and the procedure followed was essentially that described by Willgerodt.

Nine parts of cyclopentanone was mixed with thirteen parts of chloroform and six parts by weight of powdered potassium hydroxide was added over a period of several hours with constant stirring. A vigorous reaction sets in unless the mixture is kept well cooled by surrounding the reaction vessel with ice. When all of the potassium hydroxide had been added, it was allowed to stand for six days at 0–10°, being stirred occasionally. The residue was then filtered off and washed with ether. The combined filtrate and washings, after being neutralized with dilute hydrochloric acid, were washed with water and dried over anhydrous sodium sulfate. Distillation was carried out at atmospheric pressure until all of the ether, unreacted chloroform and cyclopentanone were removed. When the

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[1] Willgerodt, *Ber.*, **14**, 2451 (1881).

[2] Ekeley and Klemme, THIS JOURNAL, **46**, 1252 (1924).

[3] Howard, *ibid.*, **48**, 774 (1926).

temperature reached 140°, decomposition set in so the residual oil was steam distilled. This distillate was then treated with sodium bisulfite solution to remove traces of ketone, taken up in ether and again dried over anhydrous sodium sulfate. On fractional distillation under vacuum no definite product was obtained; it was therefore decided to treat the mixture with bromine water so that the boiling point of unsaturated impurities, formed by condensation of the ketone with itself, would be raised sufficiently to facilitate the separation. A fraction was collected which on further purification distilled at 102--102.5" at 10 mm. The yield was about 3.0% based on the total ketone used or 9.1% calculated on the amount reacting. The unsaturated impurity which has a boiling point so near that of the alcohol is cyclopentylidene-cyclopentanone.

Trichloromethylcyclopentanol-1 is a colorless oily liquid, insoluble in water, but soluble in ether, benzene, chloroform, carbon disulfide, carbon tetrachloride and glacial acetic acid; specific gravity, 1.3690^{25}_{4}; n^{25}_{D} 1.5066.

Anal. Calcd. for $C_6H_9OCl_3$: Cl, 52 29. Found: Cl, 52.03, 51.82. Mol *wt* (in benzene). Theoretical, 203.4. Found: 201.O, 205.9.

In an attempt to react chloroform and cyclohexanone by the above method, qualitative tests indicated that a small amount of the alcohol derivative was formed but apparently the tendency for this ketone to condense with itself is somewhat stronger than that of the cyclopentanone. A yield of about 15% of cyclohexylidene-cyclohexanone was obtained which was identified by means of the semicarbazone.[4] Approximately 75% did not react and apparently the remainder formed higher condensation products.

CONTRIBUTION FROM THE
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RECEIVED APRIL 17, 1931
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Isopropylcyanoacetic Acid.—Hessler[1] describes pure isopropylcyanoacetic acid as a viscous liquid. The acid obtained by treating with 10% sodium hydroxide solution under Hessler's conditions the mixture of 95% di- and 5% mono-isopropylcyanoacetic esters prepared by the author's modification of Hessler's process[2] was a viscous liquid such as he describes, but after distilling under 15 mm. pressure and keeping for a short time in ice, it developed numerous nuclei from which crystallization proceeded at laboratory temperature till the whole bulk set to a mass of plates.

Freed from traces of oil on a cooled porous plate (0°), these melted

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[4] Garland and Reid, THIS JOURNAL, 47, 2336 (1925).

[1] Hessler, THIS JOURNAL, 35, 990 (1913).

[2] Marshall, J. *Chem. Soc.*, 2754 (1931).

sharply at 31°. Calcd. for $C_6H_9O_2N$: C, 56.6; H, 7.1. Found: C, 56.55; H, 7.2.

THE IMPERIAL COLLEGE OF
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RECEIVED MAY 4, 1931
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COMMUNICATIONS TO THE EDITOR

THE CRYSTAL STRUCTURES OF ELECTRODEPOSITED ALLOYS. SILVER-CADMIUM

Sir:

The crystal structures of silver–cadmium alloys, ranging in composition from 20% Cd to 96% Cd, have been obtained from x-ray diffraction data. The alloys were deposited at room temperature according to the method of Stout [Preprint No. *29,* Trans. ***Am. Electrochem. Soc.,*** *59* (1931)], using a current density of one ampere.

In general, the structures of the alloys are quite different from those of thermal alloys of corresponding composition which have been brought to equilibrium before examination. The alloys prepared under equilibrium conditions [Astrand and Westgren, ***Z. anorg. allgem. Chem.,*** **175,** 90 (1928)] show the following phases.

Percentage Cd	
0–44	**α–solid solution of Cd in Ag**
44–49	$\alpha + \beta$
49–51	**β–C_2Cl type cubic lattice. 8'–close-packed hexagonal lattice, similar to a, obtained when β is heated above 400° and suitably quenched. It differs from ϵ in axial ratio**
51–57	$\beta + \gamma$
57–66	**γ–body-centered cubic lattice**
66–69	γ + a
69–83	**ϵ–close-packed hexagonal lattice**
83–95	$\epsilon + \eta$
95–100	**η–solid solution of Ag in Cd**

Westgren notes that β should also be formed at high temperatures in the **γ-range** but his attempts to produce it by heating the y-phase failed

The electrodeposited alloys show the following structures: (1) 40% Cd—contains the α, β' and γ phases and may contain the β phase; (2) 46–75% Cd—only the ϵ phase is deposited. The crystals show a preferred orientation with respect to the base metal, and this orientation differs with the composition; (3) 89–96% Cd—the ϵ and η phases are deposited.

Our results do not agree with microscopic data recently published by Fink and Gerapostolou [Metal *Ind.* (N. Y.), 28, 519, 562 (1930)].

It is evident that under the conditions of deposition used in these experiments the r-phase is produced throughout the greater part of the range, and is apparently a metastable phase at least through the approximate range 46–66% of Cd. This is consistent with the behavior of some pure metals, which are known to be electrodeposited in metastable forms.

It is important to know how the conditions of deposition affect the crystal structure of an alloy of any given composition, since hardness and other physical properties depend upon the structure.

We are at present investigating (1) the effect of current density and temperature on crystal structure, the composition of the deposit remaining constant; (2) the recrystallization temperatures of Cd–Ag alloys.

DEPARTMENT OF CHEMISTRY
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URBANA, ILLINOIS
CHARLES W. STILLWELL

RECEIVED APRIL 9, 1931
PUBLISHED JUNE 8, 1931

EXPLOSION DURING THE CATALYTIC REDUCTION OF NITROANISOLE IN THE LIQUID PHASE

Sir:

Brown, Etzel and Henke [*J.* Phys. Chem., **32,** 631–635 (1928)] quantitatively reduced a number of nitro compounds in the liquid phase at about 215°, under a hydrogen pressure of about 500 lb. per sq. in., using a nickel catalyst. The reduction could be made either without a solvent or with benzene and ethyl alcohol. Their work was done on small quantities (about 5 g.) of material, in a shaking autoclave maintained at the desired temperature by immersion in an oil-bath.

The writer attempted to apply this method to the reduction of *o*-nitroanisole. As no danger was anticipated, the work was done on a technical scale, using 400 g. of the nitro compound. A shaking autoclave of steel was used, of about 3000 cc. total capacity, heated electrically. The first experiment was made using benzene as a solvent, with a nickel catalyst, and gave approximately a 50% yield of amine. In the next, the solvent was omitted and the catalyst was carefully prepared to give a very active product; 250 g. of nickel nitrate was ignited at 400°, and then heated for three hours in a muffle at 560°. The oxide was reduced in the autoclave under a stream of hydrogen at a temperature of 280–300°. Four hundred grams of the nitroanisole, freshly distilled, was then added and hydrogen was passed in to a pressure of 500 lb. At a temperature of 250°, with shaking, the hydrogen was rapidly taken up, and the pressure dropped in about fifteen minutes to 250 lb. It then began to rise rapidly, and reached a total of 500 **lb.** in about five minutes. In thirty seconds more the pressure jumped to 1000 lb. The writer then opened the needle valve on the autoclave in the hope of relieving the pressure. Gas and liquid shot out of the valve, and an instant later the autoclave exploded with great violence.

The autoclave, a steel shell three-sixteenths of an inch thick by about fifteen inches long and six inches in diameter, failed by splitting open on one side. Before use, it had been tested to 1500 lb. pressure. The detonation was of sufficient violence to blow out all the windows of the laboratory and shake a large concrete building.

The explosion could not have been caused by any mixture of hydrogen and oxygen in the autoclave, as the autoclave had been thoroughly swept out with hydrogen during the reduction of the catalyst. As was indicated by the initial pressure drop, reduction was taking place very satisfactorily. It seems probable that the explosion was caused by decomposition of the nitro compound itself, possibly by auto-oxidation, or possibly by rapid oxidation by the nitro body of an intermediate product of the reduction. This may have been induced by the catalyst, which was evidently quite vigorous, and it may have been aided by local high temperature attained by the rapid reduction. In the original work of Brown, Etzel and Henke, such dangers as these were eliminated by the small scale on which they worked and by the adequate cooling afforded by the oil-bath.

The purpose of this note is to call the attention of other investigators to the dangers of this type of reduction when carried out on other than a very small scale.

MONSANTO CHEMICAL WORKS
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RECEIVED APRIL 29, 1931
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THE RAMAN SPECTRA OF FORMALDEHYDE, TRIOXYMETHYLENE, ETHYLENE GLYCOL, AND OF SOME VISCOUS LIQUIDS

Sir:

The Raman spectrum of a 37% solution of formaldehyde in water consists of at least nine lines corresponding to frequencies, expressed in wave numbers of 802, 909, 1055, 1285, 1479, 2840, 2915, 3015 and 3087. Trioxymethylene gives modified lines corresponding to 497, 579, 674, 908, 1050, 1232, 1285, 1376, 1477 and 1527 wave numbers. Ethylene glycol gives lines corresponding to 341, 491, 526, 869, 1040, 1274, 1460, 2725, 2874, 2948, 3048 and 3131 wave numbers. Except for a fairly consistent shift toward the higher frequencies, of about 25 wave numbers, the stronger Raman lines from the aldehyde solution correspond both in intensity and in distribution to those from ethylene glycol. No lines are found typical of the C=O linkage (1675–1725) for formaldehyde. On the other hand, the line at 1050 typical of C–O is fairly strong. These observations would seem to indicate the formation of methylene glycol by formaldehyde in aqueous solution. This is compatible with the observations of Auerbach and Barschall [Chem. *Zentr.*, II, 1081 (1905)] and Walker [J. *Phys.* Chem., 35, 1104 (1931)], who came to the same conclusion from cryoscopic and vapor pressure measurements. The absence of frequencies less than 800 wave numbers indicates that the concentration of higher polymers in a solution of this concentration must be small. The absence of a modified line in the 1675–1725 region for the trioxymethylene and the presence of a line corresponding to the C–O linkage may be due to the formation of a trimer in the manner suggested by Venkateswaren and Bhagavantam [*Proc.* Roy. *Soc.* (London), **128,** 260 (1930)] for paraldehyde. The presence of only three frequencies below 900 wave numbers may indicate that the polymer consists of not more than three aldehyde units. Lines corresponding to C–H linkage for the trioxymethylene are very weak and as yet have not been definitely identified.

That strong continuous Raman spectra may be a property common to viscous liquids has received some substantiation from the Raman spectra of sodium silicate, orthophosphoric acid, potassium hydrogen phosphite and ethylene glycol solutions. The continuous spectra decrease on dilution and on temperature elevation. This behavior is similar to that observed with glycerin by Venkateswaren [Indian *Journal* Phys., **3,** 105 (1928)]. This phenomenon may possibly owe its origin to intermolecular attraction, the continuous spectra arising from the probability of a large number of energy levels. The Raman spectrum of α-chloronaphthalene consists of 16 lines and shows some similarities to that of chlorobenzene and naphthalene.

A detailed account of these experiments will be communicated later.

THE GEOPHYSICAL LABORATORY
CARNEGIE INSTITUTION OF WASHINGTON
WASHINGTON, D. C.
JAMES H. HIBBEN

RECEIVED MAY 8, 1931
PUBLISHED JUNE 8, 1931

THE IONIZATION CONSTANT OF ACETIC ACID

Sir:

We have obtained a precise value of the ionization constant of acetic acid at 25° from the results of new conductance measurements, made in this Laboratory, on acetic acid, hydrochloric acid, sodium chloride and sodium acetate at low concentrations (the lowest in each case being about 0.00003 N). The principles underlying the computations are essentially those which have been outlined by one of the undersigned [MacInnes, THIS JOURNAL, **48,** 2068 **(1926)**]. The calculations take account of the change of the mobilities of the ions as required by the Debye–Hückel–Onsager theory and of the ion activities as predicted by the Debye–Hückel theory. The computations, which involve a short series of approximations, consist in estimating the proportion of ions at each acetic acid concentration by comparing the measured equivalent conductance with that of completely dissociated acetic acid, A„ at the same ion concentration. Values of A, are found by using Kohlrausch's law of independent ion migration, which is valid at the low ion concentrations involved. Applying the mass action law to the resulting degrees of dissociation we find a series of "constants," K', which, to obtain the thermodynamic ionization K, must be multiplied by the product of the ionic activity coefficients, γ^2.

It is noteworthy that to obtain a true constant the activity coefficients required are exactly those given by the Debye–Hückel theory in its limiting form

$$-\log \gamma^2 = 2 \times 0.5065 \sqrt{C_i}$$

in which C_i is the ion concentration. The results for the more dilute solutions are given in Table I.

TABLE I

RESULTS FOR THE MORE DILUTE SOLUTIONS

Concentration, equivalents per liter $\times 10^3$	Ion concn., C_i $\times 10^3$	K' $\times 10^5$	γ^2	h $\times 10^5$
0.028014	0.015092	1.7620	0.9910	1 747
.15321	.044005	1 7733	.9846	1.740
.21844	,054096	1.7766	.9830	1.746
1.0283	,12714	1.7937	9741	1 747
1.3638	.14779	1 7961	.9721	1 746
2.4139	.19992	1.8053	.9776	1.747
3.4407	.24069	1.8104	.9645	1 746
5.9115	.31895	1.8189	.9592	1.745
9.8421	.41517	1.8285	.9536	1.744

Although extraordinarily constant in the range given, at higher concentrations there is a decrease in the value of K. This variation is due to several effects which may for the present be lumped together as "effect of the medium." The bearing of this value of K on the PH scale will be discussed later and full accounts of these researches will shortly be submitted to THIS JOURNAL.

LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

D. A. MACINNES
THEODORE SHEDLOVSKY

RECEIVED MAY 9, 1931
PUBLISHED JUNE 8, 1931

THE DIRECT REACTION BETWEEN OXYGEN AND ETHYLENE

Sir:

The direct reaction between oxygen and ethylene is of general theoretical and technical interest. Study of the reaction in this Laboratory has shown that the slow non-explosive thermal reaction is complex. Two compounds have been found to be formed in the reaction whose presence has not been demonstrated before; these compounds are ethylene oxide and dioxymethyl peroxide,[1] $CH_2OHOOCH_2OH$. Investigation of the reaction at temperatures from 300 to 525° under widely different conditions has shown that the two principal primary reactions are the formation of ethylene oxide and of formaldehyde. The other reaction products, dioxymethyl peroxide, acetaldehyde, formic acid, the oxides of carbon, hydrogen and water are formed in a step-wise sequence[2] of follow reactions. At temperatures above 500° the thermal polymerization of ethylene becomes an important reaction even in the presence of appreciable amounts of oxygen and inert gases.[3]

The velocity of reaction is proportional to the cube of the ethylene concentration and is almost independent of oxygen, as has been shown by Thompson and Hinshelwood.[4] Comparison of the rates of reaction in packed and unpacked vessels shows that the reaction is mainly homogeneous. The reaction has an induction period which decreases with increase in temperature. It appears that the reaction follows a chain mechanism though it is necessary to assume that the chains can be both continued and stopped by the surface of the vessel.

Evidence of the formation of hydrogen peroxide as a reaction product has been obtained.

A full account of this work will appear shortly.

EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND CO.
WILMINGTON, DELAWARE
SAMUEL LENHER

RECEIVED MAY 16, 1931
PUBLISHED JUNE 8, 1931

INTERATOMIC FORCES IN BINARY LIQUID ALLOYS. QUANTITATIVE DETERMINATION FROM THERMODYNAMIC DATA

Sir:

It is generally agreed that the attractive force between non-polar molecules varies inversely as some high power (*e.* g., the 9th) of the distance. Langmuir [This JOURNAL, **38**,2246 (1916)] has emphasized that the forces holding together such molecules are acting almost wholly between molecules *in contact* and that, as a very good approximation, all forces acting at greater distances may be neglected. The quantitative treatment of the properties of liquids in terms of power laws of force involves great mathematical difficulties when one attempts to consider molecules of irregular shape. Langmuir has shown that the problem may be greatly simplified

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[1] Legler, *Ann.*, 217, 381 (1883); Nef, *ibid.*, 298, 202 (1897); Baeyer and Villiger, Ber., 33, 2479 (1900); Fenton, *Proc.* Roy. *Soc.* (London), A90, 492 (1914); Rieche, "Alkylperoxide und Ozonide," Theodor Steinkopff Verlag, Dresden und Leipzig, Germany, 1931, p. 48.

[2] Bone and Wheeler, J. Chem. *Soc.*, 85, 1637 (1904); Blair and Wheeler, J. *Soc. Chem. Ind.*, 42, 415T (1923).

[3] Willstatter and Bommer, *Ann.*, 422, 36 (1921).

[4] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), A118, 170 (1928).

by regarding these van der Waals forces as coming into play between molecules only at the areas of contact. By using the concepts of surface area of individual molecules, and of interfacial energy for the contact surfaces, and assuming random orientation, he has developed through the Boltzmann equation ["Colloid Symposium Monograph," **3,** *48* (1925)] an expression for the deviation of activities from Raoult's law in binary liquid mixtures. So far as I know this relation has never been tested in binary liquid alloys where the situation is much simpler than in the cases of the organic mixtures discussed by Smyth and Engel [THIS JOURNAL, **51,** 2646 (1929)]. The equation is $\ln a_1/N_1 = \beta^2 S_1 \lambda/kT$ or $\ln a_2/N_2 = \alpha^2 S_2 \lambda/kT$, where $a = p/p^\circ$, p being the partial vapor pressure, p° the vapor pressure of the pure liquid, N the mole fraction, S the surface area per molecule, λ the energy per sq. cm. of interface between the two kinds of molecules, k the Boltzmann constant, T the absolute temperature and a and β are the surface fractions of the two components in the solution defined by $\alpha = N_1S_1/(N_1S_1 + N_2S_2)$ and $\beta = N_2S_2/(N_1S_1 + N_2S_2)$. The activity a may also be evaluated from electromotive forces of concentration cells. The ordinary molecular volume V which equals molecular weight/density, must be multiplied by 0.76 to take account of cubic or hexagonal close packing in the liquid, and divided by the Avogadro number to get the effective volume of a single molecule, v $= 4/3nr^3$. From this $S = 4nr^2$.

The thermodynamic data presented herewith are based upon electromotive force measurements of N. W. Taylor [This JOURNAL, **45,** *2884* (1923)] and of Hildebrand and Sharma [ibid., 51, *467* (1929)]; density values from Hogness [ibid., **43,** *1621 (1921)*] have been used.

INTERFACIAL ENERGIES BETWEEN METAL ATOMS IN LIQUID ALLOYS

System	Temp., t	Component 1	Component 2	Log a/N $N = 0$	$S \times 10^{16}$, sq. cm.	λ Ergs/sq. cm.
Zn–Cd	540°	Zn		0.490	25.8	48.8
Zn–Cd	540°		Cd	.615	32.8	48.2
Cd–Pb	544°	Cd		.480	32.8	37.7
Cd–Pb	544°		Pb	.582	40.6	37.0
Cd–Sn	544°	Cd		.246	32.8	19.4
Cd–Sn	544°		Sn	.270	37.3	18.7
Tl–Sn	352°	Tl		.444	37.6	23.4
Tl–Sn	352°		Sn	.44	36.7	23.9
Zn–Sn	539°	Zn		.240	25.8	23.9
Zn–Sn	539°		Sn	.60	37.3	41.3

The test of the Langmuir equation lies in a comparison of the two λ values calculated for each system from log a/N and S of each component independently. For all systems except zinc–tin the agreement is good to **3%.** Since the log a_2/N_2 values for the second component of each system were evaluated by the Duhem relation they are themselves uncertain to 1 or *2%.* They are somewhat smaller than the values given in my original paper which were based upon an incorrect extrapolation. The system zinc–tin is certainly abnormal as I pointed out in my original paper in 1923. In this case influences are present which inhibit random orientation of the molecules.

The Hildebrand equation for "Regular Solutions" RT In $a_1/N_1 = bN_2^2$ or R T In $a_2/N_2 = bN_1^2$ can be strictly true only when the two components have the same surface area per molecule. S_{Tl} exceeds S_{Sn} by only 2%, and this is the reason for the result found by Hildebrand and Sharma that "so far as the variation with N is concerned, this system corresponds perfectly to the definition of a regular system given by the senior author" (THIS JOURNAL, 51, 66 (1929)].

The evidence presented thus lends support to Langmuir's equation and to the assumptions upon which it is based.

More extensive data and a fuller treatment of this problem will be presented in a later publication.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
NELSON W. TAYLOR

RECEIVED MAY 16, 1931
PUBLISHED JUNE 8, 1931

RADIOCHEMICAL EQUILIBRIUM IN AMMONIA SYNTHESIS

Sir:

The attempt to calculate chemical equilibrium or a steady state attained by alpha radiation from the known yield per ion pair of the two opposing non-thermal reactions was first made for the synthesis and decomposition of water [Lind, *Trans.* Am. *Electrochem. Soc.*, 34, 214 (1918)]. The case for ammonia is much more suitable since the system remains entirely homogeneous. The decomposition of ammonia has been measured by Wourtzel [Le Radium, **11,** 342 (1919)]. The yield in synthesis was determined in a flow system by Lind and Bardwell [THIS JOURNAL, **50,** 745 (1928)] to lie in the range $+M_{\mathrm{NH_3}}/N_{(\mathrm{N_2} + \mathrm{H_2})} = 0.2\text{–}0.3$. Choosing 0.2 as the most probable value of $+M/N$ and the round number 1.0 (from Wourtzel) for the decomposition $(-M/N)$, Lind and Bardwell calculated that the equilibrium (at 25°) would be $(1.0/1 + 0.2) = 83.3\%$ decomposition, corresponding to *9.09%* NH_3 by volume.

Later Ponsaert [Bull. *soc.* chim. Belg., **38,** 110 (1929)] redetermined the yield for synthesis as ***0.32*** and taking 1.08 from Wourtzel for decomposition calculated equilibrium at 13.5% NH_3 by volume. The actual equilibrium has now been experimentally determined by D'Olieslager and Jungers [Bull. *soc.* chim. Belg., **40,** 75 (1931)] as only *4.7%* NH_3 by volume.

In calculating the equilibrium from the yields at the beginning of the opposing reactions where back-reaction is negligible, it has been assumed that the mechanisms of the two reactions at equilibrium are independent of each other in their intermediate steps. If this were true, it would require a value of $+M/N$ in synthesis of only 0.11 in order to give a steady state at 4.7% NH_3. That the value for synthesis cannot be so low has been shown above. It therefore appears that the intermediate steps are not independent and that there must be an exchange of activation energy in the direction to produce additional decomposition.

The principal object of this communication is to point out that the shift of equilibrium from that predicted is in the right direction to be accounted for by an exchange of ionization from the elemental ions H_2^+ (16 volts) or N_2^+ (17 volts) to give NH_3^+ (11 volts). Such transfer of ionization would favor decomposition at the expense of synthesis, assuming always that H_2^+ and N_2^+ in some way cause synthesis and that NH_3^+ causes decomposition.

This same type and direction of shift may be general in other similar reactions in gaseous phase, since the larger molecules will usually have a lower ionization potential than either of its components.

An effort is being made to test this hypothesis quantitatively for ammonia by means of a complete kinetic equation which should fit the kinetics of either reaction and the equilibrium.

School of Chemistry
University of Minnesota
Minneapolis, Minnesota
S. C. Lind

Received May 20, 1931
Published June 8, 1931

THE IONIC NATURE OF THE HYDROGEN BOND

Sir:

In a recent paper, Linus Pauling [This journal, 53, 1367 (1931)] has pointed out that the hydrogen bond postulated by Huggins, Latimer and Rodebush is to be expected only of molecules having ionic characteristics and that the bond itself is ionic. The evidence that is offered by Pauling is for the most part chemical, and it might be profitable to examine the question in the light of physical data not considered by him.

Work on the Raman effect [in particular Krishnamurti, ***Nature,*** 125, 892 (1930)] has indicated that Raman lines are to be expected with atomic bonds (*i. e.*, shared electron pairs) rather than with ionic linkages. The reason for this is obscure; but at least in solutions it may be due in many cases to the magnitude of the energy states involved in the various types of molecules or "resistant groups." Raman data on the association of liquids (such as H_2O, NH_3 and SO_3) are inconclusive so far as offering information about the character of this bond. It might be possible to decide this question from the sharpness of the lines. However, in all of the work that has been done on the Raman effect of hydrates and solutions no lines have been reported that may be interpreted as showing an "atomic vibration" of the water "molecule" with respect to the metal ion. A literal application of the older conception of this bond demands that there be such lines. The observed state of affairs is to be expected on the basis of Pauling's suggestion. Furthermore, if the hydrogen ion is connected to the water molecule by means of a shared electron pair in the oxonium ion, we would expect a Raman spectrum characteristic of the latter ion. This would mean that all solutions of acids would have lines in common. An examination of the data for nitric, hydrochloric and sulfuric acids shows that this is not the case.

Another interesting example is the ammonium ion. In solution this ion has no observable Raman lines. This indicates not only that the hydrogen ion connects itself to the ammonia molecule through an ionic linkage, but that in doing so it causes the other bonds to become ionic. It is entirely possible that the case of the oxonium ion is parallel, and that each hydrogen is connected to the oxygen through an ionic linkage.

As investigations in solutions are inherently under adverse conditions, the bond may actually be intermediate in character. At least the evidence indicates quite strongly that it is not of the extreme electron pair type formerly assumed.

U. S. BUREAU OF STANDARDS
WASHINGTON, D. C.
CHARLES KASPER

RECEIVED MAY 20, 1931
PUBLISHED JUNE 8, 1931

THE CARBON–HALOGEN BOND AS RELATED TO RAMAN SPECTRA

Sir:

The purpose of the work described here was to determine the variation of the characteristics of the bond between carbon and another atom as the length and structure of the hydrocarbon chain is varied. The frequency which corresponds to the carbon–bromine bond in methyl bromide is 1.808×10^{13} per second, but in longer normal chains this is reduced to a constant value of 1.688×10^{13}. In an iso compound or in the presence of a double bond, this is reduced to about 1.61×10^{13}. These frequencies are of considerable interest, since in the simple theory they are supposed to be equal to the frequencies of the carbon–bromine bond in these compounds.

What is sometimes called the "strength of a bond" may be represented by the force constant, which for the carbon–carbon single bond is about 5×10^5 dynes per cm. The values for the carbon–halogen bond do not seem to have been calculated for monohalogens. They are given in Table I.

The force constant (a) is calculated in the ordinary way, and it is considered that the methyl group vibrates as a unit with respect to the halogen atom. In (b) a slight, somewhat arbitrary allowance has been made for the fact that this is not strictly true.

TABLE I

VALUES FOR THE CARBON–HALOGEN BOND

Compound	Wave number, cm.$^{-1}$	Frequency per second $\times 10^{-13}$	Force constant $\times 10^{-5}$ dynes *a*	*b*	Amplitude $\times 10^{10}$ cm. $n = 0$	$n = 1$
CH_3Cl[1]	712	2.135	3.14	3.02	6.7	11.6
CH_3Br[2]	603	1.808	2.70	2.60	6.65	11.5
CH_3I[2]	534	1.601	2.25	2.17	6.9	11.9

The force constants decrease from the chloride to the iodide, in somewhat the same way as the corresponding energies of dissociation. Those given in Column *(a)* are much smaller than the values of the single bonds listed by Dadieu and Kohlrausch,[1] which are (in 10^5 dynes per cm.) equal to 4.31 for *C–C* in ethane, *4.96* for C–O in methyl alcohol, and 4.89 for C–N in methylamine.

That the frequencies chosen in Table I are those characteristic of the carbon–halogen bond is shown by work on various bromides. These are listed in Table II.

TABLE II

CHARACTERISTIC WAVE NUMBERS FOR THE CARBON–BROMINE BOND IN ORGANIC BROMIDES

CH_3Br	603 (2)	$(CH_3)_2CH(CH_2)_2Br$	564
C_2H_5Br	586 (2)	$(CH_3)_2CHBr$	540
n-C_3H_7Br	563	$C_2H_5CHBrCH_3$	537
n-C_4H_9Br	563	$(CH_3)_3CBr$	538
n-$C_5H_{11}Br$	564	$CH_2:CHCH_2Br$	535
		$(CH_2)_2CHCH_2Br$	572

The remarkable fact revealed by these data is that the frequency of the carbon–bromine bond is constant in normal compounds with the exception of methyl bromide, and that it is the same for an iso compound provided the side chain is sufficiently distant from the bromine. However, an adjacent side chain, attachment to a secondary or a tertiary carbon atom, or the double bond of an adjacent unsaturated group as in allyl bromide, in all the given cases lowers the wave number from 563.5 to about 537 cm.$^{-1}$. Thus the carbon–bromine bond seems considerably weaker in this latter class of compounds (with the exception of isobutyl bromide).

It is apparent from the constant value of the wave number for the normal compounds that *the organic radical cannot vibrate as a whole with respect to the bromine atom,* for such an assumption leads to an absurd value for the force constant.

On the basis of the assumption that the effective mass of the methyl group with respect to the vibration toward bromine is 14.4 atomic weight units, the force constant for methyl bromide is 2.60×10^5 dyne/cm.

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[1] Wave number determined by Dadieu and Kohlrausch, J. *Opt. Soc. Am.*, 5, 297 (1931).

[2] Wave number determined by Cleeton and Dufford, *Phys. Rev.*, 37, 365 (1931).

(or 2.70 if CH_3 vibrates as a single unit of mass 15). If now the amyl group vibrates as a unit the force constant for amyl bromide would be 7.0×10^5 dyne/cm., or more than two and a half times larger than for methyl bromide. This is much too large.

If the force constant in all of the normal bromides is assumed to be constant and equal to 2.60×10^5 dyne/cm., the effective mass of the portion of the hydrocarbon chain which vibrates (with respect to the bromine) is 17. This indicates that the CH_2 group adjacent to the bromine possesses most of the mass which is effective. That is, the CH_2 group vibrates, but its effective mass is increased by the constraint due to its union with the rest of the hydrocarbon chain, and is influenced by the vibration of this part of the molecule.

The writers have determined the frequencies of the Raman lines of nine organic bromides. These give a large number of characteristic frequency differences as, for example, 1639 cm.$^{-1}$ for the double bond of allyl bromide, but only the values characteristic of the carbon-bromine and other carbon–halogen bonds can be discussed here. The variation in the wave number corresponding to this bond is usually not more than one unit of wave number for any one compound, and the maximum variation for any compound is two units.

The equation for the force constant (k) is

$$\nu_0 = \omega_0 \, (n' - n'') = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} (n' - n'')$$

in which n represents a quantum number, μ the mutual mass, ν_0 the fundamental frequency of the radiation, and ω_0 the fundamental mechanical frequency. A further discussion will be presented in the final paper.

Department of Chemistry
University of Chicago
Chicago, Illinois

William D. Harkins
Harold E. Bowers

Received May 22, 1931
Published June 8, 1931

PREPARATION OF UNSYMMETRICAL DIALKYL ETHYLENE DERIVATIVES

Sir:

The recent description of the preparation of α,β-unsaturated ethers by Lauer and Spielman [This journal, 53, 1533 (1931)] makes possible an extension of our nuclear synthesis of olefins [*ibid.*, 52, 3396 (1930); 53, 1505 (1931)] to include the unsymmetrical dialkyl derivatives of ethylene. The essential steps in the process are clearly represented by the scheme.

$$CH_2{=}C(R)OEt + Br_2 \longrightarrow CH_2Br{-}CBr(R)OEt \qquad (1)$$

$$CH_2Br{-}CBr(R)OEt + R'MgBr \longrightarrow CH_2Br{-}C(R')(R)OEt + MgBr_2 \qquad (2)$$

$$CH_2Br{-}C(R')(R)OEt + Zn(Alc) \longrightarrow CH_2{=}C(R')R + EtOZnBr \qquad (3)$$

Three hexenes have been prepared by this method, with the physical constants indicated.

Olefin	B. p. (760 mm.)	D_D^{20}	n_D^{20}	*MR* (Fd.)	*MR* (Calcd.)
2-Methyl-1-pentene	61.5–62.0	06831	1.3921	2934	29.44
2-Ethyl-1-butene	66.2–66.7	.6938	1.3990	29.31	29.44
2,3-Dimethyl-1-butene	56.0–56 5	.6827	1 3905	29.55	29 44

The method is being extended to the preparation of other olefins and diolefins.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

CLAUDE G. SCHMITT
CECIL E. BOORD

RECEIVED MAY 26, 1931
PUBLISHED JUNE 8, 1931

THE DECOMPOSITION OF SODIUM AZIDE BY CONTROLLED ELECTRON BOMBARDMENT

Sir:

The decomposition of solid sodium azide has been achieved by subjecting a thin film to bombardment by electrons of known velocity. The reaction was carried out in a high vacuum using an oxide filament as the source of electrons and suitable electrodes for controlling the velocity. Impacts in the gas phase were shown to be absent. The nitrogen resulting from the decomposition was detected and measured by an ionization manometer. The gas evolved was shown to be nitrogen by critical impact measurements. Rate curves taken at various electron velocities gave a sharp intercept on the voltage axis, setting the minimum potential at 12 ± 1 volts. The rate curves showed discontinuities in the region of the critical potentials of nitrogen, thus affording additional proof of the nature of the gas. At no time was any thermal decomposition observed, nor any effect at or below 11.5 volts.

These measurements are being continued with slightly improved technique. The photochemical decomposition is being studied as well and will be the subject of a later communication.

DEPARTMENT OF CHEMISTRY
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK CITY

RALPH H. MÜLLER
G. CALVIN BROUS

RECEIVED MAY 29, 1931
PUBLISHED JUNE 8, 1931

NEW BOOKS

Qualitative Chemical Analysis. BY HERMAN T. BRISCOE, Professor of Chemistry, Indiana University. The D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, 1931. v + 279 pp. Illustrated. 14.5 X 22.5 cm. Price, $2.25.

This book is typical of the Qualitative Analysis text that should be in general use in colleges. Not only are the theoretical principles underlying all analytical operations fully and clearly dealt with, but, to quote the author's own words, "proper correlation between theory and practice" is preserved throughout. The reviewer would have liked a fuller treatment of some topics like complex ions and amphoteric hydroxides and the addition of other important ones like the "salt effect," occlusion, perhaps buffer solutions and the modern method of expressing hydrogen-ion concentrations, which are not treated at all. The reviewer criticizes also the comparatively extended discussion on atomic structure, a rapidly shifting field, which has no particular place in a course in Qualitative Analysis. The Bohr atom was abandoned by Bohr himself years ago and physicists are agreed that a mechanical representation of atomic structure is, at the time of writing this review, an impossibility. The student should have been warned that some solubility products, as for example those of the sulfides, should be taken with a grain of salt. Hydrolysis, oxidation and reduction are very well treated. The laboratory separations, although perhaps not as rigid as those of A. A. Noyes, are generally satisfactory and accompanied by excellent notes in which constant application is made of the principles taught in the theoretical part, a rare accomplishment in the average run of textbooks on Qualitative Analysis.

The book is well printed and bound, free from typographical errors, the diagrams are well drawn and to the point and the reviewer feels he can recommend the book to those desiring to teach a modern course in Qualitative Analysis.

J. ENRIQUE ZANETTI

Tables annuelles de constantes et données numériques de chimie, de physique, de biologie et de technologie. (Annual Tables of Constants and Numerical Data Chemical, Physical, Biological and Technological.) Published under the auspices of the International Research Council and the International Union of Pure and Applied Chemistry by the International Committee appointed by the Seventh Congress of Applied Chemistry (London, June 2, 1909). Table des Matières des Volumes I à V. Années 1910 à 1922. (Table of Contents of Volumes I–V, 1910–1922.) Edited by G. KRAVTZOFF. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1930. lxiii + 382 pp. 22.5 X 28 cm.

As the number of volumes of Annual Tables has increased, it has become correspondingly laborious to search through them for quantitative data published during recent years pertaining to any particular subject. In the future, this labor will be considerably lessened by the use of the

General Index—the first volume of which has now appeared, covering the years 1910 to 1922.

This first volume contains an Introduction explaining the use of the Index, and a list of the French abbreviations. The latter are, however, for the most part self-evident and practically international. Next comes an Analytical Index, which is substantially a very complete table of contents. This is followed by an Alphabetical Index in French; but German, English and Italian translations have been inserted where advantageous, followed by the French equivalent. Finally, there is a Formula Index, which constitutes the bulk of the whole volume. In it, the chemical elements are arranged according to a system similar to that adopted by the new edition of the Gmelin–Kraut handbook, in which the non-metals come first, then carbon, and finally the metals arranged alphabetically according to their symbols.

A second volume of the Index is promised for 1933, covering the years 1923–1930 (Volumes VI to X). Thereafter, it is planned to issue a volume of the Index at five-year intervals. When this schedule has been attained, the labor of consulting the Annual Tables will be still further diminished. Nevertheless, in order to cover the data published during any preceding twenty years, it will still be necessary to inspect three or four volumes of the Index and two to six of the current volumes of the Annual Tables. The only method of lessening this somewhat formidable task would apparently be first to make each five-year volume of the Index cumulative, say for fifteen years, and second to decrease the lag in the appearance of these volumes behind the corresponding volumes of the Annual Tables. These remedies would, however, doubtless entail considerable additional expense.

This Index, even though it may not in the future afford the greatest possible measure of convenience, is nevertheless of very ,great value in rendering more available the unique collection of data in the Annual Tables.

ARTHUR B. LAMB

The Principles of Quantum Mechanics. By P. A. M. DIRAC, **Fellow of** St. John's **College, Cambridge. The Oxford University Press, 114 Fifth Avenue,** New York, 1930. **x + 257 pp.** 16 × **24 cm.**

The spirit and the character of this book may perhaps be best expressed by two sentences taken from it. "The new theories, if one looks apart from their mathematical setting, are built up from physical concepts which cannot be explained in terms of things previously known to the student, which cannot even be adequately explained in words at all." "The only object of theoretical physics is to calculate results that can be compared with experiment, and it is quite unnecessary that any satisfying description of the whole course of the phenomena should be given." From these quotations (though, in the last analysis, they must be seen to be entirely correct) it would be at once inferred that this is not a book for the beginner who wishes to learn quantum mechanics; and, indeed, it is rather directed to the experienced student of that subject, who wishes to study its logical foundations.

Though there is a sort of preview of the physical ideas involved in the first chapter, in general, the method of the book consists in the development of a purely abstract algebra to which the physical results are then "hung on" as representations. The reviewer is not convinced that this is necessary for a logical presentation of the theory, and it has the disadvantage that it greatly increases the difficulty of reading the book, since one has to learn two notations and the connections between them. Nevertheless, any book which presents the ideas of one who has had such a role in the development of the subject will be received with great interest, especially as most of his original work is there presented in connected form.

Having laid the foundations of the subject, the author proceeds to discuss many of its most important applications. This section of the book can be read only after thorough mastery of the ideas and notations of the first part. The last chapter treats of the relativistic theory of the spinning electron, and the author's recent work on the proton.

OSCAR K. RICE

The Quantum Theory. By FRITZ REICHE, Principal of Physics at the University of Breslau. Translated by H. S. HATFIELD, B.Sc., Ph.D., and HENRY L. BROSE, **M.A.** E. P. Dutton and Co., Inc., 286–302 Fourth Ave., New York, 1931. viii + 218 pages. 15 figs. 12.5 × 19.5 cm. Price, $2.10.

The original German edition appeared in 1920 and its English edition in 1922. The present English edition is identically the same as the 1922 edition except for the addition of a chapter of 24 pages and 64 notes and references. The preface states: "A few alterations have been made in the earlier pages. Chapter IX has been renamed. A table of contents and useful formulae and a bibliography have been added." In the new chapter the attempt is made to sketch the development of the quantum mechanics from the status of the theory in 1923. The material touched upon includes the Compton effect, de Broglie waves, Schrodinger's, Heisenberg's and Dirac's contributions to quantum mechanics, electron spin, Bose–Einstein statistics, Fermi–Dirac statistics, Raman effect among other items and finally the "Outlook of Atomic Theory in 1930"; all this in a twenty-four page chapter plus four and one-half pages of "Notes and References." The reader moderately well acquainted with the present-day status of quantum mechanics will hardly recognize in the new material more than a brief synopsis of topics while the student approaching the subject de novo will find the new chapter incomprehensible.

F. G. KEYES

Lehrbuch der Metallkunde des Eisens und der Nichteisenmetalle. (Textbook of Metal Science of Iron and the Non-Ferrous Metals.) By DR. PHIL. FRANZ SAUERWALD, Professor at the Technical High School of Breslau. Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1929. xvi + 462 pp. 399 figs. 16 × 23.5 cm. Price. RM. 29.

In writing this book the author has had three aims: first, a developed synthesis of the whole range of the science of metals, avoiding the necessity of referring the reader to many books on various special subjects with corresponding lack of correlation; second, to stimulate readers to ask and answer their own questions through the problems discussed; and third, to present the results of the author's investigations and those of his colleagues. Somewhat more than half of the book is devoted to the general science of the metallic state, alloys, and consideration of technical manufacturing processes. The remainder is concerned with the fundamental properties of iron, cast iron, steel and the non-ferrous metals. There are a number of unusual features in this work which alone should commend the book to all physical metallurgists. Among these may be mentioned the properties of metals in the liquid and gaseous states, a thorough fundamental treatment of the mechanical properties of metals, rates of reaction and diffusion, the properties of liquid alloys, technical corrosion and means for combating it, the measurement of shrinkage during solidification, and statistical methods in plant investigations. Throughout the work one finds the direct application of physical-chemical laws to metallurgical problems. One feels that the author has been substantially successful in his aims and that here is a book which every progressive physical metallurgist will wish to have in his reference library.

R. H. ABORN

Quantitative Clinical Chemistry. Vol. I. Interpretations. By JOHN P. PETERS, M.D., M.A., Professor of Internal Medicine, Yale University School of Medicine, and DONALD D. VAN SLYKE, Ph.D., Sc.D., Member of the Rockefeller Institute for Medical Research. The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Maryland, 1931. xvi + 1264 pp. 124 figs. 15 × 23.5 cm. Price $12.00.

This huge volume probably would not be interesting to many readers of THIS JOURNAL, but it should prove valuable as a reference book to clinicians. It gives a very impressive picture of the extent to which chemistry, especially analytical chemistry, is being applied in the study of diseases. Clinical chemistry is by far the most baffling field of biochemistry, and for this reason, as well as for certain other reasons, very little of its literature can be accepted without reservation until it has been repeatedly confirmed. It is therefore rather doubtful whether the fields covered by this book actually merit so large a volume, and whether it would not have been better to defer the inclusion of many observations, with their references, to later editions. The cautious reader should certainly be prepared for the probability that hundreds of original papers cited as authority for statements occurring in the book will turn out to be erroneous or misleading.

The arrangement of the material is different from what one finds in other books on clinical chemistry and is, on the whole, to be commended. There are no chapters on the chemistry of any body fluid or tissue. The headings of the twenty-one chapters into which the book is divided are as follows: Total Metabolism; Carbohydrates; Lipoids; Nan-protein Nitrogen and Nitrogen Metabolism; Urea; Ammonia; Amino Acids; Uric Acid; Creatine and Creatinine; Total Organic Acids, Lactic Acid and Ketones; Phenols; Hemoglobin; Proteins of the Blood Plasma, Urine and other Body Fluids; The Volume of the Circulating Blood; Total Base, Sodium and Potassium; Calcium; Magnesium; Carbonic Acid and Acid-Base Balance; Chlorides; Phosphorus; Sulfur. This predominantly chemical arrangement of the material has worked out very well, and it is easy to find any information contained in the book. The index is excellent.

For so large a book the text in some chapters is surprisingly meager. Chapter III, for example, on the lipoids, has over 10 pages of bibliography to only 26 pages of text. And what there is of text in this chapter is not altogether to be commended. The oxidations of the fatty acids, if touched upon at all, should have been described in more detail. The discussion of the digestion and absorption of fat is not only too brief, but is also antiquated and misleading. The essence of the subject as given, page 230, is represented by the following brief paragraph: "It was long believed that emulsified free fats could be directly absorbed; but the studies of Munk (151) conclusively proved that this was not the case and that only emulsified fatty acids could be absorbed."

It may not be possible to deny flatly that either neutral fats or fatty acids are absorbed in the form of emulsions, but Munk's quaint paper, of 1880, proved only that fatty material is absorbed about equally well whether given in the form of fats or as fatty acids. Pflüger's dictum that solution rather than emulsification is a necessary prerequisite for absorption has lost nothing in probability with the passing of time. Pflüger is not mentioned either in the text or in the bibliography.

One curious slip of the pen was found in this chapter, page 229: "Because of its choline content cholesterol has been considered as the source of bile acids."

While a slight tendency toward one-sidedness and partiality is to be detected in many other chapters, the book as a whole will prove an almost inexhaustible mine of information to the large and constantly increasing number of persons who are doing or trying to do research in the field of clinical chemistry.

OTTO FOLIN

Die Riechstoffe und ihre Derivate. (Perfumes and their Derivatives.) Edited by ALFRED WAGNER, Editor of *Die Riechstoffindustrie,* with the cooperation of ALFONS M. BURGER and F. ELZE. Part I, Aldehydes of the Aliphatic Series; Part II, Aldehydes of the Alicyclic Series; Part III, Aromatic Hydroxyaldehydes with Saturated Side Chains–Dihydroxyaldehydes—Aromatic Ether Hydroxyaldehydes with Saturated and Unsaturated Side Chains—Aroxylaldehydes; Part IV, List of Patents—Index of Patents—Author Index and Alphabetical Subject Index. A. Hartleben's Verlag, Singerstrasse 12, Vienna, 1, Austria, 1929, 1930, 1931 1431 pp. 17 X 26 cm.

This volume in the large Hartleben project on perfumes and their derivatives naturally deals primarily with aldehydes that have some actual or potential interest in connection with perfumes. In reality this interest is conceived broadly and nearly all aliphatic and alicyclic aldehydes, as well as a large number of aromatic representatives are passed in review.

Beginning with an excellent introductory chapter containing general methods of preparation and general reactions, the authors continue with the "practical part" in which the aldehydes are considered, one by one, and end with a transcript of patents which constitutes approximately a fourth of the entire volume.

In general, the description of an individual aldehyde contains an account of its history, a discussion of its structure, a complete list of sources and methods of preparation, a review of methods for its detection and quantitative estimation and extensive summaries of its derivatives. All of these matters, which may be regarded as essential to a complete description, are presented with the utmost thoroughness, and supported by innumerable references. One marvels at the patience with which this material has been accumulated and the skill with which it has been tabulated.

But one wonders also on what principles this volume has been organized, and for what manner of reader. Structural formulas of the aldehydes are followed by equally detailed formulas of oximes, hydrazones, semicarbazones which drag their tiresome lengths across the page. Descriptions of aldehydes are immersed in minute accounts of substances which add little to the picture, like cumol, cuminic alcohol, cuminic acid, para cymol and terephthalic acid in connection with cuminic aldehyde. Moreover, the authors insert a number of long papers which are printed verbatim, from periodicals that are so readily accessible as the "Berichte" and "Liebig's Annalen."

It may appear ungracious to protest that a volume offers too much, but the increasing and frequently unnecessary length of many modern treatises makes them too expensive for the individual and it seems unfortunate that a volume which, like this one, contains so much of value should be available only in those libraries in which it is not necessary to count the cost.

E. P. KOHLER

BOOKS RECEIVED

April 15, 1931--May 20, 1931

J. P. Ballantine. "The Macmillan Table Slide Rule." The Macmillan Co., 60 Fifth Ave., New York. $0.50.

G Briegleb and K. L. Wolf. "Lichtzerstreuung, Kerrrffekt und Molekulstruktur." Fortschritte der Chemir, Physik und physikalischen Chemie, Band 21, Heft 3. Verlag von Gebrddcr Borntraeger, Schoneberger Ufer 12a, Berlin, Germany. 58 pp. Subscription, M. 6; separate, M. 9.

Émile Monnin Chamot and Clyde Walter Mason. "Handbook of Chemical Microscopy." Volume II. "Chemical Methods and Inorganic Qualitative Analysis." John Wilcy and Sons, Inc., 440 Fourth Ave., New York 411 pp. $4.50.

J. J. Chartrou. "Petroles naturel ct artificiels." Librairie Armand Colin, 103 Boulevard Saint-Michel, Paris, Prance. 206 pp Fr. 10.50, unbound; fr 12, bound.

Louis J. Curtman. "Qualitative Chemical Analysis, from the Standpoint of the Laws of Equilibrium and the Ionization Theory." The Macmillan Co., 60 Fifth Ave., New York. 539 pp. $4.00.

Robert Gabillion. "Soies Artificiellcs et Matières Plastiques." Librairic Armand Colin, 103 Boulevard Saint-Michel, Paris, France. 204 pp. Fr. 10.50, unbound; fr. 12, bound.

Ernst Gellhorn, Editor. "Lehrbuch der allgemeinen Physiologie." Georg Thieme t'erlag, Antonstrasse 15/19, Leipzig C 1, Germany. 741 pp. M. 47, unbound; M. 49.50, bound.

Joshua C. Gregory. "A Short History of Atomism," from Democritus to Bohr. The Macmillan Co., 60 Fifth Avc., New York. 258 pp. $3.50.

Gustav Heller. "Über Isatin, Isatyd, Dioxindol und Indophenin." Sammlung chemischer und chemisch-technischer Vorträge, begrundet von F. B. Ahrens. Verlag von Ferdinand Enke, Stuttgart, Germany. 173 pp. RM. 13.20.

Harry N. Holmes. "Introductory College Chemistry." Revised edition. The Macmillan Co., 60 Fifth Ave., New York. 550 pp. $3.25.

Ellen Beers McGowan and Charlotte A. Waite. "Textiles and Clothing." Revised edition. The Macmillan Co., 60 Fifth Ave., New York. 344 pp. $1.32.

N. F. Mott. "An Outline of Wave Mechanics." The University Press, Cambridge, England; The Macmillan Co., 60 Fifth Avc., New York. 157 pp. $2.80.

F. H. Newman. "Electrolytic Conduction." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 441 pp. $6.50.

J. J. L. van Rijn. "Die Glykoside. Chemische Monographie der Pflanzenglykoside." Second edition, revised and enlarged by Hugo Dieterle. Verlag von Gebriider Borntrarger, W 35 Schöneberger Ufer 12a, Berlin, Germany. 620 pp. M. 48, unbound; M. 51, bound.

Julius Schmidt. "Jahrbuch der organischen Chemie." XVI Jahrgang. Die Forschungsergebnisse und Fortschritte im Jahre 1929. Verlagsbuchhandlung von Franz Deuticke, Vienna, Austria 299 pp. M. 30, unbound; M. 33, bound.

J. L. Simonsen. "The Terpenes." Vol. I. "The Simpler Acyclic and Monocyclic Terpenes and Their Derivatives." The Macmillan Co., 60 Fifth Ave., New York. 420 pp.

Ernst Stern. "Farbenbindmittel, Farbkorper und Anstrichstoffe, mit besonderer Berücksichtigung ihrer kolloidchemischen Grundlagen." Sonderabdruck aus der *Kolloidchemischen Technologie.* Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 194 pp. RM. 6.

Henry P. Talbot. "An Introductory Course of Quantitative Chemical Analysis, with Explanatory Notes." Seventh edition. Revised and rewritten by L. F. Hamilton and S. G. Simpson. The Macmillan Co., 60 Fifth Ave., New York. 253 pp $2.50.

Vlassios Vlassopoulos. "Über die sterische Hinderung bei Reaktionen von Aminosauren und Polypeptiden, zugleich ein Beitrag zum Wesen der sterischen Hinderung." Buchhandlung Gustav Fock G. m. b. H., Leipzig, Germany. 32 pp.

Clarence J. West, Editor. "Annual Survey of American Chemistry." Volume V. 1950. Published for the National Research Council by the Chemical Catalog Company, Inc., 419 Fourth Ave., New York. 629 pp. $5.00

Egyptian Government. Central Narcotics Intelligence Bureau. "Annual Report for the Year 1930." Government Press. Cairo, Egypt. 109 pp.

"Molybdenum in 1930" Climax Molybdenum Co., 295 Madison Ave., New York 104 pp.

The Journal of the
American Chemical Society

VOL. 53 JULY, 1931 No. 7

THE RADIOACTIVE CONSTANTS AS OF 1930. REPORT OF THE INTERNATIONAL RADIUM-STANDARDS COMMISSION[1,2]

BY M. CURIE, A. DEBIERNE, A. S. EVE, H. GEIGER, O. HAHN, S. C. LIND, ST. MEYER, E. RUTHERFORD AND E. SCHWEIDLER

RECEIVED JUNE 13, 1931 PUBLISHED JULY 8, 1931

Following the reorganization of the International Union of Chemistry and of the International Atomic Weights Commission, the need has arisen for the publication of special Tables of the Radioactive Constants.

This responsibility has been assumed by the International Radium-Standards Commission chosen in Brussels in 1910, which has expressed its willingness to cooperate with the International Union.

Besides the members of the Committee, the following have taken part as experts: J. Chadwick, I. Joliot-Curie, K. W. F. Kohlrausch, A. F. Kovarik, L. W. McKeehan, L. Meitner and H. Schlundt, to whom it is desired to express especial obligations.

The following report will also be published simultaneously in the *Physikalische* Zeitschrift, Review of Modern Physics, Philosophical Magazine and Journal Physique *et le* Radium.

General Remarks on Symbols and Terms

The symbols are provisionally retained as used in the texts of St. Meyer–E. Schweidler, F. Kohlrausch, and E. Rutherford, J. Chadwick and C. D. Ellis, as well as in the Physikalische Zeitschrift, 19, 30 (1918); Zeitschrift fur *Elektrochemie*, 24, 36 (1918); and Jahrb. Rad. u. *Elektr.*, 19,344 (1923).

For the three radioactive gases the use of the terms radon (Rn), thoron (Tn), and actinon (An) is recommended (*Z.* anorg. Chem., 103, 79 (1918)), and as general term for elements of atomic number 86 the retention of the word "emanations" (Em) for the three isotopes. The words emanate, emanating power, etc., are retained.

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[1] To facilitate desirable changes and additions in subsequent years it is requested that data, notes and suggestions be sent to: Prof. Dr. Stefan Meyer, Institut für Radiumforschung, Boltzmanngasse 3, IX Vienna, Austria.

[2] A summary of literature on decay constants and ranges and on absorption coefficients is to be published in other versions of this report, to appear in the July issue of the *Physikalische Zeitschrift* and of the *Review* of Modern *Physics.*

The designation "radio-lead" is restricted to the natural radioactive mixture of lead isotopes in minerals and is not used to designate RaD.

RaG, ThD and AcD shall be called uranium-lead, thorium-lead and actinium-lead, respectively. The mixture of RaG and AcD will also be designated uranium-lead.

Instead of the designation "Isotopic Weight" (Poids isotopique) as used in the earlier "Tables internationales des éléments radioactifs" for the whole numbered atomic weights or the number of hydrogen nuclei, the word "Proton number" is proposed.

Symbols:

UI, UX_1, UX_2, UII, Io, Ra, Rn, RaA, RaB, RaC′, RaC″, RaD, RaE, RaF=Po, RaG, UY, UZ.
Th, $MsTh_1$, $MsTh_2$, RdTh, ThX, Tn, ThA, ThB, ThC′, ThC″, ThD.
AcU, Pa, Ac, RdAc, AcX, An, AcA, AcB, AcC, AcC′, AcC , AcD.
Pa is for protactinium (not Proto-actinium).
Em is the joint symbol for Rn, Tn and An.

The following report contains: I, Basic Values; II, Units; III, Constants.

I. Basic Values

(1) R. T. Birge, *Phys. Rev.*, (2) 33, 265 (1929), Supplement 1.1–73, July 1929	
(1a) R. T. Birge, *ibid.*, (2) 35, 1015 (1930)	
(2) H. L. Curtis, *Bur. Stand. J. Research*, 3, 63 (1929)	c = 299790 km./sec.
(3) Michelson, 1927 (older value 299850)	c = 299796
(4) Karolus and Mittelstaedt, 1928	c = 299778
(4a) W. Grotrian, *Naturwiss.*, 17, 201 (1929)	
(5) R. A. Millikan, *Science*, 69, 481 (1929)	$e = 4.770 \cdot 10^{-10}$ E. S. U.
(6) J. A. Bearden, *Proc. Nat. Acad.*, 15, 528 (1929)	By Rontgen ray spectroscopy
(7) A. H. Compton, *Franklin J.*, 208, 605 (1929)	$e = 4.810 \cdot 10^{-10}$
(8) E. Backlin, *Nature*, 123, 409 (1929)	4.793
(9) H. A. Wilson, *Phys. Rev.*, (2) 34, 1493 (1929)	4.82
(10) W. N. Bond, *Phil. Mag.*, (7) 10, 994 (1930)	4.7797
(11) J. M. Cork, *Phys. Rev.*, (2) 35, 128 (1930)	4.821
(12) W. H. Houston, *ibid.*, (2) 30, 608 (1927)	$c/m_0 = 1.7606 \cdot 10^7$ spectroscopic
(13) H. D. Babcock, *Astrophys. J.*, 69, 43 (1929)	$1.7606 \cdot 10^7$ spectroscopic
(14) F. Kirchner, *Physik. Z.*, 31, 1073 (1930)	1.7602 Deflection of cathode rays
Ann. Physik, (5) 8, 975 (1931)	1.7598 ± 0.0025
(15) C. T. Perry and E. L. Chaffee, *Phys. Rev.*, (2) 36, 904 (1930)	1.761 Deflection of cathode rays
(16) A. Upmark, *Z. Physik*, 55, 569 (1929)	
(17) A. R. Olpin, *Phys. Rev.*, (2) 36, 251 (1930)	

Velocity of Light

$c = 2.9980 \cdot 10^{10}$ cm./sec. Literature, (1), (2), (3), (4)

II. Chemical Units

The chemical atomic weights and quantitative relations are based on O = 16.0000. The discovery of the oxygen isotopes O^{18} and O^{17} in the estimated proportions: $O^{16}:O^{17}:O^{18} = 10{,}000:1:8$ requires a sharper definition.

In contrast to the chemical definition, O = 16.0000 for the isotopic mixture, it is proposed for questions of atomic structure and radioactivity in the sense of Aston's measurements to choose $O^{16} = 16.0000$.

For the isotopic mixture in the ratios (very uncertain) given above, O = 16.0017, R. Mecke and W. H. J. Childs (*Z.* Physik, 68, 362 (1931), estimate O = 16.0035 ± 0.0003).

Corresponding to $O^{16} = 16.0000$, other values are

H = 1.0078 (Aston)	absolute.	$1\ 662 \cdot 10^{-24}$ g.
He = 4.00216 (Aston)	absolute:	$6.599_4 \cdot 10^{-24}$ g
m_0 of $O^{16}/16.00 = 1.00000$	absolute:	$1.6490 \cdot 10^{-24}$ g.
m_0 (proton) = 1.0072	absolute:	$1.661 \cdot 10^{-24}$ g
m_0 (alpha) = 4.00106	absolute:	$6\ 598 \cdot 10^{-24}$ g.
m_0 (electron) = 0.000548 for $e/m_0 = 5.2765 \cdot 10^{17}$ E. S. U.	absolute:	$9.040 \cdot 10^{-28}$ g.

Faraday Number

F = 96489 ±5 abs. coulomb (1)
96494 ±1 internat. coulomb

Elementary Charge

$e = 4.770 \cdot 10^{-10}$ E. S. U. (Millikan) (5)
($4.9 \cdot 10^{-10}$ E. S. U. by x-ray spectroscopy (6), (7), (8), (9), (10), (11)

Specific Charge

$e/m_0 = 1.760 \cdot 10^{7}$ ahs. magnet. U./g. [spectroscopic (1), electron deflection (14), (15)]
$= 5.276_5 \cdot 10^{17}$ E. S. U./g.
$1.769 \cdot 10^{7}$ abs. mag. U./g.
$= 5.303 \cdot 10^{17}$ E. S. U./g. Older deflection expts. (1), (4a), (10)

Planck's Constant

$h = 6.547 \cdot 10^{-27}$ erg. sec. (1)
$= 6.5596 \cdot 10^{-27}$ erg. sec. (10)
$= 6.591 \cdot 10^{-27}$ erg. sec. (4a)
$= 6.541 \cdot 10^{-27}$ erg. sec. (17)

Avogadro's Number

$L = Fc/e = 6.0644 \cdot 10^{23}$ mol.$^{-1}$ for $e = 4.770 \cdot 10^{-10}$
$= 6.0265 \cdot 10^{23}$ mol.$^{-1}$ for $e = 4.80 \cdot 10^{-10}$
1 Year = 365.24223 days = $3.155693 \cdot 10^{7}$ sec.
1 Sec. = $3.168876 \cdot 10^{-8}$ yr.

Derived Values

$\beta = v/c$ $c^2 = 8.988004 \cdot 10^{20}$

$$\eta = \frac{1}{\sqrt{1 - \beta^2}}$$

$m = m_0\eta$ $2e = 9.540 \cdot 10^{-10}$
$m_0c^2 = 5.9303 \cdot 10^{-3}$ for a-particles
$m_0c^2 = 8.1207 \cdot 10^{-7}$ for $e/m_0 = 5.276_5 \cdot 10^{17}$ E. S. U./g. for @-particles
$m_0c^2/{}^2e = 6.2162 \cdot 10^{6}$ for a-particles
$m_0c^2/e = 1.7034 \cdot 10^{3}$ for $e/m_0 = 5.276_5 \cdot 10^{17}$ E. S. U./g. for @-particles

Kinetic energy $E = m_0 c^2 (\eta - 1)$ for a-particles: $E = 5.9303\cdot 10^{-3} (\eta - 1)$ erg.
Kinetic energy in volt-electrons for @-particles: $E = 8.1252\cdot 10^{-7} (\eta - 1)$ *erg.*
Velocity in equiv. volts $P = 299.80E/2e = 3.1426\cdot 10^{11}E$ for or-particles
$P = 299.80E/e = 6.2851\cdot 10^{11}E$ for β-particles

Product of the magnetic field strength and the radius of curvature of the path:

$$\log R = (m_0c^2/2e)\eta\beta = 6.2162\cdot 10^{6}\,\eta\beta \text{ for a-particles}$$
$$\log R = (m_0c^2/e)\eta\beta = 1.7034\cdot 10^{3}\,\eta\beta \text{ for } \beta\text{-particles}$$
$$\lambda = hc/E = 1.9628\cdot 10^{-16}/E \text{ for } h = 6.547\cdot 10^{-27}$$
$$\lambda = hc/E = 1.9637\cdot 10^{-16}/E \text{ for } h = 6.55\cdot 10^{-27}$$

Z = number of a-particles emitted per second from 1 g. of Ra

Earlier literature to *1926,* St. Meyer–E. Schweidler, "Radioaktivitat," p. *401.*

(1) H. Jedrzejowski, *Compt. rend., 184, 1551 (1927); Ann. Physik, 9, 128 (1928)*	$Z = 3.50\cdot 10^{10}$
(2) I. Curie and F. Joliot, *Compt. rend., 187, 43 (1928)*	$3.7\cdot 10^{10}$
(3) H. J. Braddick and H. M. Cave, *Proc. Roy. Soc.* (London), *121, 368 (1928); Nature, 122,789 (1928);* also *G.* Ortner, *Wien. Ber. 138, 117 (1929); Mitt. Ra-Inst.,* Nr. *229*	*3.69*
(4) F. A. Ward, C. E. Wynn-Williams and H. M. Cave, *Proc. Roy.* SOG. (London), *125, 713 (1929)*	*3.66*
(5) S. H. Watson and M. C. Henderson, *ibid.,* **A118, 318** *(1928)* (indirect)	*3.72*
(6) G. Hoffman, *Physik.* Z., *28,729 (1927); H.* Ziegert, ***Z.*** *Physik,* 46, *668 (1928)*	*3.71*
(7) G. **Ortner** and C. **Stetter,** ***ibid.,*** 54, *475 (1929)*	*3.72*
(8) L. **Meitner** and W. **Orthmann,** ***ibid.,*** 60, *143 (1930)*	*3.68*
(9) E. Rutherford, *J.* Chadwick and C. D. Ellis, "Radiations of Radioactive Substances," *1930,* p. *63*	*3.70*

Note.—The chief source of error lies in the value for the radium equivalent of the preparation (e. g., of RaC). This arises from the decay curve of RaB–RaC. The standardization is not exact to 0.5 because the standards are not more accurate than this and on account of the different shapes of standard and unknown the comparison involves further inaccuracy. Moreover, in the washing of the preparation with alcohol to remove residual radon, RaB is dissolved in excess of RaC [Mitt. Ra. *Inst.,* No. 254; ***Wien*** Ber., 139, 231 (1930)]. The theoretical curve is thereby disturbed in the first part of the decay of the preparation so that differences of 1% in the value of active deposit result. This error would cause a minimal value of Z. Use of the value $\mathbf{3.7\cdot 10^{10}}$ is recommended in accord with lit. (9).

Ratio **Ra:U** in Old Unaltered Minerals

Earlier Literature: St. Meyer–E. Schweidler, "**Radioaktivität,**" 1927, *398,* pp. **404–406,** Lit. Nr. *7.22.23.*

V. Chlopin and M. A. **Paswick,** *Akad. Leningrad (1928)* (Russian). (In samples from the same location values varying due to chemical changes are found from *2.18* to $\mathbf{4.17\cdot 10^{-7}}$. Compare also Lind and Whittemore, THIS JOURNAL, *36,2066 (1914).*

The recommended value is $\mathbf{Ra/U = 3.4\cdot 10^{-7}}$; $\mathbf{U/Ra = 2.94\cdot 10^{6}}$.

Basic Values for the Calculation of the Number of Ion Pairs Produced by One α-Particle

$k = k_0R^{2/3}$ and calculation of velocity from $v^3 = a_0R_0$

All data refer to $0°$ and 760 mm.

As basis for k_0: $Zk = 8.18\cdot10^{15}$ (Meyer and Schweidler, "Radioaktivität," 1927, p. 189), and $Z = 3.7\cdot10^{10}$

For RaC′: $R_0 = 6.58$ cm. (see table of ranges)

$k = 8.18\cdot10^{15}/3\ 7\cdot10^{10} = ko\ 6.58^{2/3}$ $\quad k_0 = 6.296\cdot10^4$

Based on $R_0 = 6.60$ and $Z = 3.72\cdot10^{10}$ $\quad k_0 = 6.253\cdot10^4$

Based on $R_0 = 6.60$ and $Z = 3.70\cdot10^{10}$ $\quad k_0 = 6.283\cdot10^4$

Recommended: $k_0 = 6.3\cdot10^4$

For a_0, different values are obtained according to the choice of RaC′, ThC′ or Po as reference. This may mean that the relation $v^3 = aR$ is not exact and that the definition of the range (Geiger–Henderson) as the intercept of the descending straight line of the Bragg's curve with the abscissa has no theoretical basis.

For RaC′	$R_0 = 6.58$	$v = 1.022\cdot10^9$	$a_0 = 1.0790\cdot10^{27}$	$a_0^{1/3} = 1.026.109$
For ThC′	$R_0 = 8.168$	$v = 2.054\cdot10^9$	$a_0 = 1.0609\cdot10^{27}$	$a_0^{1/3} = 1.020\cdot10^9$
For Po	$R_0 = 3.67$	$v = 1.593\cdot10^9$	$a_0 = 1.1015\cdot10^{27}$	$a_0^{1/3} = 1.032\cdot10^9$
		Recommended:	$a_0 = 1.08\cdot10^{27}$	$a_0^{1/3} = 1.026\cdot10^9$

which differ only slightly from the constants in use

For [3] $R_0 = 6.60$ $\quad v = 1.922\cdot10^9$ $\quad a_0 = 1.0758\cdot10^{27}$ [4] $a_0^{1/3} = 1.0246\cdot10^9$

(Meyer–Schweidler, p. 629)

Radium content is expressed gravimetrically in grams or mg. of elemental radium, regardless of its state of chemical combination. However, it is always desirable to know the total weight and nature of the compound, with reference to Ra concentration.

Radon (Radium Emanation)

1 Curie is the quantity of Rn in equilibrium with 1 g. Ra

1 Curie Rn has the volume 0.66 cu. mm. at 0° and 760 mm.

1 Curie (Rn without decay products) can with complete utilization of the a-particles maintain by its ionization of air a saturation current of $2.75\cdot10^4$ E.S.U. (0.92 milliampere)

Sub-units are millicurie, microcurie, etc. For the Rn content of waters and gases the sub-unit milli-microcurie (10^{-9}) is frequently used.

1 Eman $= 10^{-10}$ curie per liter (10^{-13} curie/cc.) is a term used since 1921 for the Rn content of the atmosphere as a concentration unit.

1 Mache Unit (1 M. E.) is a concentration unit referred to the Rn content of 1 liter of water or gas, etc. It is that quantity of Rn per liter which without decay products and with complete utilization of the α-particles

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[3] The basic value 6.60 was the mean of the values of G. H. Henderson, *Phil. Mag.*, [6] 42, 538 (1921), 6.592, and of H. Geiger, *Z. Physik*, 8, 45 (1921), 6.608. To R_0 the corresponding value at 15° is $R_{15} = 6.963$ cm.

[4] See Rutherford, Chadwick and Ellis, Ref. (9), p. 86.

can maintain by its ionization of a ira saturation current of 10^{-3} E. S. U. 1 M. E. corresponds to $3.64 \cdot 10^{-10}$ curie/liter = 3.64 Eman.

It is recommended to extend the use of the term curie to the equilibrium quantity of any decay product of radium. One must then specify the element, as 1 curie Rn, for example. The Commission does not favor its extension to members outside the Ra family.

On the other hand, the unit quantity of any radioactive element may be expressed in terms of the mass equivalent to 1 g. of Ra with respect to the effects of the rays or to the number of atoms decaying per second.

In the latter sense one defines: 1 mg. of Ra equivalent as that quantity of any radioactive element for which the number of atoms decaying per second is the same as that for 1 mg. of Ra ($3.7 \cdot 10^7$ atoms/sec.).

Since, however, the determination of the number of atoms decaying per second can seldom be made directly, the number will much more frequently be obtained indirectly from radiation effects.

Polonium.—"1 Curie Po" = that amount which, equivalent to 1 gram of Ra, emits $3.7 \cdot 10^{10}$ a-particles per sec. "1 Curie Po" = quantity in radioactive equilibrium with'1 gram of Ra, $2.24 \cdot 10^{-4}$ g. Po.

That quantity of Po whose a-radiation directed to one side only is fully utilized to ionize air and which can support a current of 1 E. S. U. corresponds to $1.68 \cdot 10^{-10}$ g. of Po or $0.75 \cdot 10^{-6}$ curie of Po. 1 Curie of polonium would in the utilization of its rays in all directions support a saturation current in air of $2.66 \cdot 10^6$ E. S. U. 1 Microcurie of Po (one sided radiation) = 1.33 E. S. U.

Mesothorium.—"1 mg. MsTh" usually signifies the y-ray equivalent of 1 mg. of Ra–RaC, compared after absorption by 5 mm. of lead. This definition is for many reasons (dependence on the age of the preparation and on the experimental conditions (see Meyer–Schweidler, 1927, pp. 496–497)), inexact and open to criticism. All determinations of content of Ra, Rn, MsTh, Po, etc., must be exactly dated, of course.

III. Radioactive Constants[2]

. General Remarks

For U_I it is to be noted that the calculation is made on the basis $Z = 3.70 \cdot 10^{10}\ \alpha/\text{sec.}$; $Ra/U = 3.40 \cdot 10^{-7}$; Avogadro No. = $6.064 \cdot 10^{23}$, with no account taken of the branching of the Ac Series. A correction for this would be so dependent on the value of T assumed for AcU that it would have little significance at present. In any case, however, the values given above are for T and τ upper and for λ lower limits.

For UX_1, the lowest value $T = 23.8$ (1) is mentioned as well as the one preferred by the Commission.

In the Table for R, v, k (Range, Velocity, Ion Production) the directly observed values are denoted by +. The calculation of the other values far v and k was made by using the basic values denoted ++, with the data for k_0 and a_0 given on page 2441.

U_{II} gives according to the ranges of Laurence improbably low values for T (5). Direct determination (50) gives T = $3.4 \cdot 10^5$ years in good agreement with the range determinations of Hoffman–Ziegert (42). The adoption of $3 \cdot 10^5$ years is recommended.

Rn The two best determinations made recently, W. Bothe, *Z. Physik,* 16, 226 (1923), T = 3.825 ± 0.003 days, and I. Curie and C. Chamié, Compt. *rend.,* **178,** 1808 (1924); *J. phys.,* [6] 5,328 (1924), T = 3.823 ± 0.002 days, agree within the limits of experimental error. During the first day, their differences in Rn decay by the hour are scarcely noticeable in the fourth place.

For *T* = 3.823 days extended tables have been published by C. Chamié, M. Cailliet and G. Fournier [Paris, Gauthier-Villars, **1930**].

Radium E

Earlier accepted value	4.85 days	Recommended: *T* = 5.0 days, and T = 4.9 days
L. Bastings, *Phil. Mag.,* **48,** 1075 (1924)	4.985 days	
G. Fournier, *Compt. rend.,* 181, 502 (1925)	4.86 days	
L. F. Curtiss, *Phys. Rev.,* **27,** *672* (1926)	5.07 days	
J. P. McHutchison, *J. Phys.* Chem., **30,** 925 (1926)	4.87 days	

For RaC′: see Lit. (15), (16), (16a) in *Physik. Z.*, July, 1931.

For ThC′: Mme. Curie has recently calculated from the Geiger–Nuttall Law: λ = about 10^9 sec.$^{-1}$. In view of the great uncertainty attaching to the values for ThC′, O. Hahn and L. Meitner propose to be content with the statement: T = 10^{-6} sec.

AcC″: A. F. Kovarik points out that 150 curves are found to give T = 4.71 min., while Albrecht has only 9 curves for T = 4.76 min. Both values are given in the table.

URANIUM FAMILY

At. wt. = atomic weight; P. no. = proton number; at. no. = atomic number; yr. = years; d. = days; h. = hours; m. = minutes; s. = seconds; T = half period; τ = average life; λ = decay constant; ( ) indicates earlier values still in use

		T	λ	τ	Literature
Uranium I	UI	$4.4 \cdot 10^9$yr.	$1.6 \cdot 10^{-10}$yr.$^{-1}$	$6.3 \cdot 10^9$yr.	
At. wt.	238.14	$1.4 \cdot 10^{17}$s.	$5.0 \cdot 10^{-18}$s.$^{-1}$	$2.0 \cdot 10^{17}$s.	*Cf* "Remarks" above
At. no.	92				
P. no.	238				
Uranium X_1	UX_1	24.5d.	$2.83 \cdot 10^{-2}$d.$^{-1}$	35.4d.	51
		$2.12 \cdot 10^6$s.	$3.28 \cdot 10^{-7}$s.$^{-1}$	$3.05 \cdot 10^6$s.	
At. no.	90	23.8d.	$2.90 \cdot 10^{-2}$d.$^{-1}$	34.4d.	1
P. no.	234	$2.06 \cdot 10^6$s.	$3.37 \cdot 10^{-7}$s.$^{-1}$	$2.97 \cdot 10^6$s.	
Uranium X_2	UX2	1.14m.	0.61m.$^{-1}$	1.64m.	(51) (3a)
(Brevium)	91	68.4s.	$1.01 \cdot 10^{-2}$s.$^{-1}$	98.7s.	2, 3
ca. 99.65%	234				
Uranium Z	UZ	6.7h.	0.103h.$^{-1}$	9.7h.	
ca. 0.35%	91	$2.4 \cdot 10^4$s.	$2.87 \cdot 10^{-5}$s.$^{-1}$	$3.5 \cdot 10^4$s.	
	234				
Uranium II	UII	3.10^5yr.	$2.3 \cdot 10^{-6}$yr.$^{-1}$	$4.3 \cdot 10^5$yr.	
	92	$9.4 \cdot 10^{12}$s.	$7.4 \cdot 10^{-14}$s.$^{-1}$	$1.4 \cdot 10^{13}$s.	4, 5
	234				

URANIUM FAMILY (Concluded)

		T	A	τ	Literature
Uranium Y	UY	24.6h.	$2.82\cdot10^{-2}$h.$^{-1}$	35.5h.	
ca 3%	90	1.03d.	0.675d.$^{-1}$	1.48d.	
	231 or 230	8.88.104s.	$7.81\cdot10^{-6}$s.$^{-1}$	$1.28\cdot10^{5}$s.	

IONIUM–RADIUM FAMILY

		T	λ	τ	Literature
Ionium Io		$8.3\cdot10^{4}$yr.	$8.3\cdot10^{-6}$yr.$^{-1}$	$1.2\cdot10^{5}$yr.	
At, no.	90	$2.6\cdot10^{12}$s.	$2.6\cdot10^{-13}$s.$^{-1}$	$3.8\cdot10^{12}$s.	7, 8, 8a'
P. no.	230				
Radium Ra		1590yr.	$4.36\cdot10^{-4}$yr.$^{-1}$	2295yr.	
	88	$5.02\cdot10^{10}$s.	$1.38\cdot10^{-11}$s.$^{-1}$	$7.24\cdot10^{10}$s.	9
	226				
Radon Rn		3.825d.	0.1812d.$^{-1}$	5.518d.	
At. no.	86	$3.305\cdot10^{5}$s.	$2.097\cdot10^{-6}$s.$^{-1}$	$4.768\cdot10^{5}$s.	10
P. no.	222	3.823d.	0.1813d.$^{-1}$	5.515d.	*Cf.* Remarks
		$3.303\cdot10^{5}$s.	$2.098\cdot10^{-6}$s.$^{-1}$	$4.765\cdot10^{5}$s.	
Radium A **RaA**		3.05m.	0.227m.$^{-1}$	4.40m.	11
	84	183s.	$3.78\cdot10^{-3}$s.$^{-1}$	264s.	51
	218				
Radium B **RaB**		26.8m.	$2.59\cdot10^{-2}$m.$^{-1}$	38.7m.	
	82	$1.61\cdot10^{3}$s.	$4.31\cdot10^{-4}$s.$^{-1}$	$2.32\cdot10^{3}$s.	
	214				
Radium C **RaC**		19.7m.	$3.51\cdot10^{-2}$m.$^{-1}$	28.5m.	
	83	$1.18\cdot10^{3}$s.	$5.86\cdot10^{-4}$s.$^{-1}$	$1.71\cdot10^{3}$s.	12
	214				
Radium C' **RaC'**		*ca.* 10^{-6}s.	10^{6}s.$^{-1}$	10^{-6}s.	13, 14
99.96%	84				15, 16
(99.97%)	214				16a
Radium C'' **RaC''**		1.32m.	0.525m.$^{-1}$	1.9m.	
0.04%	81	79.2s.	$8.7\cdot10^{-3}$s.$^{-1}$	115s.	17
(0.03%)	210				
Radium D **RaD**		22yr.	0.0315yr.$^{-1}$	31.7yr.	
	82	$6.94\cdot10^{6}$s.	$1.00\cdot10^{-9}$s.$^{-1}$	$1.00\cdot10^{9}$s.	18, 19, 20
	210				
Radium E **RaE**		4.9d.	0.141d.$^{-1}$	7.07d.	
		$4.26\cdot10^{5}$s.	$1.63\cdot10^{-6}$s.$^{-1}$	$6.13\cdot10^{5}$s.	21
	83 or	5.0d.	0.139d.$^{-1}$	7:2d.	
	210	$4.32\cdot10^{5}$s.	$1.61.10^{-6}$s.$^{-1}$	$6.22\cdot10^{5}$s.	
Radium F **RaF(Po)**		140d.	$4.95\cdot10^{-3}$d.$^{-1}$	202d.	22, 23
Polonium	84	$1.21\cdot10^{7}$s.	$5.73\cdot10^{-8}$s.$^{-1}$	$1.75\cdot10^{7}$s.	
	210				
Radium ***G*** **RaG**					
Uranium lead	206.016				
	82				
	206				

ACTINIUM FAMILY

		T	λ	τ	Literature
Actinium Uranium					
AcU		*ca.* 10^8 to 10^9yr.			24
Uranium Y, see Uranium Family					
Protactinium Pa		$3.2\cdot10^4$yr.	$2.17\cdot10^{-5}$yr.$^{-1}$	$4.6\cdot10^4$yr.	24a, 24b, 25
	91	$1.01\cdot10^{12}$s.	$6.86\cdot10^{-13}$s.$^{-1}$	$1.46\cdot10^{12}$s.	
	231				
Actinium Ac	89	13.5yr.	$5.15\cdot10^{-2}$yr.$^{-1}$	19.4yr.	26
		$4.23\cdot10^8$s.	$1.63\cdot10^{-9}$s.$^{-1}$	$6.12.10^8$s.	
	227	20 yr.	$3.4\cdot10^{-2}$yr.$^{-1}$	29 yr.	
		$6.3\cdot10^8$s.	$1.1\cdot10^{-9}$s.$^{-1}$	$9.2\cdot10^8$s.	
Radioactinium RdAc		18.9d.	$3.66\cdot10^{-2}$d.$^{-1}$	27.3d.	27, 28
	90	$1.63\cdot10^6$s.	$4.24\cdot10^{-7}$s.$^{-1}$	$2.36\cdot10^6$s.	
	227				
Actinium X AcX		11.2d.	$6.17\cdot10^{-2}$d.$^{-1}$	16.2d.	27, 51
	88	$9.7\cdot10^5$s.	$7.14\cdot10^{-7}$s.$^{-1}$	$1.40\cdot10^6$s.)	
		11.4d.	$6.08\cdot10^{-2}$d.$^{-1}$	16.4d.	
	223 or	$9.85\cdot10^5$s.	$7.06\cdot10^{-7}$s.$^{-1}$	$1.42\cdot10^4$s.	
Actinon An		3.92s.	0.177s.$^{-1}$	5.66s.	29, 51
	86				
	219				
Actinium A AcA		2.10^{-3}s.	347s.$^{-1}$	$2.88\cdot10^{-3}$s.	30
	84				
	215				
Actinium B AcB		36.0m.	$1.93\cdot10^{-2}$m.$^{-1}$	51.9m.	31
	82	2.16.103s.	$3.21\cdot10^{-4}$s.$^{-1}$	$3.12\cdot10^3$s.	
	211				
Actinium C AcC		2.16m.	0.321m.$^{-1}$	3.12m.	27
	83	130s.	$5.35\cdot10^{-3}$s.$^{-1}$	187s.	
	211				
Actinium C′ AcC′		*ca.* 5.10–3s.	ca. 140s.$^{-1}$	*ca.* 7.10^{-3}s.	
	84				
0.32%	211				
Actinium C″ AcC″		4.76m.	0.145m.$^{-1}$	6.87m.	32
99.68%	81	286s.	$2.43\cdot10^{-3}$s.$^{-1}$	412s.	
		4.71m.	0.146m.$^{-1}$	6.83m.	
	207 or	283s.	$2.44\cdot10^{-3}$s.$^{-1}$	410s.	
Actinium D					
AcD	207.016(?)				
Actinium **lead**	82				
Pb^{207}	*207*				

THORIUM FAMILY

		T	λ	τ	Literature
Thorium Th		$1.8\cdot10^{10}$yr.	$4.0\cdot10^{-11}$yr.$^{-1}$	$2.5\cdot10^{10}$yr.	33
At. wt.	232.12	$5.6\cdot10^{17}$s.	$1.2\cdot10^{-18}$s.$^{-1}$	$8.0\cdot10^{17}$s.	
At. no.	90				
P. no.	232				

THORIUM FAMILY (*Conclude1*)

		T	λ	τ	Literature
Mesothorium 1 $MsTh_1$		6.7yr.	0.103yr.$^{-1}$	9.7yr.	
	88	$2.1\cdot10^8$s.	$3.26\cdot10^{-9}$s.$^{-1}$	$3.05\cdot10^8$s.	
	228				
Mesothorium 2 $MsTh_2$		6.13h.	0.113h.$^{-1}$	8.84h.	34
	89	$2.21\cdot10^4$s.	$3.14\cdot10^{-5}$s.$^{-1}$	$3.18\cdot10^4$s.	
	228				
Radiothorium RdTh		1.90yr.	0.365yr.$^{-1}$	2.74yr.	35
	90	$6.0\cdot10^7$s.	$1.16\cdot10^{-8}$s.$^{-1}$	8.65.10's.	
	228				
Thorium X	ThX	3.64d.	0.190d.$^{-1}$	5.25d.	
	88	$3.14\cdot10^5$s.	$2.20\cdot10^{-6}$s.$^{-1}$	$4.54\cdot10^5$s.	
	224				
Thoron Tn		54.5s.	$1.27\cdot10^{-2}$s.$^{-1}$	78.7s.	36
	86				
	220				
Thorium A ThA		0.14s.	4.95s.$^{-1}$	0.20s.	37
	84				
	216				
Thorium B ThB		10.6h.	$6.54\cdot10^{-2}$h.$^{-1}$	15.3h.	
	82	$3.82\cdot10^4$s.	$1.82\cdot10^{-5}$s.$^{-1}$	$5.51\cdot10^4$s.	
	212				
Thorium C ThC		60.5m.	$1.15\cdot10^{-2}$m.$^{-1}$	87.3m.	38
	83	$3.63\cdot10^3$s.	$1.91\cdot10^{-4}$s.$^{-1}$	$5.24\cdot10^3$s.	
	212				
Thorium C' ThC′		10^{-9}s.	10^9s.$^{-1}$?	10^{-9}s.??	
65%	84	or $<10^{-6}$	$>10^6$s.$^{-1}$	$<10^{-6}$s.	
65.7%	212				40
Thorium C″ ThC″		3.1m.	$2.24\cdot10^{-1}$m.$^{-1}$	4.47m.	39
35%	81	186s.	$3.73\cdot10^{-3}$s.$^{-1}$	286.3s.	
34.3%	208				40
Thorium D ThD					
	208.016(?)				
Thorium lead	82				
Pb^{208}	208				

QUANTITIES IN RADIOACTIVE EQUILIBRIUM

			M in mass units	
		T	**For Ra = 1**	**For UI = 1**
	UI	$1.39\cdot10^{17}$s.	$2.94\cdot10^6$	1.00
	UX_1	$2.12\cdot10^6$	$4.4\cdot10^{-5}$	$1.5\cdot10^{-11}$
		$(2.06)\cdot10^6$	$(4.3)\cdot10^{-5}$	
99.65%	UX_2	68.4	$1.4\cdot10^{-9}$	$5\cdot10^{-16}$
0.35%	UZ	$2.4\cdot10^4$	$1.7\cdot10^{-8}$	$6\cdot10^{-16}$
	UII	$9.4\cdot10^{12}$	$2.0\cdot10^2$	$6.7\cdot10^{-5}$
3%	UY	$8.88\cdot10^4$	$5.6\cdot10^{-8}$	$1.9\cdot10^{-14}$
97%	Io	$2.6\cdot10^{12}$s.	52.7	
	Ra	$5.02\cdot10^{10}$	1.00	
	Rn	$3.303\cdot10^5$	$6.47\cdot10^{-6}$	

QUANTITIES IN RADIOACTIVE EQUILIBRIUM (*Concluded*)

			M in mass units	
		T	For Ra = 1	For UI = 1
	RaA	183	$3.52\cdot10^{-9}$	
	RaB	$1.61\cdot10^{3}$	$3.04\cdot10^{-8}$	
	RaC	$1.18\cdot10$	$2.23\cdot10^{-8}$	
99.96%	RaC′	*ca.* 10^{-6}	*ca.* $2\cdot10^{-19}$	
0.04%	RaC″	79.2	$6\cdot10^{-13}$	
	RaD	$6.94\cdot10^{8}$	$1.28\cdot10^{-2}$	
	RaE	$4.26\cdot10^{5}$ (4.9d.)	$7.9\cdot10^{-6}$	
		$4.32\cdot10^{5}$ (5.0d.)	$8.0\cdot10^{-6}$	
Po =	RaF	$1.21\cdot10^{7}$	$2.24\cdot10^{-4}$	
	M for Ra = 1 and 3% Branching Fraction			
	Pa	$1.01\cdot10^{12}$s.	0.62	
	Ac	$4.23\cdot10^{8}$	$2.5\cdot10^{-4}$	
		($6.3\cdot10^{8}$, 20yr.)	($3.7\cdot10^{-4}$)	
	RdAc	$1.63\cdot10^{6}$	$9.8\cdot10^{-7}$	
	AcX	$9.7\cdot10^{5}$	$5.8\cdot10^{-7}$	
	An	3.92	$2.27\cdot10^{-12}$	
	AcA	$2\cdot10^{-3}$	$1.14\cdot10^{-15}$	
	AcB	$2.16\cdot10^{-3}$	$1.21\cdot10^{-9}$	
	AcC	130	$7.2\cdot10^{-11}$	
0.32%	AcC′	*ca.* 10^{-3}	*ca.* $2\cdot10^{-18}$	
99.68%	AcC″	286	$1.57\cdot10^{-10}$	
		(283)	$1.55\cdot10^{-10}$	

QUANTITIES IN RADIOACTIVE EQUILIBRIUM

			M in mass units	
		T	For Th = 1	For MsTh$_1$ = 1
	Th	$5.6\cdot10^{17}$s.	1.00	$2.7\cdot10^{9}$
	MsTh$_1$	$2.1\cdot10^{8}$	$3.68\cdot10^{-10}$	1.00
	MsTh$_2$	$2.21\cdot10^{4}$	$3.88\cdot10^{-14}$	$1.05\cdot10^{-4}$
	RdTh	$6.0\cdot10^{7}$	$1.05\cdot10^{-10}$	0.286
	ThX	$3.14\cdot10^{5}$	$5.41\cdot10^{-13}$	$1.47\cdot10^{-3}$
	Tn	54.5	$9.23\cdot10^{-17}$	$2.50\cdot10^{-7}$
	ThA	0.14	$2.32\cdot10^{-19}$	$6.31\cdot10^{-10}$
	ThB	$3.82\cdot10^{4}$	$6.23\cdot10^{-14}$	$1.69\cdot10^{-4}$
	ThC	$3.63\cdot10^{3}$	$5.92\cdot10^{-15}$	$1.61\cdot10^{-5}$
65%	ThC′	*ca.* 10^{-9}	*ca.* 10^{-27}	*ca.* $3\cdot10^{-18}$
	or	10^{-6}	10^{-14}	$3\cdot10^{-15}$
35%	ThC″	186	$1.04\cdot10^{-16}$	$2.83\cdot10^{-7}$

Remarks on "Range" and "Ion Production."—Comparison of the results of different investigations shows that the ranges are not defined with sufficient sharpness to justify the use of three decimal places. Limitation to two places is therefore proposed.

In general, the values of H. Geiger [Z. *Physik,* 8, 45 (1921)] supplemented by those of G. H. Henderson [*Phil. Mag.*, [16] 42, 538 (1921)] and the later values (Lit. 41) are the ones used in the following. For U_{II} see the note on page 2443. For RaC′ Mmes. M. Curie and I. Joliot-Curie have made the following summary

	R_{15}	**Recommended**
H. Geiger, *Z. Physik*, 8, 45 (1921)	6.971	
G. H. Henderson, Phil. Mag., 42, 538 (1921)	6.953	6.95 or
I. Curie and F. Béhounek, J. *Phys. Rad.*, 7,125 (1926)	6.96	6.96
G. I. Harper and E. Salaman, Proc. Roy. *Soc.* (London), 127, 175 (1930)	6.94	

Since the basic value for RaC′ which has been used up to the present (cf. page 2441) is the mean of the values of Geiger and of Henderson, $R_0 = 6.600$ or $R_{15} = 6.963$, it appears advisable to retain it and to round off R_{15} as 6.96.

There is no agreement yet on the range of a-particles of ThC. Both values $R_{15} = 4.78$ and 4.72 are, therefore, reported.

For the discussion of ranges refer especially to the measurements of S. Rosenblum, *Compt.* rend., 190, 1124 (1930), and the sections in Rutherford, Chadwick and Ellis (51), page 82, et *seq.*, and the table on page 86. If one is content with two decimal places for the velocity, then the relation $v^3 = aR$ gives sufficient accuracy for the normal ranges.

The basic value for ion production by a-particles is that for RaC′: k = 2.2·10⁵ (cf. page 2441).

For the velocity of α-particles from ThC Rutherford, Chadwick and Ellis (51) choose $1.701 \cdot 10^9$ cm./sec., while Mmes. M. Curie and I. Joliot-Curie propose $1.698 \cdot 10^9$ cm./sec.

RANGES AT 0° AND 760 MM. IN AIR (R_1); AT 15° (R_{15})
Velocity (v) and ion production (k)

	R_0	R_{15}	v	k	Literature
UI	2.53	2.67	$1.40 \cdot 10^9$	$1.16 \cdot 10^5$	M.–Schw. (42)
	2.59	2.73	1.41	(1.18)	41, 51
UII	2.96	3.12	1.47	1.29^+	42
	3.11	3.28	1.50	(1.33)	41, 43, 51
Io	3.03	3.19	1.48	1.31	M.–Schw. 41
Ra	3.21	3.39	1.51	1.36^+	42
Rn	3.91	4.12	1.61	1.55	M.–Schw.
RaA	4.48	4.72	1.69	1.70	
RaC	3.9	4.1	1.61	1.55	48a
RaC′	6.600^{++}	6.96	1.922^{++}	2.20^{++}	M.–Schw.
	(6.58)	(6.94)			44, 48
Po	3.67	3.87	1.593^+(1.58)	149	45
	(3.72)	(3.92)	(1.59)	(1.50)	44, 46
Pa	3.48	3.67	1.55	1.44	M.–Schw.
RdAc	(4.43)	4.68	1.68	(1.69)	52
and	(4.77) and	4.34	1.64	(1.67)	
AcX	4.14	4.37	1.65	1.61	
An	5.49	5.79	1.81	1.95	
AcA	6.24	6.58	1.89	2.12	
AcC	(5.22)	(5.51)	(1.78)	(1.88)	48a
and →	(4.82) and →	(5.09)	(1.73)	(1.79)	
AcC′	(?6.2?)	(?6.5?)	(1.9?)	*ca.* 2	

Absorption Coefficients for β- and γ-Rays.—Beta and gamma rays are at present best characterized by their spectra. An extensive reproduction of such spectra would exceed the limits of these first tables issued by the Radium-Standards Commission.

The following summaries are cited

L. Meitner, "Handbuch der Physik," by H. Geiger and K. Scheel, Bd. XXII, 1926; St Meyer and E. Schweidler, "Radioaktivitat," Teubner, 1927; K. W. F. Kohlrausch, "Radioaktivitat," Bd. XV, Handb. d. Experimentalphysik, W. Wien and F. Harms, 1928; A. F. Kovarik and L. M. McKeehan, "Radioactivity," Bull. of the National Research Council, Nr. 51, Washington, 1929; I. Joliot-Curie, "Données numériques de Radioactivité, Tables annuelles de constantes et donneés numériques," Paris, 1930; E. Rutherford, J. Chadwick and C. D. Ellis, "Radiations from Radioactive Substances," Cambridge, England, 1930.

The absorption coefficients (μ) are in the expression $I = I_0e^{-\mu x}$, somewhat deficiently defined, but for practical measurements and for radioactive identification they constitute very useful data and are therefore given in the following table, as well as the velocity limits for β-rays. μ/ρ is the mass absorption coefficient (ρ = density); D = thickness for half absorption, $0.69315/\mu$. All data refer to aluminum as absorbing material.

BETA RAYS

Sub-stance	Type of decay	μ in cm.$^{-1}$ Al	μ/ρ	D in cm. Al	Litera-ture	Magnetic spectrum, velocity limits in 10^{10} cm./sec.	Remarks[a]	Accompany-ing γ-rays
UX_1	β	460	170	0.0015	9	1.44-1.74	3L.[b] 1 Bd.	No nuclear y-rays
UX_2	β	18	6.75	0.038	9	2.46–2.88	2 Bd.	Weak nuclear y-rays
UZ	β	270 to 36	100 to 13.5	0.0026 –0.019	11	?	?	?
Ra	α	312	116	0.00222	4	1.56–2.04	3 L.	1 Nuclear γ-line
RaB	β	890: 80: 13	330: 29.5: 4.84	0.00078: 0.0087: 0.053	1	1.08–2.47	31 L.	9 Nuclear γ-lines
RaC + C″	a + β	50: 13	18.5: 4.84	0.0139: 0.053	1	1.14–2.96	63 L.	11 Nuclear y-lines
RaD	β	5500	2037	0.000126	8	0.96–1.20	5 L.	1 Nuclear 7-line
RaE	β	45.5	16.9	0.0152	13	2.05-2.84	1 Bd.	Weak nuclear γ-ray
UY	β	ca. 300	110	0.0023	10	?	?	?
Pa	α	126	47	0.0055	14, 16	1.47–2.35	12 L.	3 Nuclear γ-lines
Ac	β	?	?	?	?	?	?	?
RdAc	α	175	65	0.004	14	0.66–2.3	49 L.	10 y-lines
AcX	α	?	?	?		0.88–2.22	21 L.	5 y-lines
AcB	β	ca. 1000	370	0.0007	2	1.49	1 L. ?	
AcC AcC″	$\alpha + \beta$ β	29	10.7	0.024	5	2.25–2.56	8 L.	3 Nuclear y-lines
$MsTh_1$	β	. ?	?	?		?	?	?
$MsTh_2$	β	40: 20	14.8: 7.4	0.018 –0.034	3	1.09–2.90	31 L.	8 γ-Lines
			150	0.0017	6	1.19–1.53	6 L.	

BETA RAYS (Concluded)

Substance	Type of decay	μ in cm.$^{-1}$ Al	μ/ρ	D in cm. Al	Literature	Magnetic spectrum. velocity limits in 10^{10} cm./sec.	Remarks	Accompanying y-rays
ThB	β	153	57	0.0045	5.7	1.88–2.99	5 L.	2 Nuclear γ-lines
ThC	$\alpha + \beta$	14.4	5.35	0.048	7			
ThC″	β	21.6	8.0	0.032	7	0.91–2.87	37 L.	11 Nuclear γ-lines
K	β	74: 49	27.4: 18	0.0094 :0.014	15			Weak γ-rays
Rb	β	700: 190:	260: 70	0.001 :0.0037	15, 19			
		900	333	0.0077	12			

GAMMA RAYS

μ_{Al} is arranged to show the assumed origin of the radiation

Substance	Type of decay	M-series	L-series	K-series	Nucleus		Number of lines	
UX$_1$	β	..	24	0.7	. . . . . .		1	
UX$_2$	P	..	..	..	..	0.14	..	
Ionium	a	1088	22.7	0.41	..	...	..	
Radium	a	354	16.3	..	0.27	...	1	
RaB	β	230	40	0.57	..	...	10	
RaC + C"	a	..	..	1.49	0.23	0.127	11	
RaD	β	..	45	1.17	..	...	1	(Lit. 22)
RaE	β	..	..	..	0.24	...	..	
RaF	a	2700	46	..	Like RaC		(Lit. 20, 21)	
Pa	α	..	..	..	..	...	3[a]	(Lit. 16)
RdAc	a	..	25	..	..	0.19	10	
AcX	a	..	..	..	..	...	5	
AcB	β	120	31	0.45	..	...	..	
AcC″	β	..	..	..	..	0.198	3	
MsTh$_2$	β	..	26	..	..	0.116	8	
ThX	a	..	..	..	..	...	2	(Lit. 17)
ThB	β	160	32	0.36	..	...	3	
ThC″	β	..	..	..	..	0.096	11	
K	β	From F = 0.19				0.065		(Lit. 18)
		From P = 0.59				0.14		(Lit. 19)

[a] Bands (UX$_1$ to ThC″) have their origin in the primary (nuclear) β-rays; lines in the photo-electrons of the γ-rays.

[b] L, line; Bd., band.

[CONTRIBUTION FROM THE CHEMICAL SCHOOL OF THE UNIVERSITY OF MELBOURNE]

A NEW FORM OF BUBBLE COUNTER FOR MEASUREMENT OF GAS EVOLUTION

BY E. A. BUDGE

RECEIVED MAY 15, 1930 PUBLISHED JULY 8, 1931

The measurement of the volume of gas evolved during the progress of a reaction in which a gas is one of the products is a well-known method of measuring reaction velocity coefficients. The estimation of the rate of evolution of the gas by timing evolution of gas bubbles of uniform volume is a very attractive experimental method, and if the counting can be performed automatically the method becomes almost ideal. Various appliances to carry out bubble-counting of this kind have been described in the literature at various times. For instance, Bose[1] has used such a method in his studies of photosynthesis.

During an investigation on the rate of decomposition of hydrogen peroxide in the presence of hydrochloric acid, the author was led to devise an apparatus which proved quite useful for the purpose. The starting point was a simple apparatus which was in use in England.[2] In this apparatus, however, the bubbles were formed at the mouth of a bell-shaped tube immersed mouth-downward in a vessel of water. It was found that this form of bubbler was unsatisfactory, as the volume of the bubbles was not constant under varying rates of bubbling and over long periods. Finally the author devised the form of apparatus shown in Fig. 1.

In this figure, A shows the top of the reaction flask, from which the gas to be measured (in this case oxygen) is being evolved. The gas passes by way of the rubber connection B and the tube C to the bubbler D, which is immersed in the water of the thermostat. The gas issues from D in distinct bubbles of constant size. This constancy of size is ensured by the U-shaped bend of capillary tubing which is so fused on that the change of internal diameter shall be as sudden as possible. On account of the surface tension of the water in the capillary tube, the meniscus does not leave it; the bubble breaks off when the gas–water interface has reached F and the interface immediately retreats to E. The volume of the bubble is therefore rigidly defined by the dimensions of this capillary in comparison with the total volume of gas space in the apparatus. Each time a bubble breaks away there is a diminution in the pressure of the gas enclosed in the apparatus. This variation of pressure causes an oscillation in the level of the mercury in the U-shaped tube G, and this oscillation is made to operate an electrical make-and-break by means of a platinum wire H sealed through the lowest part of the U and another platinum wire J so arranged that the mercury in rising will make contact with it. When a bubble breaks away from D and the gas–water interface moves smartly from F to E, the sudden fall of pressure causes the mercury in G to fall rapidly away from the platinum wire J and thus break the circuit. In this circuit is a 2-volt battery, a regulating resistance and a relay. This relay switches on and off a stronger current fur-

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[1] Bose, "The Physiology of Photo-synthesis," Longmans, 1924, p. 21.

[2] *School Science Review, 4, 139 (1923).* (A more detailed description which was referred to in this review could not be traced.)

nished by a 60-volt battery which operates a counter such as is used for counting telephone calls. The make and break of this higher-voltage circuit is through a pair of arc light carbons, one of which is furnished with a screw adjustment. By this means fouling of the contacts owing to sparking is rendered innocuous. There are a few further points worth mentioning with regard to the low-voltage contact G. A large part of the U-tube of G is made of capillary tubing in order to render the contact "dead beat" in its action by damping out oscillations of the mercury column which might lead to false contacts. A few drops of distilled water are placed above each mercury surface in G to act as a lubricant and prevent sticking of the mercury. To minimize sparking when contact with the wire J is broken, a condenser is placed in parallel with this gap. The absolute elimination of sparking at this contact is desirable, as it results in fouling of the contact and uncertain counting during the course of a long run. This sparking causes a brownish cloud, presumably finely divided mercury, to form in the water. This can be removed by flushing out the widened portion of the tube with distilled water from a wash bottle with a fine jet. If the surface of the mercury becomes covered with a scum, this is removed by adding a trace of nitric acid to the water by touching it with a platinum wire that has been dipped in dilute nitric acid. If this is done, the wide tube must soon afterward be well flushed out with water, as otherwise a deposit of mercurous nitrate will soon put the contact out of action. Contact was found to be more certain when the platinum wire J was connected to the positive pole of the cell, owing to the well-known effect of the nature of the charge of a mercury surface on its surface tension. As the mercury rises toward J its potential is negative toward the water and in consequence the increase of surface tension tends to depress the meniscus; but as soon as the mercury touches the wire J, this negative potential becomes zero. In consequence the surface tension decreases and the resulting small rise of the mercury meniscus renders contact certain and the mercury appears to adhere to the wire. When the mercury meniscus is jerked away from the wire as a bubble breaks away at D, the depression of the meniscus, due to the increased surface tension, effectively prevents any second contact. This phenomenon was found to be a very important protection against the effects of chance vibration. The point needing most attention, however, is the preservation of a bright clean surface at the mercury meniscus by the prevention of sparking. This calls for a small current at the contact J and a sensitive relay. The clicking of the counter could be heard even in an adjacent room and, although this is rather trying to the nerves over a long period, one subconsciously listens to the clicks and soon learns to appreciate the slightest variation from regular working, which gives timely warning of any incipient trouble at the contact.

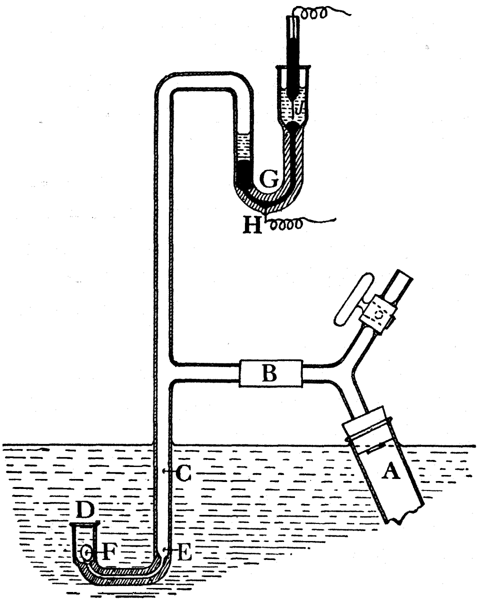

Fig. 1.—Diagrammatic view of the bubble counter.

For testing the equality of the volume of the bubbles a useful accessory is a piece of capillary tube of suitable internal diameter, which is placed horizontally against a scale and calibrated by a mercury thread in the usual manner. One end of this capillary is bent vertically downward and expanded into a bell-shaped mouth. This dips below the water in the bath and enables a single bubble to be caught. The other end of the capillary is also bent downward and carries a stopcock. When the tube is filled with water, it acts as a siphon and by opening the stopcock the bubble caught in the bell may be brought to a convenient place in the tube for measurement of its volume.

A serious limitation on the usefulness of the apparatus lies in the necessity for the constancy of the total volume of gas in the tubes of the counter and any apparatus to which it is connected. Also this gas volume must not be too large or a series of bubbles is formed at each emission instead of a single one. A gradual change in this gas volume can be allowed for by measuring the volume of the bubbles at various times by means of the accessory capillary tube; but, where this gas volume is not subject to change, the apparatus is very convenient for such purposes as the measurement of reaction velocity by gas evolution, since both the total volume of gas evolved and also the rate of evolution of the gas are easily obtained by readings of the dial.

The author desires to express his sincere thanks to Professor E. J. Hartung for the generous manner in which he has made available facilities for carrying out this work and for his very helpful criticism and advice.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OP PENNSYLVANIA]

INACCURACY IN THE DETERMINATION OF MERCURY BY DIRECT PRECIPITATION AS MERCURIC SULFIDE FROM ACID SOLUTION[1]

BY E. P. FENIMORE AND E. C. WAGNER

RECEIVED NOVEMBER 18, 1930 PUBLISHED JULY 8, 1931

The direct precipitation of mercury as sulfide from acid solution is a procedure whose accuracy has for many years remained apparently unquestioned.[2]

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[1] This paper is constructed from a portion of the doctorate thesis of Edward P. Fenimore, University of Pennsylvania, 1929.

[2] Fresenius–Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, Inc.. New York, 1903, Vol. I, p. 366; Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Drechsel, Bern, 1913, Vol. II, p. 412; Treadwell–Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1924, Vol. II, 6th ed., p. 172.

It was planned to use this method for control purposes in the development of a new distillation procedure (to be described in a later paper) for determination of mercury in organic compounds. Trials with known amounts of mercury, however, yielded results which were too high. Continued study confirmed this unexpected finding, and showed the sulfide to be contaminated, *e. g.*, with chlorine, the impurity being greater in the presence of dissolved salts in quantity.

Experimental

The concentration of mercury was in all trials less than 0.1 g. per 100 cc. Precipitations were made in Erlenmeyer flasks, hydrogen sulfide being introduced under slight pressure at room temperature. The washed precipitates were extracted for one to two hours in a Wiley apparatus; a second extraction was found to be without effect. The Gooch crucibles were prepared with thick mats of fine asbestos, with underlying disks of filter paper.[3]

Each crucible was conditioned by passing through it a solution whose composition, etc., duplicated that of the liquid to be filtered in the analysis; these wash-liquids, however, contained no hydrogen sulfide. This treatment was repeated until it was certain, after drying at 100–105°, that the weight was constant within 0.0001 g.

The materials analyzed were two specimens of mercuric chloride and one of precipitated oxide, all of determined purity.

Results obtained with various conditions of precipitation are given in Table I.

TABLE I

ANALYTICAL RESULTS

Conditions	Mercury taken, g.	Mercuric sulfide, g.	Mercury found, g.	Error. g.
1 Precipitation from solution about **0.2** N in HCl, and free from salts	0.36378	0.42275	0.36449	+0.0007
	.2218	.2577	.2222	+ .0004
	.2216	.2586	.2230	+ .0014
	.2216	.2581	.2225	+ .0009
	.3695	.4294	.3702	+ .0007
	.3226	.3756	.32385	+ .0012
	.3384	.3940	.3397	+ .0013
	.3631	.4227	.3645	+ .0014
Variations in procedure				
(a) Solution saturated with H_2S in cold, boiled, cooled and resaturated	.2225	.2596	.2238	+ .0013
	.2237	.2608	.2249	+ .0012
(b) Dilute solution: 0.09 g. of Hg in **400 cc.**	.0902	.1052	.0907	+ .0005
	.0890	.1042	.0898	+ .0008
(c) Dilute Hg solution added slowly to excess H_2S water	.2219	.2585	.2229	+ .0010
	.2216	.2578	.2223	+ .0007

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[3] White, THIS JOURNAL, 42, 2355 **(1920).**

TABLE I (*Concluded*)

Conditions	Mercury taken, g	Mercuric sulfide, g.	Mercury found, g.	Error, g
3 Precipitation from solution acid with H_2SO_4 and containing $MnSO_4$, as in method of White	0.0923	0.10885	0.0939	+0.0016
	.1389	.1632	.1407	+ 0018
	.1022	.12015	.1036	+ 0014
	.1345	.1572	.1355	+ .0010
3 Precipitation from acid solution containing KI and much NaCl and Na_2SO_4, as in distillation method	.0980	.1208	.1042	+ 0053
	.1205	.1470	.1268	+ 0063
4 Modified Volhard method, in presence of KI	.2262	.2644	.2280	+ .0018
	2223	.2585	.2229	+ .0006
3 Double precipitation: HgS from iodide solution rich in salts dissolved in Na_2S and reprecipitated by NH_4NO_3	0943	.1141	.0984	+ .0041
	1122	.1347	.1161	+ .0039

Discussion

The average error of the first eight trials, made under conditions most favorable to accuracy, was +0.34%. The larger error (about 1%) in series 2 will affect gravimetric results by White's method, though it may in practice be compensated by loss of mercury during the decomposition or by loss in weight of Gooch crucibles not properly conditioned. Presence of iodide or of salts in excess (series 3, 4, 5) increased the positive error markedly. The unfavorable effect of iodide was reported by Wegelius and Kilpi,[4] and several methods to avoid its interference have been proposed, including the solution of the impure sulfide in sodium sulfide and reprecipitation by Volhard's method.[5]

The Volhard procedure, when applied to solutions which contain only the mercury salt and at most the salts from neutralization of a little acid, has been established as accurate. Trials by Rauschenbach[6] yielded results only 0.06% low. One of the writers (W.) has tested the method in comparison with the thiocyanate titration, with several electrolytic methods,[7] and against purified mercuric chloride, results by the several methods being practically identical.

Some of the sulfide precipitates of series 1 were in part removed from the crucibles, ignited with lime and tested for chlorine. A considerable contamination was shown (9.8 mg. of AgCl); a blank on the lime, etc., was negative.

An explanation for the lack of purity of mercuric sulfide precipitated from acid solution is suggested by the intermediate "compounds" whose

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[4] Wegelius and Kilpi, *Z. anorg. Chem.*, 61, 413 (1909).

[5] Dunning and Farinholt, THIS JOURNAL, 51, 804 (1929); Johns, Peterson and Hixon, *ibid.*, 52, 2820 (1930); Pretzfeld, *ibid.*, 25, 198 (1903).

[6] Treadwell–Hall, Ref. 2, 3d ed., 1911, p. 170.

[7] Smith, "Electro-Analysis," P. Blakiston's Sons, Philadelphia, 1918, 6th ed., pp. 101, 102, 104.

visible formation is a feature of the precipitation. The mechanism of mercuric sulfide formation was studied by Smith and Semon,[8] who concluded that five consecutive reactions are involved. The intermediate compounds were represented to be (1) $[Hg(SH)_2 \cdot Hg]X_2$, (2) $[HgSHg]X_2$, (3) $[Hg(SHg)_2]X_2$, (4) $[Hg(SHg)_2](SH)_2$. It is clear that pure mercuric sulfide will result only if none of these intermediate compounds survives.

There must be considered also the ability of mercuric sulfide to combine with or adsorb other molecules. Striking evidence of this was provided by qualitative tests[9] in which freshly precipitated and well-washed mercuric sulfide was introduced into solutions of mercuric chloride, sulfate, nitrate and acetate, and the mixtures well shaken and filtered, the filtrates in every case being free from mercury. During the precipitation of mercury by hydrogen sulfide the newly formed sulfide would probably be especially active in this way. The success of Volhard's method in the absence of salts in excess may be due to the circumstance that sulfide formation requires only transposition of $[SHgS]Na_2$ to the ammonium compound, which on heating decomposes irreversibly due to escape of ammonia and hydrogen sulfide.

Summary

The direct precipitation of mercuric sulfide from acid solution by hydrogen sulfide yields an impure product which is too heavy. In the presence of salts in excess, and of iodide, the positive error is increased. These effects appear to be due to the ability of precipitated mercuric sulfide to cause co-precipitation of other molecules, and perhaps to the nature of the mechanism by which the sulfide is formed. Volhard's procedure is accurate when applied to solutions which contain the mercury salt and not much else, but presence of salts in quantity, and especially of iodide, leads also to high results.

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[8] Smith and Semon, Tars JOURNAL, 46,1325 (1924).

[9] Privately communicated by Dr. J. H. Miiller.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OHIO STATE UNIVERSITY]

THE ABSORPTION SPECTRA OF COBALTOUS COMPOUNDS. III. THE PYRIDINE AND QUINOLINE COMPLEXES AND SOLUTIONS

BY WALLACE R. BRODE

RECEIVED JANUARY 9, 1931 PUBLISHED JULY 8, 1931

In the earlier papers of this series[1,2] the absorption spectra of cobaltous chloride, bromide and iodide, in solution in the corresponding halogen acids, were measured (Fig. 1). The data presented in these papers showed the cobalt and halogen atoms to be definitely bound together. The change in molecular weight in going from chloride to bromide to iodide caused a proportional shift in the position of the absorption band. No attempt was made to distinguish between the effect produced by the solvent and that produced by the halogen in combination with the cobalt, since each halide was measured in solution in the corresponding halogen acid. By an application of composite curve analysis,[3] the absorption bands were found to be resolvable into a series of component bands of multiple integral frequency. The same series of multiples appeared in the analysis of the absorption band of each of the cobalt halides, but the frequency of any given component band was different, as was also the frequency interval, between the component bands, for the chloride, bromide and iodide.

A discussion of the various theories concerning the color changes of cobalt solutions and molecular configuration of cobalt halides will not be undertaken until additional data have been obtained. However, certain more important papers bearing on the experimental work involved must of necessity be considered. A good review of much of the literature on this subject is to be found in a recent paper by Bassett.[4] Hantzsch[5] has shown, in a study of the absorption spectra of cobalt chloride in pyridine, that the color change from pink to blue, caused by the application of heat to the pyridine solution, is similar to that of an aqueous solution of cobalt chloride. The absorption spectrum of the blue pyridine solution indicated the possible existence of a composite curve, similar to that shown in the case of cobalt chloride in hydrochloric acid. A preliminary examination of the absorption spectra of hot solutions of cobalt chloride, cobalt bromide and cobalt iodide, in pyridine, made by Dr. R. A. Morton and the author[6] at the University of Liverpool, gave the results similar

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[1] Brode, *Proc. Roy. Soc.*, 118A, 286 (1928).

[2] Brode and Morton, *ibid.*, 120A, 21 (1928).

[3] Brode, *Bur. Standards J. Research*, 2, 520 (1929).

[4] Bassett, *J. Chem. Soc.*, 1784 (1930).

[5] Hantzsch, *Z. anorg. Chem.*, 159, 273 (1926).

[6] *Then* a Fellow of the John Simon Guggenheim Memorial Foundation.

to those indicated in Fig. 2. These results were only qualitative in nature, due to the relatively high temperatures required to produce a reasonable concentration, particularly for the iodide salt. Recent observations on these cobaltous halides in quinoline (Fig. 2) have given quantitative data, since the blue solutions are stable at room temperature, so that solutions of a definite concentration of the cobalt halide can be easily measured at a constant temperature. Although there is a marked difference in the molecular weight and other physical properties of the two solvents, pyridine and quinoline, absorption bands of nearly identical shape and frequency were obtained for each of the three halides. This would indicate an absence of solvent effect and the probability that neither pyridine nor quinoline is directly bound to the cobalt. On the other hand, the change in shape and frequency position of the absorption bands with a change of the halogen would indicate that there must be a direct connection between the cobalt and the halogen atoms.

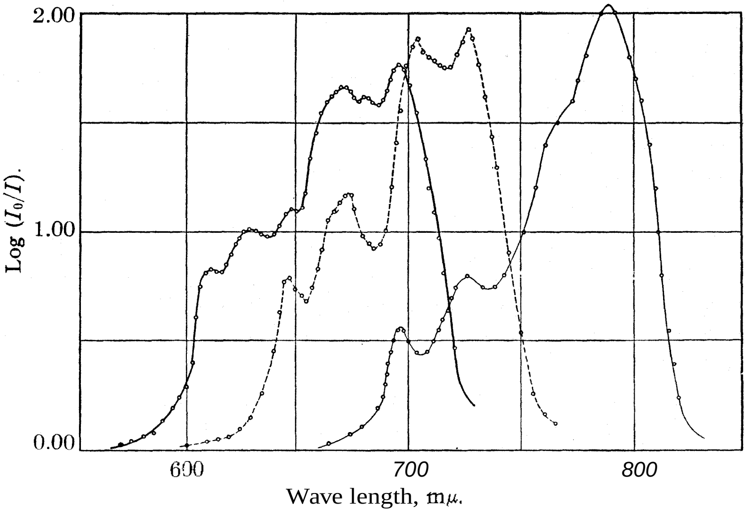

Fig. 1.—The absorption spectra of cobaltous halides in their corresponding halogen acids: ——, $CoCl_2$ in HCl; - - - - - -, $CoBr_2$ in HBr; —○—, CoI_2 in HI.

When one compares the absorption spectra of the cobaltous halides in pyridine solution with those of the same salts in concentrated halogen acids one notes a marked difference. The shift in the position of the. absorption band toward the red end of the spectrum as one goes from chloride to bromide to iodide is much greater in acid solution than in the pyridine or quinoline solution. It will also be noted that for any given halide as, for example, the chloride, the absorption band in acid solution is of lower frequency than for the same salt in pyridine or quinoline.

These larger differences in frequency and the general displacement to lower frequency values in acid solution may be attributed to either of the following causes: (a) to the direct combination of the cobalt atom with a greater number of halogen atoms, or (b) to the effect of the solvent medium which in the acid solution is different for each salt studied.

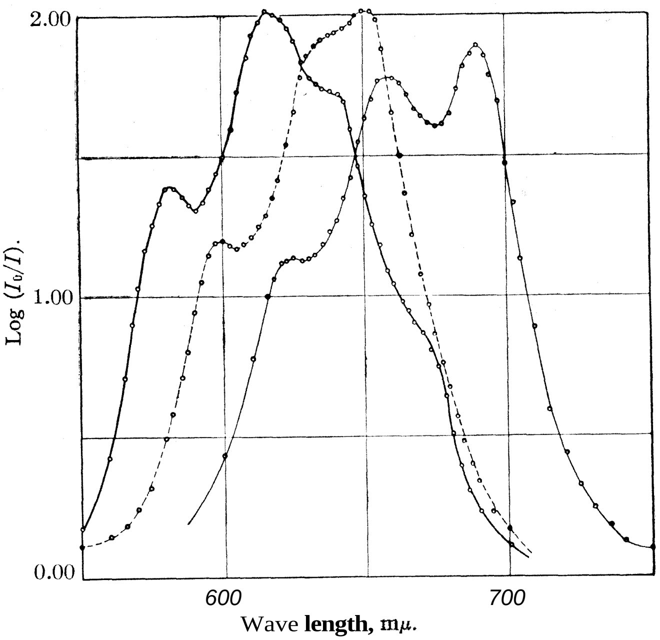

Fig. 2.—The absorption spectra of cobaltous halides in quinoline: ———, $CoCl_2$; - - - - - -, $CoBr_2$; ———, CoI_2. (Identical or nearly identical curves were obtained from cobalt quinolinium halides in quinoline and cobalt halides and cobalt pyridinium halides in pyridine.)

From the above observations it would seem that one has to deal here with two distinct systems of vibrations:[7] that characteristic of the acid solution and that characteristic of solution in an organic base such as pyridine or quinoline. In the present state of our knowledge of these composite absorption bands it is not possible to say whether the differences between the two series of absorption bands are due to a change in the component members. When the data from the halogen acid series (which will be referred to as the "HX" system) and the pyridine–quinoline series (which will be referred to as the "Py–Q" system) are compared on a

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[7] For purposes of comparison and discussion, a system will be defined as an electronic configuration which produces a series of absorption bands that remain similar in shape and multiple relations even though the mass of the molecule may be changed, *i. e.*, by a change from Cl to Br to I.

frequency scale in place of the wave length scale as used in this paper, it will be noted that either of the above possibilities would be supported by the data.

In a recent article Percival and Wardlaw[8] have described the preparation of cobalt pyridinium and cobalt quinolinium halides, to which they have assigned a constitution involving the $CoCl_4''$ ion. The blue cobalt solutions have been associated by many writers with the possible existence of this ion in solution. The above-mentioned compounds are, however, among the first to be isolated in which such a group has been formulated for a solid substance. The general method of preparation of these compounds was to mix in an alcoholic solution, pyridine (or quinoline) hydrochloride (bromide or iodide) with an equimolecular amount of the corre-

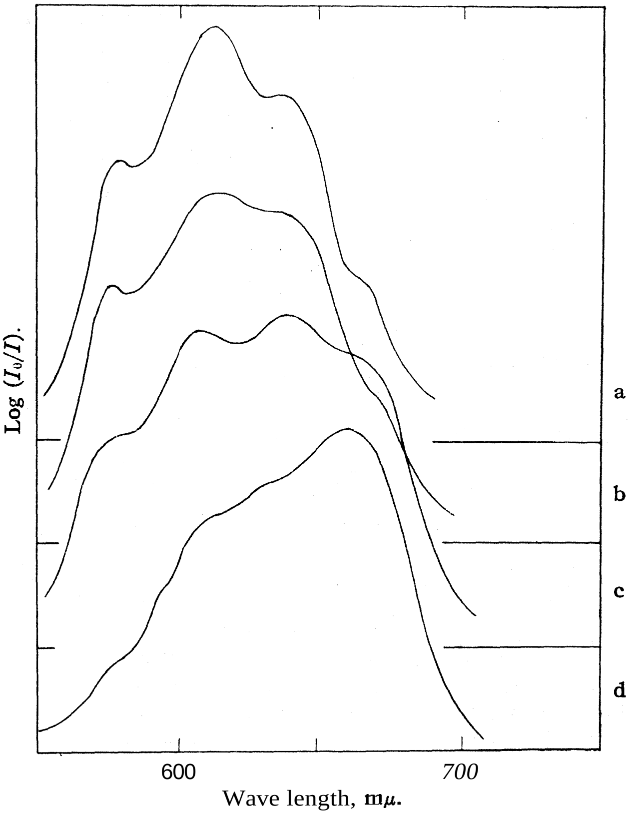

Fig. 3.—(a) The absorption spectra of cobaltous chloride–pyridine complex ($CoPy_2Cl_2$) in $CHCl_3$; (b) $CoPy_2Cl_2$ in $CHCl_3$ + C_2H_5OH; (c) $CoPy_2Cl_2$ in C_2H_5OH; (d) $(PyH)_2CoCl_4$ (cobaltous pyridinium chloride) in C_2H_5OH.

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[8] Percival and Wardlaw, *J. Chem. Soc.*, 1505 (1929).

sponding cobaltous halide. The cobalt pyridinium (or quinolinium) halide formed by this reaction was filtered off and recrystallized from alcohol. All of these compounds crystallized with ease from alcohol, yielding needle-shaped crystals in the case of the pyridine derivatives and plates in the case of the quinoline derivatives. Because of the possibility of confusion of these compounds with those described in the following paragraph, analyses were made on these complexes and the results of Percival and Wardlaw were confirmed.

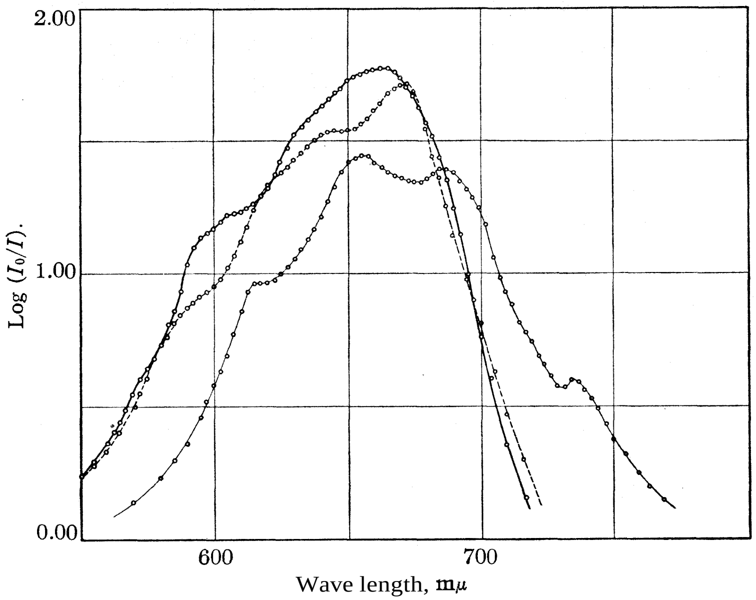

Fig. 4.—The absorption spectra of cobalt quinolinium halogen complexes ($(QH)_2CoX_4$) in absolute ethyl alcohol: X = Cl, ———; Br, - - - - -; and I, ———. The cobalt pyridinium complexes gave identical curves.

Percival and Wardlaw did not refer to the work of Hantzsch,[5] Reitzenstein[9] or Grossmann,[10] who prepared similar compounds by the interaction of cobaltous halides with pyridine or quinoline in alcohol solution. These authors have assigned formulas of the general type $Co(C_5H_5N)_2X_2$ and $Co(C_9H_7N)_2X_2$ to such compounds. The relation between these cobalt halogen complexes may well be represented by the equation

$$\underset{(I)}{CoPy_2Cl_2} + (2HCl) \rightleftharpoons \underset{(II)}{CoCl_2\cdot Py_2\cdot 2HCl} \rightleftharpoons \underbrace{CoCl_2 + 2Py\cdot HCl}_{(III)}$$

According to Percival and Wardlaw the formula for compound (II) should be written as $(PyH)_2CoCl_4$. Since compounds of both types (I)

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[9] Reitzenstein, *Ann.*, 282, 275 (1894).

[10] Grossmann, *Ber.*, 37, 1256 (1904).

and (II) can be recrystallized from alcohol solutions without change in composition and since both give blue solutions, a study of their absorption spectra should offer valuable information with regard to the nature of these complexes. The cobalt chloride–pyridine complex (Compound I) gave in alcohol an absorption spectrum quite similar to the absorption spectrum of cobalt chloride in pyridine (Fig. **3**). While the band intensities of the former did not exactly correspond with those (Fig. 2) of cobalt chloride in pyridine or quinoline, their frequency positions were the same, and it was further shown that the band intensities could be altered without changing the position of the bands by the use of other solvents such as ligroin and chloroform. In these latter solvents there is a general sharpening of the bands while in alcohol there seems to have been a broadening and flattening of the bands. The same effects were noted in a study of the absorption spectra of the quinoline complex, which, though of a markedly different color from the pyridine complex in the crystalline state, gave an almost identical absorption spectrum in alcohol solution.

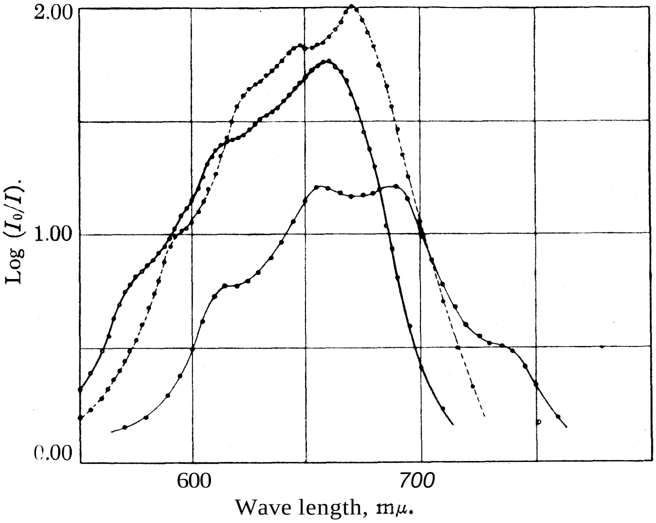

Fig. 5.—The absorption spectra of cobaltous halides in ethyl alcohol: Cl, ——; Br, ------; and I, —·—

The absorption spectra of the cobaltous pyridinium and quinolinium chlorides (11), bromides and iodides (Fig. 4) in alcohol were quite different from the absorption spectra of the corresponding cobalt halides in pyridine and quinoline. A comparison of the curves of these pyridinium and quinolinium complexes in alcohol with those of the corresponding cobalt halides in alcohol (Fig. 5) showed that for the same halogen nearly identical absorption spectra were obtained. These facts suggest a reaction similar to that indicated from (II) to (III) in the above equation, and that the cobalt halide absorption spectrum in alcohol was not influenced by the pyridinium or quinolinium chloride present. An exact analysis of the curves is not possible due to the broad flat nature of the component portions of the alcohol bands. There is some question as to whether there is a distinct alcohol system of absorption, similar to the "HX" and "Py–Q" systems or whether the curve (Fig. 4) is formed by an equilibrium between the "HX" and "Py–Q" systems. The addition of very small amounts of quinoline to a solution of cobalt chloride in alcohol produces the absorption spectra characteristic of cobalt chloride in quinoline, (Fig. 7), and in a like manner the addition of small amounts of hydrochloric acid and lithium chloride to the neutral alcohol solution of cobalt chloride produces absorption spectra which are characteristic of cobalt chloride in hydrochloric acid (Fig. 6). Gróh[11] made a study of this latter reaction and concluded that the alcohol solution of cobalt chloride contained equimolecular amounts of Co^{++} and $CoCl_4''$ ions and that the change in color on addition of the halogen containing salt such as lithium chloride is due to an increase in the concentration of the $CoCl_4''$ ion with a corresponding decrease in the amount of the Co^{++} ion, the latter ion being responsible for the pink color of cobalt solutions. The data here presented would seem to indicate a change in the nature of the blue absorption spectrum rather than a mere intensification of the alcohol bands, and hence does not support Gróh's proposed mechanism. As another example of difference of intensity of components of the same system under different conditions, the changes in intensities of the 595 mμ and 695 mμ bands are worth noting.

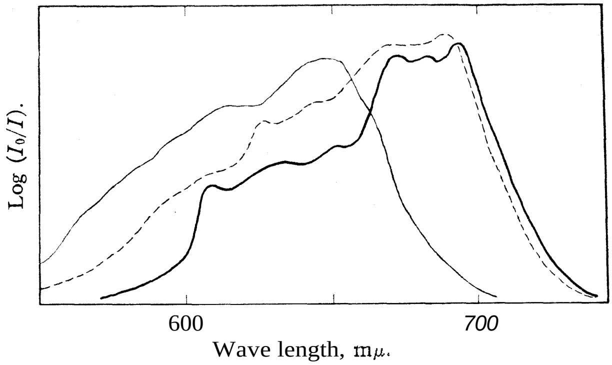

Fig. 6.—The absorption spectra of $CoCl_2$; in concentrated HCl, ———; in a 3% solution of LiCl in alcohol, - - - - - -; and in ethyl alcohol, ———.

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[11] Gróh, Z. *anorg.* Chem., 162,321 (1927); 146,305 (1925).

The addition of small amounts of halogen ions, either as quinolinium chloride or free hydrochloric acid, had no apparent effect on the absorption bands of cobaltous chloride in quinoline. Also, the addition of quinolinium chloride to the alcohol solution of cobalt chloride had no effect on the absorption band, indicating that all of the cobalt ions have the same amount of halogen.

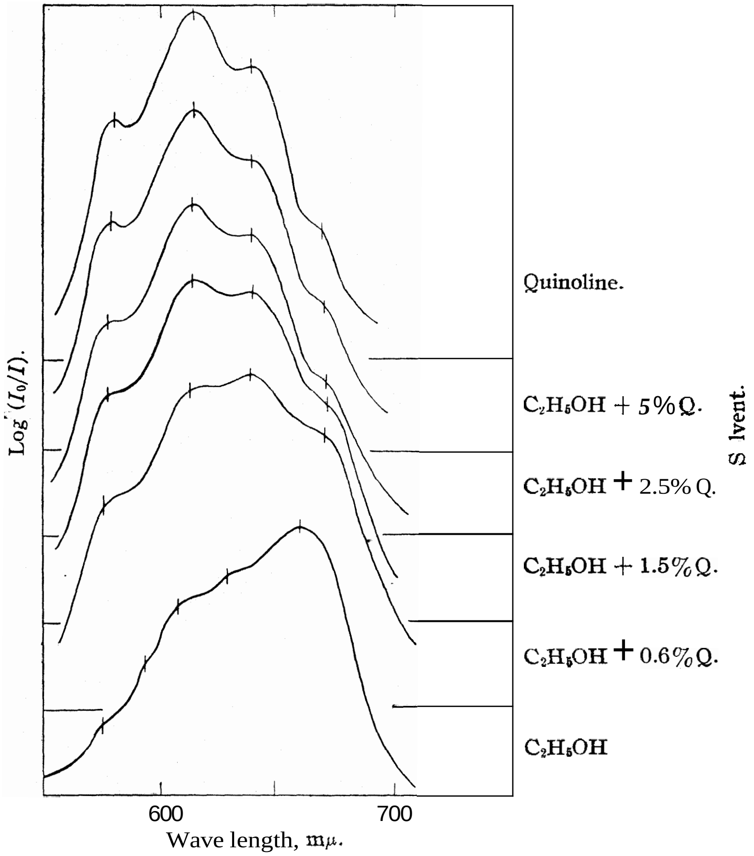

Fig. 7.—The change from the alcohol absorption to the "Py–Q" system of absorption caused by the addition of quinoline to a solution of $CoCl_2$ in ethyl alcohol.

If the alcohol solutions are to be considered as representing an intermediate or equilibrium state between the "HX" and "Py–Q" systems, then it should be possible to go directly from one system to another by the addition of one solvent to a cobalt solution of the other. A few of the curves obtained from nearly fifty solutions of varying concentration of hydrochloric acid and quinoline are presented in Fig. 8. These curves were selected to show representative conditions and transition stages.

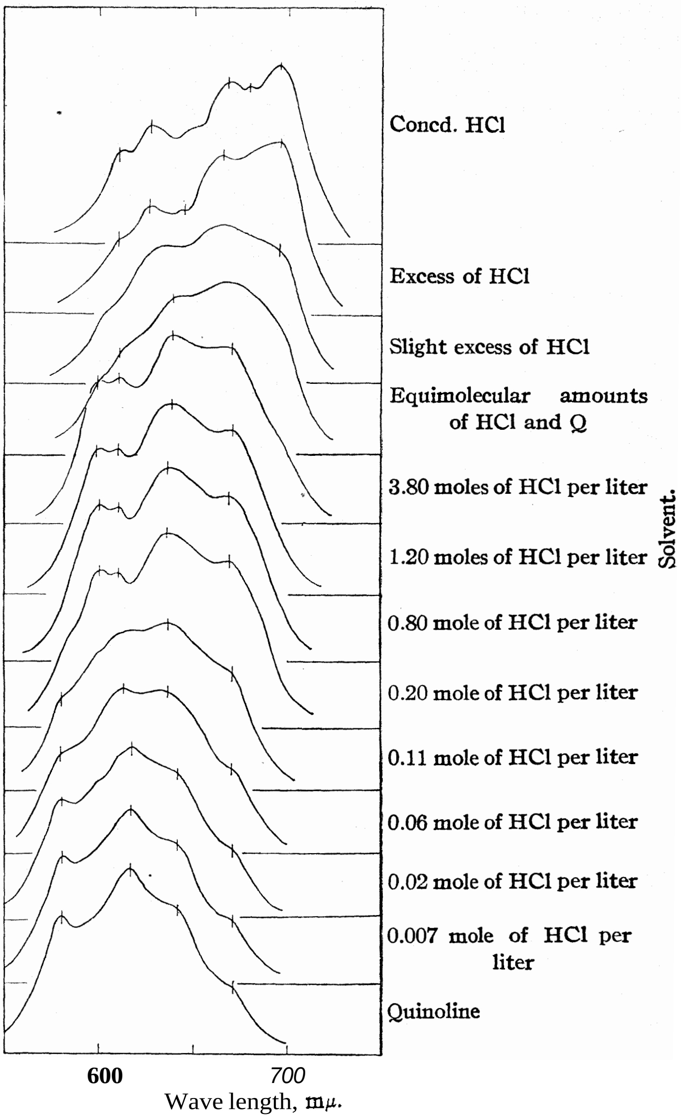

Fig. 8.—The change from the "Py–Q system, through the "intermediate" system to the "HX" system, caused by the addition of HCl to a solution of $CoCl_2$ in quinoline. (The curves in this figure are only a few of the some fifty curves, observed at various Q–HCl concentrations. They have been chosen to show characteristic stages or transition points in the change of the absorption systems. The concentration of $CoCl_2$ in all solutions was approximately 0.0043 mole per liter.)

Over a considerable concentration range there is no apparent effect on the general nature of this intermediate absorption band, and only after a concentration of acid in excess of the quinoline is reached do the " HX or acid system bands appear. While the intermediate band obtained in this "HX"–"Py–Q" equilibrium is not identical with the alcohol band, the close similarity in position and shape, allowing for some solvent effect, would argue for the existence of an "intermediate" system of absorption as well as for the "HX" and "Py–Q" systems.

Experimental

The observations recorded in the figures in this paper, with the exception of Fig. 1, were made on a Bausch and Lomb spectrophotometer which was equipped with a modified DuBoscq colorimeter attachment which permitted the use of all glass cells and the rapid variation of cell thickness by changing the position of the glass plungers. The data are recorded in wave length values expressed in millimicrons (meters $\times 10^{-9}$), as abscissa and in extinction coefficients, expressed as log I_0/I, as ordinates.

Cobalt chloride was prepared by dissolving cobalt carbonate in C. P. hydrochloric acid, recrystallizing from water and drying at 120° in the presence of dry hydrogen chloride. The anhydrous cobalt chloride was kept at 100° in a closed container until used. The sample was analyzed and checked for both cobalt and halogen. The cobalt was determined by the sulfate fusion method and the halogen by the standard silver chloride method.

A convenient means of determining the amount of cobalt present in any sample was to evaporate the solution to a small volume or to dryness and make up to the original volume with concentrated hydrochloric acid. The presence of such impurities as quinolinium hydrochloride, sulfates, nitrates or other halides in small amounts were shown by experiment to have no influence on the absorption bands of the hydrochloric acid solution. The hydrochloric acid solutions follow Beer's law throughout a wide concentration range. Because of its general shape, location and intensity, the band at 625 mμ was chosen for reference purposes (Fig. 1).

The molecular extinction coefficient for cobalt chloride in concentrated hydrochloric acid was found to be **335.5** at $\lambda = 625$ mμ and this value was used to determine the cobalt content of other solutions. In compounds where the halogen content might vary, such as the pyridine and quinoline complexes, separate halogen determinatious were made to insure that the correct compound was being used. The earlier data on the halogen acid solutions[1] were obtained from weighed samples of the supposed hexa hydrate. From the above analyses it is shown that the water content was not as supposed, so that the data as published represent the absorption of 0.7225 g. of the anhydrous cobaltous chloride per liter (Fig. 1).

Summary

A spectrophotometric study has been made of cobalt chloride, cobalt bromide and cobalt iodide dissolved in pyridine and quinoline, and the relation between the data observed and those previously presented on the corresponding acid solutions has been discussed. Although the data of this paper are in contradiction to some of the data and theories published or offered by others on the nature of cobalt colors, no attempt has been made to explain the actual constitution of the cobalt complexes. Discussion on this point is reserved for a later paper which will be presented after the publication of the cobalt alkaline solution data.

1. Evidence has been presented to substantiate the existence of three absorption systems in blue cobalt solutions, namely, the halogen acid system, the pyridine–quinoline system and a possible intermediate system.

2. The fact that the cobalt halides gave identical absorption spectra in both pyridine and quinoline supports the theory that the cobalt atom is not directly connected to the pyridine or quinoline molecule, since with the markedly different molecular weights of pyridine and quinoline, one would expect a shift in the absorption bands or a change in the component intensities with such a change in molecular weight. On the other hand, the nature of the holding or partial valence forces in complexes may be such that the effects produced would be too small to observe.

3. The change in frequency of the absorption bands with a change of halogen in the pyridine–quinoline system is similar to that previously observed in the halogen acid system, but of smaller magnitude, indicating a possible cobalt complex involving fewer halogen ions and more ions common to all three compounds.

4. Cobalt pyridinium and quinolinium halogen complexes give in alcohol the same absorption spectra as the pure cobalt halide in alcohol, indicating the non-existence of pyridinium or quinolinium complexes in the alcohol solution.

5. By a change of solvents it has been possible to alter the intensity of components of absorption bands without shifting their frequency position. If identical band positions but different extinction coefficient values are to be taken as indication of equilibrium isomers,[12] then the data presented on the absorption spectra of the cobalt quinoline and pyridine chloride complexes in alcohol and in chloroform would support the contention of Hantzsch[5] that isomeric forms of these complexes can exist.

COLUMBUS, OHIO

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[12] Morton, *J. Chem. Soc.*, 706 (1926).

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OR THE UNIVERSITY OF PENNSYLVANIA]

AN ANHYDROUS DISTILLATION METHOD FOR THE DETERMINATION OF CERTAIN METALS IN ORGANIC COMPOUNDS. I. THE DETERMINATION OF MERCURY1

BY E. P. FENIMORE AND E. C. WAGNER

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In the method described below, the sample is decomposed by concentrated sulfuric acid and ammonium (potassium) persulfate in a special apparatus, and mercury is distilled out as chloride by passing a stream of hydrogen chloride and heating to the temperature of distillation of the sulfuric acid (external temperature about 260–310°). The mercuric chloride is collected in water, and is determined by an adaptation of Jamieson's iodate method. Presence of chlorine or bromine introduces no difficulty, but that of iodine necessitates certain changes in the procedure. The method is believed to be general.

It appears that no similar procedure has been described. The volatilization of certain metals as anhydrous halides is employed in the analysis of minerals which are advantageously decomposed by heating in a stream of chlorine, carbon tetrachloride, etc. The wet distillation of metallic chlorides volatile with steam is familiar in the case of arsenic, and Biltz[2] separated arsenic, antimony and tin in this way. Strecker and Riedemann[3] observed mercuric chloride to pass over in part with arsenic, and upon this fact Strecker and Conradt[4] based a procedure for quantitative (though relatively slow) distillation of mercury in steam containing hydrochloric and hydrobromic acids.

In the elaboration of a complete procedure including the decomposition and anhydrous distillation outlined above, it was necessary finally to determine mercury in a solution containing hydrochloric and sulfuric acids and sulfur dioxide, or the salts formed by their neutralization. The nature of the solution excluded Volhard's thiocyanate titration. The iodimetric method of Rupp[5] yielded in five trials with pure mercuric chloride results which were concordant but somewhat high. Isolation of mercury as metal by excess stannous chloride, the washed globules being dissolved in nitric acid and titrated with thiocyanate,[6] was subjected to trial,

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[1] This paper is constructed in large part from the doctorate thesis of Edward P. Fenimore, University of Pennsylvania, 1929.

[2] Biltz, *Z. anal. Chem.*, 81, 82 (1930).

[3] Strecker and Riedemann, *Ber.*, 52, 1935 (1919).

[4] Strecker and Conradt, *ibid.*, 53, 2113 (1920).

[5] Rupp, *ibid.*, 39, 3701 (1906); 40, 3276 (1907); *Chem.-Ztg.*, 32, 1077 (1908); Smith, *Am. J. Pharm.*, 83, 311 (1911); Kolthoff and Keyzer, *Chem. Abstracts*, 14, 3035 (1920); Kolthoff, *ibid.*, 17, 1106 (1923).

[6] The method of Krieckhaus: Low, "Technical Methods of Ore Analysis," John Wiley and Sons, Inc., New York, 1922, 9th ed., p. 159.

a filter being used to retain floating particles of mercury otherwise lost during the washing by decantation. Results were satisfactory when the quantity of mercury was 0.2–0.3 g. (average error, −0.1%), but with 0.1 g. or less of mercury the results were barely acceptable or considerably too low.[7]

Determination of mercury as sulfide by precipitation with hydrogen sulfide was found to yield high results. With dilute solutions of mercuric chloride about 0.03 normal in hydrochloric acid the errors averaged +0.34%, and in presence of salts the errors were larger. This matter is discussed in another paper.[8]

The iodate method of Jamieson,[9] in which mercury is precipitated as $ZnHg(SCN)_4$, which is titrated with standard iodate solution in presence of hydrochloric acid, was found to be satisfactory, the small errors averaging 0.0001 g. For precipitation from the solution obtained in the distillation method, an increase in the concentration of the precipitating reagent was found necessary. The accuracy under the conditions adopted was nearly as high as that of the original method. For comparison purposes the method of White was adopted.[10] The sample, in warm (not hot) concentrated sulfuric acid, was decomposed by addition of powdered permanganate in small portions, the diluted liquid cleared by chlorine-free hydrogen peroxide, and the mercury titrated with thiocyanate solution standardized under the same conditions against pure mercury metal. Tests of this procedure, using pure (99.98%) mercuric acetate, and sucrose to provide oxidizable matter, showed it to be satisfactory, results for mercury averaging 0.04% low. This comparison method is not applicable to compounds which contain halogen, presence of which both increases danger of loss of mercury during the rather vigorous decomposition and excludes the convenient thiocyanate titration.

Distillation Method for Determination of Mercury in Organic Compounds.—The complete apparatus is illustrated in the figure.

1. Decomposition **and** Distillation.—Receiver M contains about 20 cc. of water, and the trap N about 5 cc. Stopcock P is closed. Tube p extends just to the surface of the water in M, and the latter is supported in a beaker of cold water.

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[7] Willard and Boldyreff, THIS JOURNAL, 52, 569 (1930), determined mercury gravimetrically as metal following reduction by stannous chloride, and, using quantities of mercury never less than 0.14 gram, found it necessary to apply an additive correction of 0.0010 g.

[8] Fenimore and Wagner, *ibid.*, 53, 2453 (1931).

[9] Jamieson, *J. Ind. Eng. Chem.* 11, 296 (1919); "Volumetric Iodate Methods," The Chemical Catalog Co., Inc., New York, 1926, p. 42.

[10] White, THIS JOURNAL, 42, 2350 (1920). The method of Eschka, in the modification described by Whitmore ("Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, p. 365), proved to be somewhat uncertain. The lime method is cumbersome and inclined to yield low results, and the modification by Bouton and Duschak [U. S. Bur. Mines Technical Paper No. 227, 1920] for mineral analysis has *not* been developed for use with organic mercury compounds.

The sample, containing not more than **0.15** g. of mercury, is weighed in a small glass cup, introduced into the decomposition flask G, and dissolved in **4–5** cc. of fuming sulfuric acid, with warming if necessary. To the cooled liquid is added **10** g. of powdered ammonium persulfate (or 12 g. of potassium persulfate), and then **15** cc. of concd. sulfuric acid is introduced in such way as to wash off any powder adhering to the ground surface H.[11] The decomposition flask is put in place, funnel F is charged with **5** cc. of concd. sulfuric acid, and connections are made as shown in the figure.

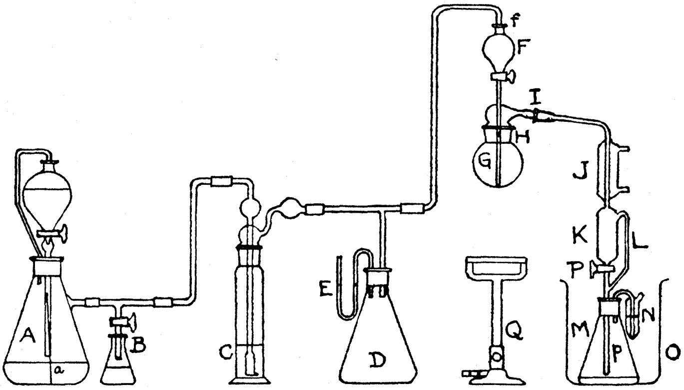

Fig. **1.—A,** HCl generator; NH_4Cl and concd. HCl in flask, concd. H_2SO_4 in funnel. Rod *a* causes acid to enter steadily and not by drops; B, pressure release; flask contains water; C, concd. H_2SO_4 drier and bubble-counter; D, safety flask; E, manometer (concd. HCl); F, funnel of **25** cc. capacity; G, decomposition flask of **100** cc. capacity; H and I, ground joints; J, water condenser; K, reservoir of 6–7 cc. capacity; L, vapor by-pass; M, receiver, capacity **150** cc.; N, trap, capacity **15** cc.; O, cooling bath; Q, ring burner.

Flask G is heated cautiously until oxidation starts, shown by gentle effervescence, and decomposition is completed by judicious heating, with occasional cooling if necessary. When active bubbling ceases, the stopcock F is opened, a stream of hydrogen chloride *(2* or **3** bubbles per second) is started, and the flask is heated rapidly until sulfuric acid distils. Mercuric chloride volatilizes in part far below its boiling point, collecting at first in the upper parts of the flask. As the temperature rises the mercuric chloride passes over rapidly, and eventually most of it is washed into reservoir K by the sulfuric acid which distils. When 5–6 cc. of acid has collected in K, the heating is stopped, the stream of hydrogen chloride is checked, and the apparatus separated at I, the receiving unit being kept assembled.

For compounds which decompose normally the operations just described can be completed in less than thirty minutes. There should be no odor of hydrogen chloride, as the generator sketched permits good control of the gas stream, and as absorption of hydrogen chloride in M is complete.

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[11] If the substance is too actively attacked by the oxidizing mixture to permit addition of all the persulfate at one time, the sample is treated with **5** cc. of fuming acid and **10** cc. of concd. sulfuric acid, and persulfate is added in small portions while cooling the (open) flask. The ground surface is then rinsed with 5 cc. of concd. sulfuric acid, and the analysis continued as described above.

2. Determination of Mercury in Absence of Iodine. (a) Precipitation of Zinc Mercuric Thiocyanate.—The acid in K is allowed to enter M by drops, regulated by the stopcock, the flask being rotated and cooled during the addition. The parts JKL are washed out partially with water (about 10 cc.) introduced at I. Tube p is thrust to the bottom of the flask, a rubber tube is attached to the outlet of the trap, and the acid liquid is forced up into JKL by gentle blowing, and is then allowed to recede. This is repeated several times, to dissolve any lumps of mercuric salt adhering to the glass. The flask M is disconnected and the associated parts washed with numerous small portions of water. If the foregoing operations have been completed properly, the volume at this point will be about 60 cc., and should not exceed 80 cc

To oxidize sulfur dioxide, fresh bromine water is added (or, if the volume already approaches the stated maximum, vapors from the mouth of a bromine bottle are "poured" into the flask) until a yellow color persists. The solution is neutralized with pure sodium hydroxide, added as a saturated solution and with cooling until the yellow color disappears. The liquid is then barely acidified with hydrochloric acid (yellow color), and an excess of 5 cc. of 6 N hydrochloric acid is added.[12]

To the cold solution, whose volume should not exceed 100 cc., there is added 25 cc of the stronger Jamieson reagent (a filtered solution containing 73 g. of $ZnSO_4 \cdot 7H_2O$ and 125 g. of KSCN per liter), the liquid is mixed and allowed to stand for thirty minutes or longer. The precipitate is filtered with gentle suction on a 9-cm. paper supported by a filter cone. The flask is rinsed with wash liquid (2 cc. of the stronger Jamieson reagent in 450 cc. of water), and precipitate and filter paper are washed five or six times with the same liquid.

(b) Titration.—The filter paper and precipitate are put into a 250-cc. glass-stoppered Erlenmeyer flask, treated with 45 cc. of cold hydrochloric acid (1 volume of water and 3.5 volumes of concd. acid) and 6–7 cc. of chloroform, and titration with standard potassium iodate solution (about 25 g. per liter, standardized as suggested below) is begun at once, with continual rotation of the flask. After the color has become pale, titration is continued cautiously, with shaking of the stoppered flask after each addition, until the last tint in the chloroform is just discharged. The end-point is very sharp.

Standardization of Iodate Solution.—If pure iodate is used the solution will have almost exactly the theoretical mercury equivalent ($Hg \approx 6KIO_3$). It seems better, however, to standardize the solution against pure mercury or mercuric salt by the Jamieson procedure. For this purpose the mercuric solution is acidified with 5 cc. of 6 N hydrochloric acid, diluted to 50 cc., precipitated with 25 cc. of Jamieson's reagent (the weaker reagent, see paragraph 3), and the filtration and titration conducted as outlined above.

Accuracy tests of the distillation procedure applied to pure mercuric chloride arc summarized in Table I.

TABLE I

ACCURACY TESTS OF DISTILLATION PROCEDURE USING PURE MERCURIC CHLORIDE[a]

$HgCl_2$ taken, g.	Hg taken, g.	Hg found, g.	Error, g.
0.1479	0.1092	0.1094	+0.0002
.1249	.0922	.0920	− .0002
.1363	.1006	.1006	.0000
.0997	.0736	.0736	.0000

[a] No organic material was present, and no persulfate was used; otherwise the procedure described was employed.

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[12] The small excess of free bromine is later reduced by the thiocyanate.

Results for organic mercury compounds are given in Table III. An analysis can be completed in less than two hours.

3. Determination of Mercury in the Presence of Iodine.—Most of the iodine volatilizes before mercuric chloride does so in quantity. The formation of mercuric iodide in the receivers makes it necessary to wash them out with potassium iodide solution. The mercury then cannot be precipitated by Jamieson's reagent. It is therefore first separated as metal by addition of zinc dust, excess of zinc dissolved in dilute hydrochloric acid, mercury and residual zinc dissolved in nitric acid, and mercury precipitated by Jamieson's original method. The procedure is as follows.

After the distillation, reservoir K is emptied into M, 10 cc. of 10% potassium iodide solution introduced at I, and liquid from M forced up into JKL and held there until all mercuric iodide has dissolved. These parts and the trap are washed with water as described in 2(a). The volume of the liquid should be about 75 cc.

To oxidize sulfur dioxide a strong solution of iodine in potassium iodide is added until the color persists. One gram of zinc dust is suspended in a little water and added in small portions to the solution. The flask is covered, and when evolution of hydrogen moderates (five to ten minutes) the amalgam, excess zinc, and a small brown precipitate (apparently mercuric sulfide) are filtered with suction on a glass filtering crucible (30 cc.), and washed well with water. The crucible is placed upright in a 150-cc. beaker, and 25 cc. of 6 N hydrochloric acid added (about 5 cc. in the beaker and 20 cc. in the filtering crucible). The beaker is covered and the acid warmed (not boiled) until the amalgam is reduced to a small mass, stiff in consistency and mossy in appearance. If this treatment is continued until the amalgam becomes liquid, and especially if the acid is boiled, there is danger of loss of mercury. The filtering crucible is replaced in its holder, the acid drawn through, and filter and amalgam washed well with water. The lump of amalgam is dropped into flask M, and the filtering crucible is replaced in its holder, with flask M beneath as receiver. The crucible is treated with several cc. of strong bromine water (no suction), and then with about 2 cc. of hot concd. nitric acid. This treatment dissolves any particles of amalgam and also the small dark precipitate. After a minute the liquid is drawn through the filter, which is treated with several successive portions of hot concd. nitric acid, using in all about 5 cc. of nitric acid. The filter is finally washed with two small portions (1–2 cc.) of water. The flask is warmed until the amalgam dissolves, the solution diluted to about 25 cc. and cooled. Bromine water is added until the color persists.

The liquid is neutralized with strong sodium hydroxide solution, and acidified with 2 cc. of 6 N hydrochloric acid; an acidity much higher than this may lead to interaction of nitric acid and thiocyanate during the precipitation. The solution is cooled, diluted to 50 cc., and mercury precipitated by addition of 25 cc. of Jamieson's reagent (29 g.

TABLE II

ACCURACY TESTS OF SEPARATION OF MERCURY FROM STRONGLY ACID SOLUTION BY ZINC DUST[a]

Hg taken, g.	KI present, g.	Hg found, g.	Error, g.
0.1042	None	0.1041	−0.0001
.1042	None	.1045	+ .0003
.1042	2	.1046	+ .0004
.0521	2	.0517	− .0004
.0521	2	.0518	− .0003
.1033	2	.1032	− .0001

[a] The mercury solutions contained 10 cc. of concd. hydrochloric acid and 5 cc. of concd. sulfuric acid, but no sulfur dioxide; otherwise the procedure was that described.

of $ZnSO_4 \cdot 7H_2O$ and 50 g. of KSCN per liter, obtained by diluting two volumes of the stronger reagent with three volumes of water). The liquid becomes deep red due to iron from the zinc. After an hour or more the precipitate (yellow-tinted when obtained by this procedure) is filtered, washed and titrated as outlined in 2(a) and (b).

Accuracy tests of the zinc separation of mercury are summarized in Table II.

Results for determination of mercury in presence of iodine are given in Table III

TABLE III

DETERMINATION OF MERCURY IN ORGANIC COMPOUNDS

	Distillation method		Comparison method
Compound	**Sample, g.**	**Mercury, %**	**Mercury, %**
Diacetatomercuriphenol	0.1508	66 36	
	.1537	66.40	66.43
	.1522	66.36	66.29
	.16045	66.41	
	.14895	66.30	
		Av. 66.37	**Av.** 66.36
Mercury *p*-ditolyl	0.19945	51.74	
	.1984	51.76	51.92
	.19335	51.98	51.85
	.2004	51.73[a]	
	.1998	51.87[a]	
		Av. 51.82	**Av.** 51.89
n-Butyl mercury mercaptide	0.2000	61.14	Contained $HgCl_2$:
	.2206	61.06	not analyzable
		Av. 61.10	
Mercurated fluorescein Na-salt	0.3048	31.23	30.63
	.3045	31.19	30.66
		Av. 31.21	**Av.** 30.65
p-Aminophenylmercuriacetate	0.2009	59.78	60.05
	.2055	59.84	60.06
		Av. 59.81	**Av.** 60.06
Mercuric cyanide	0.1534	79.34	79.44
			79.35
			Av. 79.39
Mercurated *p*-nitrotoluene (mostly HgO)	0.1311	89.66	89.32
	.1363	89.74	89.49
		Av. 89.70	**Av.** 89.41
Dibromo-hydroxymercurifluorescein	0.3576	27 89	
	.3543	27 71	27.87[b]
	.3599	27.71	27.66[b]
		Av. 37.77	**Av.** 27.77
Diacetatomercuriphenol with 0.1 g. *diiodofluorescein* added in trials by distillation method	0.1505	66.35	
	.1421	66.41	
	.1454	66.35[c]	
	.1448	66.54[c]	
		Av. 66.41	(66.36)

[a] These two analyses run in ninety-three minutes each. [b] Mercury determined as sulfide following hot decomposition by White's method. [c] These two analyses together were completed in six hours elapsed time, with eighty-minute precipitation intervals.

4. Analytical Results for Some Organic Mercury Compounds.—Results by the new method, in comparison with those obtained by the comparison method, are shown in Table III.

Comments.—The use of potassium dichromate for the oxidation gave satisfactory decompositions, but it was found impossible to distil out all the mercury as chloride, retention by anhydrous chromic sulfate seeming to occur. The use of persulfate and concd. sulfuric acid for decomposition of organic samples was apparently new at the time this work was first described (1929), though several chemists had earlier used persulfate with water or dilute sulfuric acid.[13] Recently Thompson and Oakdale[14] applied persulfate and fuming sulfuric acid in the determination of halogens in organic compounds by a modification of the Baubigny–Chavanne–Robertson method.

In presence of iodine, the preliminary displacement of mercury from the distillate liquid requires zinc dust. Qualitative trials showed that 1 g. of finely granular zinc was ineffective, whereas half as much zinc dust added as a suspension removed mercury completely in a few minutes.

The principal impurities in the zinc dust were iron (0.03%) and lead (0.1%). As these metals are concentrated in the zinc amalgam during the hydrochloric acid treatment, their effects upon results by Jamieson's method were studied. Iron yielded of course a strongly colored solution, and the precipitate was tinted, but the effect of even ten times the iron present in 1 g. of zinc dust was nil. In the presence of lead the precipitate was yellow-tinted, as it was in analyses following separation of mercury by zinc, and a positive error rather regularly entered the results. No relationship could be established between the quantity of lead and the magnitude of the error, although the color of the precipitate deepened as the quantity of lead was increased. .These results, however, indicate the advisability of using zinc dust as free as possible of impurities.

The trap N is probably not essential, no evidence of presence of mercury in it having been obtained.

Acknowledgment is made to Dr. H. S. Lukens and to Dr. W. M. McNabb for helpful suggestions.

Summary

In the method described for determination of mercury in organic compounds the sample is decomposed by persulfate and concentrated sulfuric acid, mercury is distilled out as chloride by heating in a stream of hydrogen chloride, and is precipitated as zinc mercuric thiocyanate and determined by iodate titration. In presence of iodine, mercury in the distillate liquid is

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[13] Newbery, J. *Chem. Soc.*, 127, 1751 (1925); Duret, *Compt. rend.*, 167, 129 (1918); Rupp and Lehmann, *Arch. Pharm.*, 251, 1 (1913); *Chem. Abstracts*, 7, 1151 (1913); H. Meyer, "Analyse," Springer, Berlin, 1922, 4th ed., p. 313.

[14] Thompson and Oakdale, THIS JOURNAL, 52, 1195 (1930).

first precipitated by zinc dust, excess zinc dissolved in hydrochloric acid, the residual amalgam dissolved, and mercury determined by the iodate method.

Trials of the procedure with a variety of compounds and in presence of halogens and of sulfur showed it to be apparently of general applicability. The method has the advantage that in presence of halogens it eliminates the danger (which otherwise attends decompositions by acid agents) of loss of mercury by volatilization.

Presence of iodine prolongs the analysis, but in its absence the method is at least as rapid as others of comparable accuracy and applicability.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF BRITISH COLUMBIA]

STUDIES IN THE RARE EARTHS. I. THE PREPARATION OF THE BROMATES OF CERIUM GROUP RARE EARTHS

BY J. ALLEN HARRIS[1]

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Historical

The method of separating the rare earth elements that proved successful in permitting of the concentration of illinium was a fractional crystallization of samarium rich fractions obtained from a double magnesium nitrate series of rare earths, as the bromates, the cerium, lanthanum and praseodymium having been removed completely prior to the conversion to the double magnesium nitrate. This latter crystallization permitted of the separation of the bulk of the neodymium from the remaining elements but experience seems to prove that in such a series the illinium concentrates with the neodymium, rendering its detection difficult, the order of solubility of these salts being such that we have an increase with increasing atomic weight.[2]

From such a study, then, it would appear to be most advantageous to submit the original material to a preliminary, rather than to a subsequent crystallization as the bromates. The serial order of solubilities would then become, erbium, lanthanum, yttrium, holmium, praseodymium, dysprosium, neodymium, terbium, illinium, gadolinium, samarium, and europium (least soluble), thus permitting of a more efficient separation of the illinium and neodymium.[2,3]

Introduction

The standard method of preparing the bromate is that of James, and was used extensively by him in his classical work on the yttrium group earths.

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[1] National Research Fellow.

[2] Harris with Hopkins, THIS JOURNAL, 48, 1585 (1926).

[3] James, *ibid.*, 48, 2871 (1926).

The dried earth oxalates are mixed to the consistency of a thin paste with concentrated sulfuric acid, warmed to expel excess of acid, and finally heated strongly to convert to the anhydrous sulfates. These, on cooling, are pulverized and sifted, with constant stirring, into ice water; care being necessary to prevent the formation of a basic salt. This solution is then added a little at a time to a saturated solution of freshly precipitated barium bromate in a large steam heated evaporating dish equipped with a mechanical stirrer, care being taken to ensure the presence of excess barium in the solution. On final addition of the sulfate, the precipitated barium sulfate is removed by filtration and the solution of rare earth bromates crystallized by evaporation.

This method, while extremely annoying, in that it involves the evolution of copious fumes of oxides of sulfur over a considerable period, due to the decomposition of the acid by the oxalate radical, yields anhydrous sulfates of the yttrium group earths, even when considerable amounts of neodymium are present, which dissolve to a neutral solution, fairly readily when added slowly to large volumes of ice water.

It has been the experience of the writer, however, that when all of the members of the cerium group earths (with the exception of cerium) are present, together with certain of the yttrium group earths, it is almost impossible to remove the last traces of acid from the more basic members, without decomposing the sulfates of the less basic earths. If decomposition takes place, these basic salts will not dissolve. On the other hand, if any trace of acid is permitted to remain, although ready solution is effected, total decomposition of the bromates during final concentration of the solution invariably results.

At the suggestion of Professor Georges Urbain, of the Sorbonne, the following method was developed, and has been used extensively by the writer with excellent results, affording sulfates of the cerium group earths that are readily soluble in water, even at room temperature, yielding solutions that are neutral although considerable amounts of lanthanum be present.

Procedure

The dried earth oxalates are ignited to the oxides, weighed and the amount of sulfuric acid necessary for their conversion to the sulfates calculated, measured out and diluted considerably. After thorough moistening of the oxides with water to permit of ready penetration by the acid, the acid is added very slowly in small portions, the liquor being allowed to reach neutrality before subsequent addition. When the point is reached at which the solution shows little or no tendency to become neutral, the mixture is transferred to a hot-plate, and warmed until neutralization is again effected. The process of addition is continued until all of the acid has been added.

If upon final addition the liquor again attains neutrality, a little more dilute acid is added, so that a feebly acidic solution is maintained over the sulfate residue. The mixture is then allowed to evaporate slowly on the hot-plate and when thoroughly dry the sulfates may be removed, pulverized and then heated strongly to remove any excess acid. The evolution of fumes is thus reduced to a minimum, and when the anhydrous sulfates are obtained, as evidenced by cessation of evolution of the oxides of sulfur, they are quickly transferred to a dry and previously weighed container, roughly weighed, and transferred while still hot to a bell jar which is immediately evacuated.

From the weight of the sulfates, the amount of water necessary for their solution is calculated and measured into a large conical precipitation flask. When cool, the sulfates are taken in small portions from the bell jar and sprinkled with vigorous stirring into the water, where they dissolve very readily. In this manner it is possible to obtain a concentrated solution of the sulfates, containing no basic salts, which is neutral to litmus. The solution may now be transferred to an evaporating dish and gently evaporated until crystals begin to form at the edges of the container.

If the barium bromate solution is prepared in advance, so as to contain quantities of salt sufficient to precipitate the sulfate ion, the conversion to the bromates may be effected in the minimum of time and with small volumes of solution.

In conclusion the writer wishes to express his appreciation to the International Education Board and the National Research Council for furnishing funds to permit of the writer's working with Professor Urbain, to whom the writer is also deeply grateful.

Summary

Difficulty is experienced when attempting to prepare a neutral solution of cerium group rare earth sulfates, by igniting the oxalates with sulfuric acid, and dissolving the residue in ice water.

A method is outlined for the preparation of concentrated neutral solutions of these sulfates, by the conversion of the oxides to the sulfates and dissolving in water at room temperatures.

This method eliminates waste of sulfuric acid, annoying prolonged evolution of fumes, the use of ice water, loss of time required in conversion to the bromate and subsequent evaporation of large volumes of solution.

VANCOUVER, CANADA

[CONTRIBUTION FROM THE INSTITUTE OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF COPENHAGEN]

A KINETIC STUDY OF SOME REACTIONS OF DIAZOACETIC ESTER IN BENZENE SOLUTION

BY J. N. BRÖNSTED AND R. P. BELL

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1. Introduction

In the extended theory of acid and basic catalysis[1] the effect of acids in accelerating chemical reactions is looked upon as due to a direct interaction between the molecules reacting and the molecule of the catalyzing acid. In a basic medium like water the catalysis produced by the addition of an acid A may be a compound effect of both A and the hydrogen ion "formed by dissociation." In non-basic media where no protolytic[2] reaction with acids is possible, acid catalysis ought to be of a simpler character.

With the purpose of broadening the foundation of the extended theory we have in the present investigations studied several reactions of diazoacetic ester in benzene solutions. The reaction of this substance with water in the presence of acids according to the equation

$$CHN_2COOC_2H_5 + H_2O \longrightarrow CH_2OHCOOC_2H_5 + N_2 \qquad (1)$$

has long been known as an example of hydrogen-ion catalysis, and kinetic measurements of this reaction have been extensively used as a method for determining hydrogen-ion concentration in aqueous solutions. Provided that the solutions are so dilute that salt effects can be neglected, the velocity of reaction (1) is directly proportional to the concentration of "hydrogen ion," which in aqueous solutions is actually H_3O^+. It has been shown[3] that the reaction has a large linear salt effect. Similarly, when various alcohols are used as solvents, the velocity of the reaction

$$CHN_2COOC_2H_5 + ROH \longrightarrow CH_2ORCOOC_2H_5 + N_2 \qquad (2)$$

is determined by the concentration of the solvated hydrion, though in these media, where the dielectric constant is much less than that of water, primary salt effects are much higher, and are of importance even at low concentrations.'

In the presence of some acids, *e. g.*, the halogen acids and nitric acid, a side reaction takes place.[4]

$$CHN_2COOC_2H_5 + HX \longrightarrow CH_2XCOOC_2H_5 + N_2 \qquad (3)$$

The velocity of this reaction is in aqueous solution proportional to the concentrations of both the hydrogen ion and the anion of the acid. Ex-

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Bronsted, "Acid and Basic Catalysis," p. 250.

[2] Bronsted, *Z. angew. Chem.*, 43, 229 (1930).

[3] Brönsted and Duus, *Z. physik. Chem.*, 117, 299 (1925).

[4] Rredig and Ripley, *Ber.*, 40, 4015 (1907).

amination of the data of Bredig and Ripley[4] and those of Lachs[6] shows that the salt effect is in this case "exponential" in type, as would be expected for a reaction involving two charged molecules[6] and that also numerically there is a fair agreement with the theoretical formula for such a reaction.

Thus in water and the alcohols it appears that acid catalysis in the general sense[7] is at the most very small compared with catalysis by the solvated hydrion. Hantzsch[8] has found an increase of catalytic activity with increasing concentration for the halogen acids in aqueous solution, which he attributes to catalysis by the undissociated molecules. However, in drawing this conclusion, no account has been taken of the fact that the change of acid concentration causes a very considerable change of medium. In fact, if the primary salt effect found at low concentrations[3] is assumed to be linear up to the high acid concentrations used by Hantzsch, it is sufficient to account approximately for the increase of catalytic power observed. Furthermore, the reaction of diazoacetic ester with the halogen acids is complex (see equations (1) and **(3)** above) and the hypothesis of Hantzsch, that the initial stage in the reaction with acid determining the velocity of the reaction is the same in each case, is a pure assumption. Snethlage[9] considers that his results in ethyl alcohol solution show catalysis by the undissociated picric acid molecule, but this view has been shown to be inconclusive owing to the presence of an unknown, but probably large, secondary salt effect.[1]

In aprotic solvents, unable to solvate the free hydrogen ion, acids will not be ionized, and any phenomena of acid catalysis observed must be attributed to acid molecules in general. It is in fact well known that many organic reactions are powerfully catalyzed by solutions of acids in "inert" solvents.[10] The rearrangement of diazoamino compounds in basic solvents, which has been studied extensively by Goldschmidt[11] and his co-workers, probably constitutes an example of general acid catalysis, though it is possible to attribute at least a part of the catalysis to ions such as C_6H_5-NH_3^+, which in these solvents are nothing more than solvated hydrions. In the case of diazoacetic ester, there will not in general be any possibility

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[5] Lachs, Z. *physik. Chem.*, **73**, 291 (1910).

[6] Bronsted, "Acid and Basic Catalysis," Chap. IV; *Z. physik. Chem.*, 102, 169 (1922); 115, 337 (1925).

[7] Bronsted, "Acid and Basic Catalysis," Chap. VIII.

[8] Hantzsch, 2. *physik. Chem.*, 125,251 (1927); *Ber.*, 58,612 (1925).

[9] Snethlage, Z. *physik. Chem.*, 85,211 (1913).

[10] For example, see Lowry and Magson, J. *Chem. Soc.*, 93, 117 (1908); Lapworth, *ibid.*, **85**, 30 (1904); Blanksma, *Rec. trav. chim.*, 21,366 (1902); 22,290 (1903).

[11] Goldschmidt and Reinders, *Ber.*, 29, 1469, 1899 (1896); Goldschmidt, Johnsen and Overwien, *Z. physik. Chem.*, 110, 251 (1924); Goldschmidt and Overwien, *ibid.*, [A] 134,354 (1929); Goldschmidt, *Z. Elektrochem.*, 36,662 (1930).

of reaction with the solvent itself in such a case, but it is possible to study the reaction of the ester with the acid added, or with a third substance. Such a study is of interest from two main points of view: (a) the catalytic properties of acid molecules in inert solvents, and (b) the molecular state of carboxylic acids in such solvents.

The only previous work on the kinetics of reactions. with diazoacetic ester in non-dissociating solvents is that of Hantzsch[12] with a variety of acids and solvents. These investigations, however, are not of such a character as to permit of any conclusion regarding the nature or mechanism of the reaction. Hantzsch considers that the reactivity of any acid toward diazoacetic ester is a measure of its "strength," but as has been pointed out by v. Halban[13] this is not allowable, since we are considering a different chemical reaction in each case, and not the same reaction catalyzed by different acids. Even admitting Hantzsch's unproved and improbable assumption that the first step, and that which determines the velocity, is the formation of a diazonium salt, it would not justify the relation proposed between reaction velocity and acid strength in any ordinary sense of this word.

The present investigation deals exclusively with benzene solutions. The reaction of diazoacetic ester has been studied with the following acids: monochloroacetic, dichloroacetic, iodoacetic, nitroacetic, formic, α-bromopropionic, α,β-dibromopropionic and picric.

Measurements have also been made for acid mixtures, and for the rate of reaction of diazoacetic ester with phenol, catalyzed by these acids.

2. Materials

Unless otherwise stated, the products used were of "zur Analyse" grade from Merck or Kahlbaum.

Benzene was allowed to stand for periods ranging from two weeks to several months over phosphorus pentoxide, and was finally refluxed and distilled over fresh phosphorus pentoxide in an all-glass apparatus. It was stored in a container protected by mercury seals and phosphorus pentoxide tubes, and when making up a solution only dried air came in contact with the solution and the stock of benzene. All solutions when made were kept in a desiccator.

Monochloroacetic acid was recrystallized from pure benzene, and dried in vacuo over sulfuric acid.

Dichloroacetic acid was redistilled, and the fraction boiling at 191–192.5° was used.

α,β-Dibromopropionic acid was recrystallized from ligroin, and dried in vacuo over sulfuric acid.

α-Bromopropionic acid was purified by partial freezing, and dried in vacuo over sulfuric acid.

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[12] Hantzsch, Z. *Elektrochem.*. 24, 201 (1918); 29, 221 (1923); *30,* 194 (1926); *Z. physik. Chem.*, 125,251 (1927).

[13] V. Halban, Z. *Elektrochem.*, 29,434 (1923).

Iodoacetic acid was prepared by the method of Abderhalden and Guggenheim.[14] It was recrystallized from a mixture of one volume of benzene and six volumes of ligroin, and dried in vacuo over sulfuric acid, The acid and its solutions were kept in the dark.

Nitroacetic acid was prepared according to the directions given by Steinkopf[15] and Pedersen.[16] It was recrystallized from chloroform. Only freshly made samples were used.

Formic and picric acids were used without further purification.

Phenol was dried in vacuo over sulfuric acid and kept in the dark.

A test of the purity of the acids was afforded by titration of the stock solutions, which were prepared from weighed amounts of acid. The figures thus obtained corresponded to a purity of 99% or better.

Diazoacetic ester was prepared from a 20% alcoholic solution. The alcohol was removed by standing in a vacuum desiccator over sulfuric acid until the weight had fallen to 5% of its original value. The purity of the product thus obtained was tested by measuring the volume of nitrogen evolved when a weighed amount of the ester reacted in a $N/20$ aqueous solution of perchloric acid. The values obtained for various samples ranged between *97.8* and *99.1%* purity. A further check on the purity, which also served as a test of the simple nature of the reaction between diazoacetic ester and monochloroacetic acid, was as follows. A weighed amount of ester was allowed to react with a known excess of monochloroacetic acid in benzene at room temperature. After standing for some weeks (it being known from kinetic measurements that this period corresponded to practically complete reaction), the solution was poured into water and the residual monochloroacetic acid immediately titrated with alkali. The values obtained for the amount of acid which had reacted were 95–98% of the values calculated from the weight of ester taken.

The ester was not kept as such, but was immediately dissolved in **pure** benzene to give a stock solution about $N/10$ volume normally. These solutions were perfectly stable over long periods, as was shown by the fact that the volume of nitrogen obtained **from** a given amount of solution remained appreciably constant for at least several months.

3. Measurements

The reactions were followed by measuring the pressure of the nitrogen evolved in a closed system. The apparatus used is shown in Fig. 1. The reacting solution (volume 20 cc.) was contained in the flask **A** (volume 40 cc.) which was in a thermostat at 15 ± 0.01°. The flask was shaken to and fro mechanically with an amplitude of about 2 cm., and the rate of shaking was maintained constant by a centrifugal regulator. It was connected by the flexible glass tubing B to the mercury manometer C. The reaction flask was closed by an unlubricated ground cap D, sealed with mercury, and the vacuum side of the manometer by a mercury seal E. At F was a porous plug of gypsum, as described by Prytz.[17] The tube G served to introduce mercury into the manometer, and was afterward sealed off.

The method of carrying out an experiment was as follows. The required

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[14] Abderhalden and Guggenheim, ***Ber.*, *41*, 2853 (1908).**

[15] Steinkopf, *ibid.*, ***42*,3925 (1909).**

[16] Pedersen, ***Trans. Faraday Soc.*, *23*,316 (1927).**

[17] Prytz, ***Det. kgl. danske Videnskab. Selskab. Forh.*, 293 (1904).**

acid solution was introduced into A by means of pipets protected by calcium chloride tubes, standard solutions of known strength being employed. The diazoacetic ester solution was introduced by a small pipet, D immediately closed, the shaking started, and the apparatus evacuated through H for two to four minutes with a good water suction pump, the taps J and K being open. (On account of the high vapor pressure of benzene, the use of a better pump is unnecessary at this stage.) J and K were then closed and the mercury caused to rise in the manometer by introducing a little air through F. This was effected by pushing a small plug of cotton wool (which contains sufficient air entangled) through the mercury above F, and pressing it upon the upper surface of the gypsum. J and K were then opened, and the right-hand side of the manometer evacuated with a Cenco Hyvac oil-pump. Finally, J was closed and mercury allowed to rise in the seal E by admitting a little air through K.

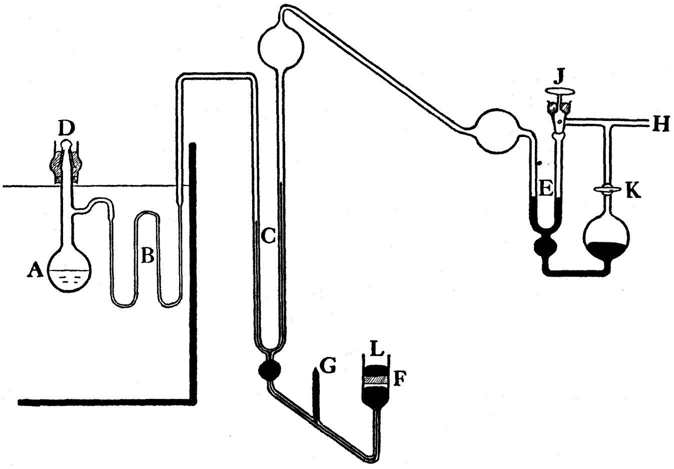

Fig. 1.

The apparatuses were mounted in pairs on a common shaking mechanism. The pressure was measured at intervals by reading the heights in the two manometer limbs, correct to 0.01 cm., using small lenses. The total pressure change for the reaction of 0.0002 gram molecule of ester was about 48 mm. of mercury.

The chief possibility of a systematic error in the results lies in the presence of dissolved gases in the benzene solutions which are probably not completely removed by the short period of evacuation employed. This probably accounts for an occasional irregularity observed in the first few readings, but a steady state appeared to be rapidly reached. A longer period of evacuation is inadvisable, owing to the possibility of appreciable alteration in the concentration of the solutions by the evaporation of benzene. The mutual concordance of the results obtained with periods of evacuation varying from two to four minutes shows that no appreciable error from this source is present. Since the vapor pressure of benzene at 15° changes by about 3 mm. for 1° temperature change, temperature fluctuations of more than 0.03° will affect the manometer reading. A control of ±0.01° is therefore adequate.

4. Calculation of Velocity Constants

All concentrations are expressed as gram formula weights per liter of solution at 15°. The concentration of ester present in most experiments was 0.0075-0.011 N. In a few experiments with acid concentrations less than 0.1 N, the ester concentration was about 0.005 N, and in the experiments with the two most dilute solutions of dichloroacetic acid, about 0.0025 N. Thus the ester concentration was in no case more than 8% of that of the other reactant, and in most cases considerably less, so that the course of an experiment may be expected to follow fairly closely the monomolecular law. This was in fact found to be the case, and all velocity constants given have been calculated by the method of Guggenheim.[18] In three experiments with monochloroacetic acid, an end-point was measured experimentally and used to calculate the constants in the usual manner. The same values were obtained as by Guggenheim's method. The number of readings taken in one experiment was 40–60. In calculating the constant decadic logarithms were used, *i. e.*, the constants given in the tables are

$$k_1 = \frac{d \log_{10} c}{dt}$$

the unit of time being the minute.

5. Results for Carboxylic Acids

The acids which were studied over a large range of concentrations were monochloroacetic, dichloroacetic, α,β-dibromopropionic and α-bromopropionic. Most experiments employed benzene purified as described above, but a few, marked *, were made with Merck's benzene "zur Analyse," which had not been further treated. No difference was detectable between the two sets of results.

Since the concentration of acid never changed by more than 8% during the course of the experiment, and usually by much less, we have taken the monomolecular velocity constant (k_1) to refer to the mean of the initial and final concentrations of acid (c).

It is at once obvious from the figures that in no case is the reaction velocity even approximately proportional to the concentration of acid. As may be seen from Figs. 2 and 3, the velocity in the range of concentrations considered is more nearly proportional to the square of the concentra-

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[18] Guggenheim, *Phil. Mag.*, [2]7, 538 (1926).

TABLE I

MONOCHLOROACETIC ACID

c	$k_1 \times 10^4$	$\sqrt{k_1} \times 10^2$	$k_1/c \times 10^4$
0.0573	0.618	0.79	10.8
.0765	0.902	0.95	11.8
.0906	1.38	1.18	15.2
.0909*	1.68	1.30	18.5
.122*	2.46	1.57	19.0
.123*	2.43	1.56	19.8
.129	2.67	1.64	20.6
.156	3.86	1.97	23.2
.167*	4.17	2.04	25.0
.167	4.50	2.12	27.0
.243*	8.04	2.84	33.3
.249*	7.94	2.82	31.9
.253	8.80	2.97	34.8
.281	11.5	3.40	40.8
.312*	12.0	3.48	38.6
.314*	12.4	3.52	39.6
.338	16.6	4.08	48.1
.366*	17.0	4.14	46.5
.413*	21.0	4.59	51.0
.424	22.5	4.75	53.1
.491*	33.1	5.77	67.4
.510	33.8	5.82	66.5
.638	44.8	6.70	70.0

DICHLOROACETIC ACID

c	$k_1 \times 10^2$	$\sqrt{k_1} \times 10^2$	$k_1/c \times 10^2$
0.0248	0.328	0.574	13.2
.0313	0.630	0.795	20.1
.0406	0.922	0.961	22.7
.0424*	0.902	0.951	21.3
.0504	1.37	1.17	27.1
.0625*	1.70	1.30	27.2
.0681	1.98	1.42	29.1
.0810*	2.69	1.64	33.2
.0901	3.59	1.89	39.9
.0980	3.84	1.97	39.3
.106	4.66	2.16	44.0
.114	5.56	2.36	48.7

α,β-DIBROMOPROPIONIC ACID

c	$k_1 \times 10^4$	$\sqrt{k_1} \times 10^2$	$k_1/c \times 10^3$
0.0286	0.940	0.971	3.28
.0566	2.79	1.67	4.93
.0910	6.08	2.41	6.68
.113*	7.70	2.78	6.83
.141	11.8	3.44	8.38
.204	18.9	4.35	9.29
.295	32.9	5.67	11.1
.397	50.9	7.14	12.8
.489	70.2	8.39	14.4

α-BROMOPROPIONIC ACID

c	$k_1 \times 10^5$	$\sqrt{k_1} \times 10^2$	$k_1/c \times 10^4$
0.0934	3.01	0.549	3.23
.121	4.46	0.669	3.70
.248	14.2	1.19	5.70
.326	22.1	1.49	6.78
.393	30.7	1.75	7.81
.502	48.2	2.19	9.78

tion, and we have found that the results are expressed within the experimental error by equations of the form

$$k_1 = \alpha c^2 + \beta c \qquad (4)$$

where a and β are constants for each acid. The only exceptions to this relation are the results for the two most dilute solutions of dibromopropionic acid, which do not agree with the equation representing the remainder of the results for this acid. The values of a and @ in equation (4) were determined by plotting k_1/c against c and measuring the slope and intercept of the straight line thus obtained. The values are as given in Table II.

It has previously been found by Nernst and Hohmann[19] that the re-

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[19] Nernst and Hohmann, *Z. physik. Chem.*, 11,361 (1893).

TABLE II

EXPERIMENTAL DATA

	α	β
Monochloroacetic	1.20 × 10^{-2}	4.5 × 10^{-4}
α,β-Dibromopropionic	2 35 × 10^{-2}	5 2 × 10^{-3}
α-Bromopropionic	1.58 × 10^{-3}	1.75 × 10^{-4}
Dichloroacetic	3 34	8 4 × 10^{-2}

action velocity of amylene with various carboxylic acids in both amylene and benzene solutions is also proportional to the square of the acid concentration. They explain this relation by assuming that the velocity is proportional to the concentration of double molecules, which are in equilibrium with a much greater concentration of single molecules. It is doubtful whether this view is correct for amylene solutions and it is certainly untenable both for the benzene solutions employed by Nernst and Hohmann, and for those studied in the present work, since cryoscopic molecular weight determinations show the acids to be present almost entirely as double molecules at the concentrations concerned.[20] We must therefore conclude that the reaction with diazoacetic ester (and probably also with amylene) is kinetically of the second order with respect to the double molecules, which may thus be said to catalyze their own reaction. This conception is further supported by the results given later for the reaction of mixtures of acids.

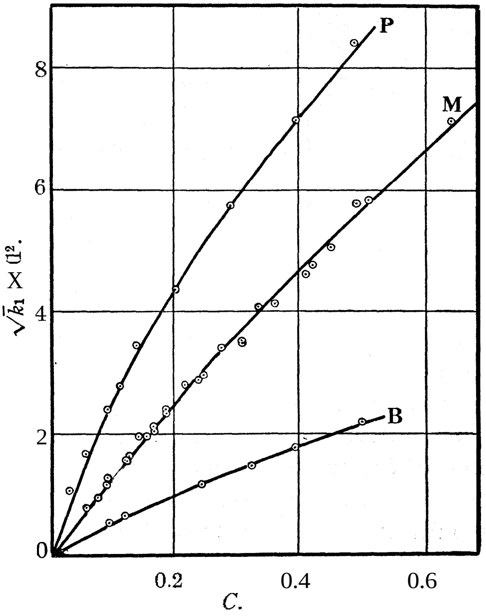

Fig. 2.—B, α-bromopropionic acid; M, monochloroacetic acid; P, α,β-dibromopropionic acid.

Goldschmidt has previously found[21] that the reaction of carboxylic acids with aniline to give anilides in aniline solution is of the second order with respect to the acid, and has termed these reactions "autocatalytic." In the case of aniline as a solvent the state of affairs may be more complex than in benzene solutions, owing to the formation of the anilinium ion,

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[20] See, *e.* g., Tollens, *Ber.*, 48, 489 (1915); Celincev and Kozlov, *J. Russ. Phys.-Chem. Soc.* [Sect. chim], **46,** 718 (1916); Walden, *Bl. Acad. Petrograd.*, *6,* Ser. *8,* 1161 (1914); Rabinowitsch, *Z. physik. Chem.*, **132,** 83 (1928)

[21] Goldschmidt and Wachs, *ibid.*, 24, **353** (1898); Goldschmidt and Brauer, *Ber.*, 39, **97** (1906).

which may have catalytic properties. The same applies to the self-esterification of di- and trichloroacetic acids in alcohol solution, which has also been found by Goldschmidt[22] to be a second order reaction, though in this case it seems probable that the catalytic agent is the acid molecule itself, since the addition of di- and trichloroacetates causes but little diminution in catalytic power.

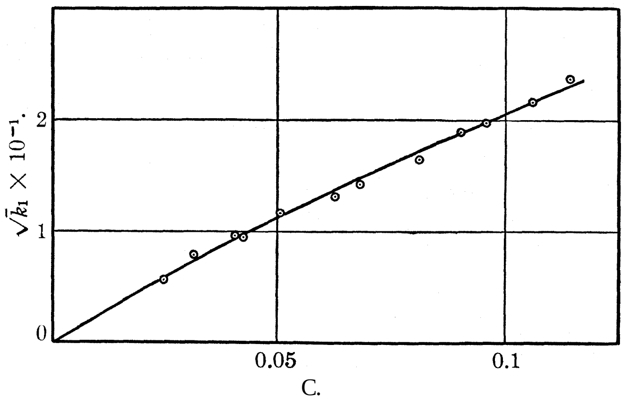

Fig. 3.—Dichloroacetic acid.

If the partial conversion of double molecules into single molecules leads to an increase in reaction velocity, we have a qualitative explanation of the form of equation (4), though it is impossible at present to give a fully quantitative interpretation. In the presence of two species of acid molecules there are theoretically four possible catalytic reactions, two of which are practically indistinguishable. On this basis of classical kinetics we should expect the total velocity to be given by an equation of the type

$$k_1 = a_1[(\mathrm{HA})_2]^2 + a_2[\mathrm{HA}]^2 + a_3[\mathrm{HA}][(\mathrm{HA})_2] \qquad (5)$$

where a_1, a_2 and a_3 are constants. For small concentrations of such molecules and values of a_1, % and a_3 of the same order of magnitude the member containing a_2 would tend to vanish. The experimental accuracy is however not sufficient to make the equation thus appearing distinguishable from equation (4). It is possible that the lack of agreement with equation (4) shown by the two most dilute solutions of α,β-dibromopropionic acid is due to the fact that a considerable fraction of the acid is present as single molecules. (Cryoscopic measurements show[20] that this acid is much less completely associated than monochloroacetic acid at the same concentrations.)

If the equilibrium between double and single molecules can be expressed by the simple mass law equation

$$\frac{[\mathrm{HA}]^2}{[(\mathrm{HA})_2]} = K \qquad (6)$$

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[22] Goldschmidt, *Ber.*, 29, 2212 (1896); *Z. Elektrochem.*, 15, 4 (1909); *cf.* also Michael and Wolgast, *Ber.*, 42, 3161 (1909); Kailan, *Monatsh.*, 29, 805 (1908).

we have for nearly complete association

$$[\mathrm{HA}] = \sqrt{\frac{Kc}{2}} \qquad [(\mathrm{HA})_2] = \frac{c}{2}$$

and equation (6) becomes

$$k_1 = \frac{a_1}{4}c^2 + \frac{a_2}{2}Kc + \frac{a_3}{2}\sqrt{\frac{K}{2}}\,c^{3/2} \tag{7}$$

What evidence there is, however, goes to show that equation (6) does not hold for carboxylic acids in inert solvents: in other words that the mass action law is not strictly applicable for such solutions. Previous attempts to calculate an association "constant" have not been successful[23] and calculations on the basis of the cryoscopic data of Peterson and Rodebush[24] for very dilute benzene solutions of acetic acid give no constant value for K in equation (7). The results of partition experiments are often quoted as evidence for a simple mass law equilibrium between single and double molecules but it has been found by Szyszkowski[25] that the presence of hydrated molecules invalidates the usual treatment of these results, and it has been recently shown[26] that Szyszkowski's method of correcting this treatment is based on false assumptions.

There is, however, nothing very surprising in the failure of such solutions to obey the gas laws. It seems to be the general view that such deviations are principally confined to ionic solutions, where they are caused by interionic forces. It is necessary, however, also to take into consideration the interaction of dipole fields, which in solvents of low dielectric constant are considerable and can lead to departures from simple behavior in just the same manner as interionic forces. In the case of a dipole gas, the magnitude of this effect has been evaluated quantitatively by Falkenhagen[27] and shown to agree with experiment for several gases. In benzene solution one would expect the double molecule to be more "normal" than the single molecule and thus the constant K to increase with increasing dilution. Recent work of Briegleb,[28] however, seems to show that not only the single carboxylic acid molecules, but also the double ones, have fairly large dipole moments, which introduces some uncertainty in the above conclusion.

Side by side with this departure from simple thermodynamic behavior, we must also anticipate a kinetic "dipole effect" (analogously to kinetic salt effect), so that the constants a_1, a_2 and a_3 of equation (6) are probably not strictly constant over a large range of concentrations. An example

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[23] Trautz and Moschel, Z. anorg. *Chem.*, *155*, 13 (1926); Brown and Bury, *J. Phys. Chem.*, 30,694 (1926).

[24] Peterson and Rodebush, *ibid.*, 30,094 (1926).

[25] Szyszkowski, *Z. phys. Chem.*, *131*, *180* (1927).

[26] Bell, *ibid.*, [A]150, *20* (1930).

[27] Falkenhagen, *Physik.* Z., 23, *887* (1922).

[28] Briegleh, *Z. physik. Chem.*, [B] 10, 205 (1930).

of this type of effect is afforded by the results of Bugarsky[29] on the velocity of the reaction between alcohol and bromine in inert solvents. Bugarsky interprets the abnormalities observed by assuming an equilibrium between double and single alcohol molecules governed by the mass, only the double molecules reacting with bromine. Apart from the improbability of the last assumption, cryoscopic measurements show that the activity coefficient of alcohol in inert solvents changes in a manner which cannot be explained by the simple equilibrium

$$2C_2H_5OH \rightleftharpoons (C_2H_5OH)_2$$

and it seems more reasonable to consider such solutions as containing only single molecules, which show an abnormal thermodynamic behavior owing to the strong inter-dipole forces. Bugarsky's results then appear as a consequence of the corresponding kinetic abnormality of these molecules.

These considerations of deviations from simple behavior leave unaffected the main conclusions, *i.* e., (a) that the reaction is mainly a second order reaction involving two double molecules, and (b) that the values of α in equation (4) and Table II represent at least approximately the specific reaction velocities of the double molecules.

It may be noted that the values of α increase in the same order as the electrolytic dissociation constants in water.

6. Results for Picric Acid

These results are given separately in Table III, since they differ fundamentally from those for the carboxylic acids.

TABLE III

RESULTS FOR PICRIC ACID

c	0.068	0.083	0.104	0.136
$k_1 \times 10^5$	2.93	3.68	5.33	6.60

Owing to the limited solubility of picric acid, it was not possible to study more concentrated solutions. The results are plotted in Fig. 4, from which it is seen that the reaction velocity is directly proportional to the concentration, not to its square. Picric acid also differs from the carboxylic acids in not forming double molecules, but it is strange that such a strong acid should not show "self-catalysis," particularly as it will be shown later that it is capable of catalyzing the reactions of monochloroacetic acid and of phenol with the ester. It is of course possible that a catalyzed reaction is present with picric acid alone, but is obscured by a faster non-catalyzed reaction.

7. Results for Mixtures of Acids

If two different acids are present together in the same solution, we have the added possibility of what one may term a cross-catalysis, *i.* e., that each

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[29] Bugarsky, *Z. physik. Chem.*, 71, 705 (1910).

acid may catalyze the reaction of the other. Thus if the molecules of each acid remain unchanged by mixing, we should expect a total reaction velocity greater than the sum of velocities for the two acids when present separately at the same concentrations. Actually we must anticipate, in the case of the carboxylic acids, the formation of a new species of complex double molecules (cf. Szyszkowski's results on the solubility of mixtures of acids in benzene).[25] Since the number of possible catalytic reactions is thus still further increased, this will in general give rise to a further increase of reaction velocity, though it may in some cases give a decrease if the two acids concerned have very widely differing reactivities, but are present in comparable amounts.

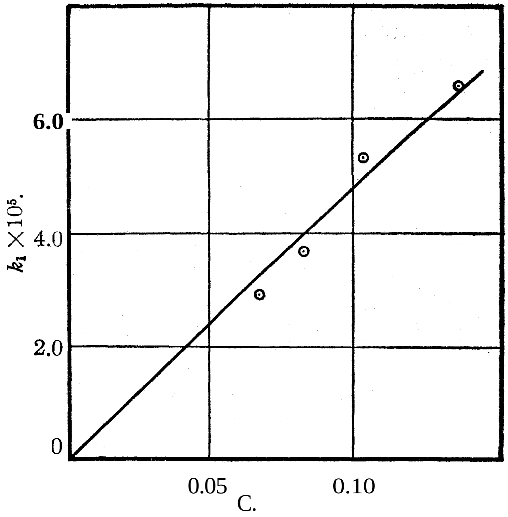

Fig. 4.—Picric acid.

The experimental results for acid mixtures are given in Table IV. As for single acids, the concentrations given are the mean of the initial and final concentrations, the latter differing at the most by a few per cent.

TABLE IV

c_A, c_B = concentrations of the two acids
k_1 = observed velocity constant for the mixture
k_A, kg = velocity constants for the two acids when present singly at concentrations c_A and c_B, calculated from equation (4) and Table II.
$p = k_1 - k_A - k_B$
$n = 100\, p/(k_A + k_B)$

(a) Dichloroacetic acid (A) + monochloroacetic acid (B)

c_A	c_B	$k_1 \times 10^3$	$k_A \times 10^3$	$k_B \times 10^3$	$p \times 10^3$	n
0.0407	0.114	7.13	8.46	0.21	−1.44	−16.6
.0411	.190	7.48	8.63	.54	−1.69	−18.5
.0409	.337	7.92	8.57	1.56	−2.21	−21.9

(b) α,β-Dibromopropionic acid (A) + a-bromopropionic acid (B)

c_A	c_B	$k_1 \times 10^3$	$k_A \times 10^3$	kg × 10^3	$p \times 10^6$	n
0.151	0.203	0.1315	0.1220	0.0100	−0.5	±0.0
.151	.320	.1362	.1220	.0218	−7.6	−5.3

(c) Dichloroacetic acid (A) + α,β-dibromopropionic acid (B)

c_A	c_B	$k_1 \times 10^3$	$k_A \times 10^3$	kg × 10^3	p × 103	n
0.0418	0.289	12.6	8.88	4.70	−0.94	−6.9
.0412	.155	9.28	9.03	1.25	−1.00	−9.7

TABLE IV *(Concluded)*

(d) α,β-Dibromopropionic acid (A) + monochloroacetic acid (B)

c_A	c_B	c_Ac_B	$k_1 \times 10^3$	$k_A \times 10^3$	$kg \times 10^3$	$p \times 10^3$	n
0.0457	0.240	0.0110	1.32	0.189	0.850	0.284	27.3
.0925	.240	.0222	2.11	0.566	.850	.699	49.5
.153	.241	.0369	2.96	1.25	.858	.852	39.0
.229	.151	.0347	3.45	2.24	.360	.850	32.6

(e) Dichloroacetic acid (A) + a-bromopropionic acid (B)

c_A	c_B	$k_1 \times 10^3$	$k_A \times 10^3$	$k_B \times 10^3$	$p \times 10^3$	n
0.0409	0.00973	8.14	8.99	0.00	−0.85	− 9.5
.0409	.0195	6.66	8.99	.01	−2.24	−24.8
.0409	.0389	6.18	8.99	.02	−2.83	−31.4
.0409	.0973	4.68	8.99	.04	−4.35	−48.1
.0409	.176	4.81	8.99	.08	−4.26	−47.1
.0409	.353	4.58	8.99	.26	−4.67	−50.4

(f) Monochloroacetic acid (A) + a-bromopropionic acid (B)

c_A	c_B	c_Ac_B	$k_1 \times 10^4$	$k_A \times 10^4$	$k_B \times 10^4$	$p \times 10^4$	n
0.243	0.0931	0.0226	9.65	8.13	0.30	1.22	14.7
243	142	.0345	10.4	8.13	0.57	1.73	19.9
.243	.246	.0598	12.5	8.13	1.39	3.03	31.8
243	352	.0855	15.9	8.13	2.58	5.21	48.7

(g) Monochloroacetic acid *(A)* + picric acid (B)

c_A	c_B	c_Ac_B	$k_1 \times 10^4$	$k_A \times 10^4$	$k_B \times 10^4$	$p \times 10^4$
0.169	0.0331	0.0056	5.18	4.19	0.16	0.83
.169	.0510	.0086	5.73	4.19	.24	1.30
.169	.0795	.0134	6.80	4.19	.38	2.23
.169	.0980	.0166	7.20	4.19	.47	2.54
.169	.112	.0190	8.44	4.19	.53	3.72
.298	.0220	.00652	13.52	11.96	.16	1.46
.298	.0379	.0113	14.10	11.96	.18	1.96
.298	.0604	.0180	15.56	11.96	.29	3.31
.298	.0696	.0207	15.66	11.96	.33	3.37
.298	.0950	.0284	17.38	11.96	.45	4.97

For the three acid pairs (d), (f) and (g) an increase of velocity is found, and it is seen from Figs. 5 and 6 that this increase is roughly proportional to the product of the acid concentrations, as would be expected if the effects of cross-association can be neglected. For the acid pairs (a) and (e) the effect is a reduction. For this last pair, dichloroacetic and α-bromopropionic acids, the dichloroacetic acid concentration was the same in each experiment, and in Fig. 7 the percentage reduction is plotted against the concentration of a-bromopropionic acid. It is seen that at high concentrations the reduction tends to a constant value. Since the velocity attributable to the reaction of the a-bromopropionic acid is only a small fraction of the total velocity, this constant value can be interpreted as corresponding to a total conversion of dichloroacetic acid molecules into complex double molecules. For the acid pairs (b) and (c), the effect observed is small, and is probably compounded of both the above influences.

8. Acid Catalysis in the Reaction of Alcohol and Phenol

When the two acids react simultaneously with diazoacetic ester, it is impossible from measurements of the nitrogen evolved to deduce the velocities of the separate reactions involved. Such measurements cannot therefore be used to compare the catalytic activities of different acids for the same reaction. This may however be possible if we can find a suitable substance of low acidity whose reaction with the ester is catalyzed by acids. The catalyzing acid will itself react simultaneously but this can be corrected for on the assumption that its reaction velocity is unaffected by the presence of the second substance.

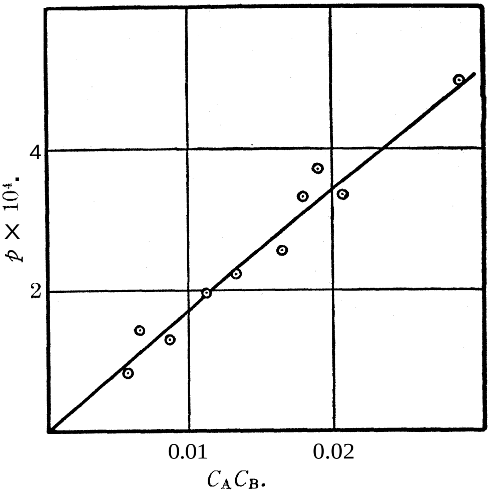

Fig. 5.—Monochloroacetic + picric acids.

The first substance tried was ethyl alcohol, which is known to react according to the equation

$$CHN_2COOC_2H_5 + C_2H_5OH \longrightarrow C_2H_5OCH_2COOC_2H_5 + N_2$$

which reaction is catalyzed by solvated hydrogen ions in aqueous and alcoholic solutions. Experiments in benzene solution with mixtures of mono-

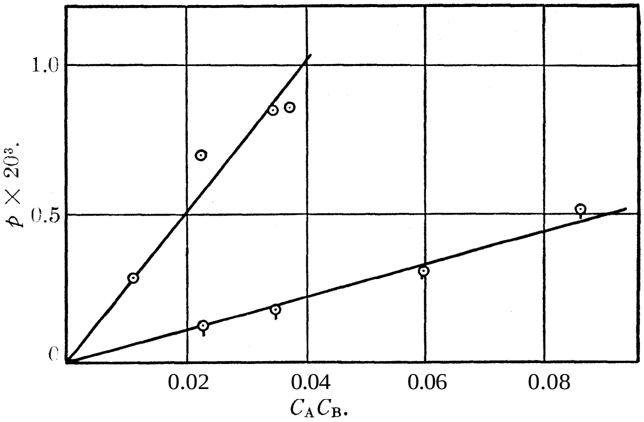

Fig. 6.—⊙, α,β-Dibromopropionic + monochloroacetic acids; ♀, monochloroacetic + a-bromopropionic acids.

chloroacetic acid and alcohol showed, however, that alcohol caused a very large decrease in velocity instead of the expected increase. The figures given in Table V were obtained.

TABLE V

c_1 = concentration of monochloroacetic acid; c_2 = concentration of alcohol

c_1	0.220	0.220	0.220
c_2	0	0.685	1.10
$k_1 \times 10^5$	67.0	2.6	1.3

There is thus present some complicating effect, possibly due to association of the alcohol and acid molecules.

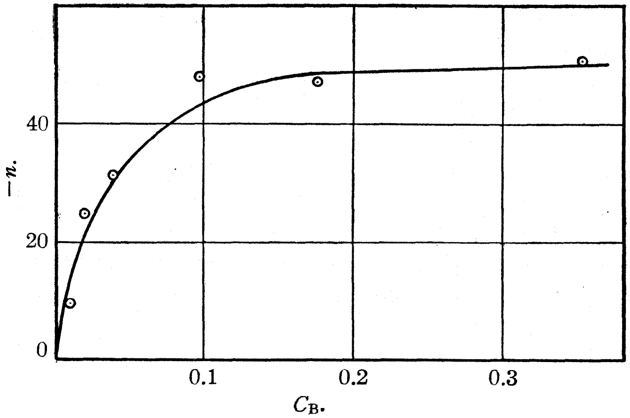

Fig. 7.—Dichloroacetic + α-bromopropionic acids.

A few experiments were also carried out to test whether the presence of small quantities of water would have any appreciable effect on the results obtained (Table VI).

TABLE VI

c_1 = concentration of acid; c_2 = concentration of water; k_1' = velocity constant in absence of water

Monochloroacetic Acid

c_1	c_2	$k_1 \times 10^4$	$k_1' \times 10^4$
0.141	0.043	3.92	3.03
.184	.056	5.70	5.50

Dichloroacetic Acid

c_1	c_2	$k_1 \times 10^4$	$k_1' \times 10^4$
0.0524	0.043	95.4	135

It is seen that the effect is sometimes positive and sometimes negative, but that it is small enough to exclude any uncertainty in the experimental results due to the presence of traces of water.

With benzene solutions of picric acid, however, the addition of alcohol gives rise to an increase in velocity, which must be attributed to the reaction of alcohol with the ester. The results are given in Table VII, the concentrations being as usual the mean of the initial and final values.

TABLE VII

c_A = concentration of picric acid; c_B = concentration of alcohol; k_1 = observed velocity constant, k_A = velocity constant for picric acid alone; $p = k_1 - k_A$

c_A	c_B	$k_1 \times 10^4$	$k_A \times 10^4$	$p \times 10^4$	c_Ac_B
0.0495	0.685	1.94	0.24	1.70	0.0344
.070	.685	2.70	.33	2.37	.0480
.105	.685	3.80	.50	3.30	.0719
.140	.685	5.60	.67	4.93	.0960
.140	1.03	8.40	.67	7.73	.144

It is seen from Fig. 8 that p is directly proportional to c_Ac_B, which is what we should expect for the catalyzed reaction of the alcohol. A single experiment with picric acid + butyl alcohol gave an increase almost identical with that for ethyl alcohol.

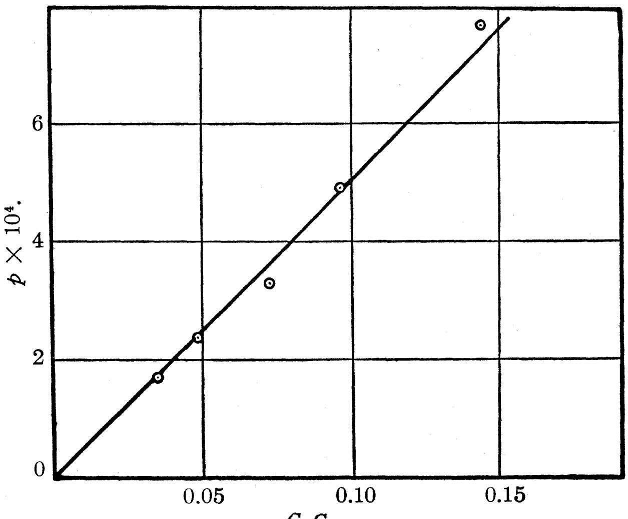

Fig. 8.—Picric acid + ethyl alcohol.

The addition of phenol was next tried, and was found to give an increase of velocity with all the acids studied. This increase we attribute to the reaction

$$CHN_2COOC_2H_5 + C_6H_5OH \longrightarrow C_6H_5OCH_2COOC_2H_5 + N_2 \qquad (8)$$

catalyzed by the acid present. We have not been able to find any reference to the formation of phenoxyacetic ethyl ester by this reaction, but the corresponding reaction of diazomethane

$$CH_2N_2 + C_6H_5OH \longrightarrow C_6H_5OCH_3 + N_2$$

takes place readily. Since phenoxyacetic ester is a liquid boiling at 250°, and will be accompanied by the products of reaction of the acid itself (which are not reported in Beilstein, but which probably have similar boiling points), we have not attempted to isolate the products of reaction. The chief evidence that the increase of velocity is due to reaction (8) is afforded by the kinetic measurements themselves.

Preliminary experiments showed that phenol alone gave no measurable reaction with diazoacetic ester in benzene solution. The most extensive experiments were carried out with monochloroacetic acid, and are given in Table VIII. The concentrations of both phenol and acid are the mean of initial and final concentrations differing by, at the most, a few per cent.

TABLE VIII

c_A = concentration of acid; c_B = concentration of phenol; k_1 = observed velocity constant; k_A = calculated velocity constant for acid alone; $p = k_1 - k_A$

Monochloroacetic Acid (A) + Phenol (B)

c_A	c_B	$k_1 \times 10^4$	$k_A \times 10^4$	$p \times 10^4$	c_Ac_B
0.216	0.085	7.90	6.57	1.33	0.0184
.0778	.426	2.02	0.96	1.06	.0331
.0930	.426	3.02	1.46	1.56	.0396
.217	.256	9.50	6.60	2.90	.0555
.155	.426	6.21	3.46	2.75	.0660
.217	.426	10.90	6.70	4.20	.0924
.218	.597	12.90	6.63	6.27	.130
.312	.426	19.65	12.76	6.89	.133

It is seen from Fig. 9 that the velocity of the catalyzed reaction can be represented by the equation

$$p = lc_Ac_B \tag{9}$$

where "l" is a constant. For the same reasons as those given in section (5), we must conclude that "l" is at least approximately the catalytic constant for the double monochloroacetic molecule. "Medium effects" and effects due to the presence of single molecules cannot be detected within the limits of accuracy obtained. A single experiment with o-chlorophenol + monochloroacetic acid gave a value of p only slightly greater than with phenol.

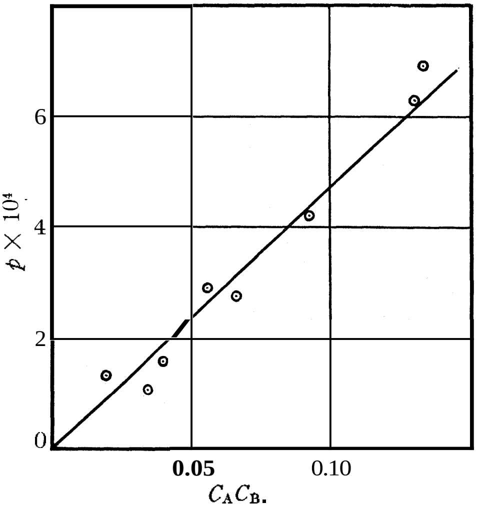

Fig. 9.—Monochloroacetic acid + phenol.

We have not tested equation (9) extensively for any other acids, but have preferred to carry out a few experiments for a number of different acids, and to calculate the values of "l" assuming equation (9) to hold. Even if the values so obtained are only provisional, a comparison for acids of widely varying strength is of great interest. Table IX contains such results, the notation being the same as that employed in Table VIII.

For α,β-dibromopropionic acid the values of k_A are obtained from the curve in Fig. 2. For iodoacetic and formic acids these values were obtained by carrying out an experiment without phenol. For these two acids approximate values have been calculated for the specific reaction velocities of the double molecules α by assuming that

$$k_A = \alpha c_A^2 \tag{10}$$

TABLE IX

Iodoacetic Acid (A) + Phenol (B)

c_A	c_B	$k_1 \times 10^5$	$k_A \times 10^5$	$p \times 10^5$	c_Ac_B
0.173	0.256	12.20	5.9	6.30	0.0444
.173	.426	14.7	5.9	8.8	.0737
.181	.426	21.3	6.5	14.8	.0772

$\alpha = 2.0 \times 10^{-3}$ $l = 1.4 \times 10^{-3}$

Formic Acid (A) + Phenol (B)

c_A	c_B	$k_1 \times 10^5$	$k_A \times 10^5$	$p \times 10^5$	c_Ac_B
0.208	0.426	15.8	3.20	13.6	0.089
.240	.426	18.9	4.12	17.8	.102
.259	.426	27.6	7.80	10.8	.110
.320	.426	27.3	7.30	20.0	.136

$\alpha = 8.0 \times 10^{-3}$ $l = 1.6 \times 10^{-3}$

α,β-Dibromopropionic Acid (A) + Phenol (B)

0.0588	0.426	38.0	28.2	10	0.0250
.0944	.426	111	60.8	50	.0403
.146	.426	161	117	54	.0622

$l = 8.5 \times 10^{-3}$

Picric Acid (A) + Phenol (B)

0.0704	0.426	5.50	3.43	2.07	0.0301
.106	.426	9.03	5.04	3.99	.0452

$l = 8.4 \times 10^{-4}$

With dichloroacetic acid it was found that the addition of phenol to solutions of 0.05–0.1 normality caused no measurable change of velocity. However, by decreasing the acid concentration greatly, while keeping the phenol concentration fairly high, the phenol reaction became the predominant one, as was shown by the fact that the course of these reactions was strictly monomolecular, in spite of the fact that the acid concentration was smaller than that of the ester. Experiments were carried out with constant acid concentration and varying phenol concentration, and the total reaction velocity plotted against c_Ac_B. The slope of the best straight line thus obtained was taken as the catalytic constant.

A similar procedure was adopted for nitroacetic acid, which is too little soluble in benzene to measure at high concentrations (Table X).

TABLE X

Dichloroacetic Acid (A) + Phenol (B)

c_A	c_B	$k_1 \times 10^5$	$c_Ac_B \times 10^4$
0.00204	0.171	9.1	3.49
.00204	.256	10.6	5.22
.00204	.342	11.1	6.99
.00204	.426	12.3	8.70

$l = 1.0 \times 10^{-1}$

Nitroacetic Acid (A) + Phenol (B)

c_A	c_B	$k_1 \times 10^5$	$c_Ac_B \times 10^3$
0.00720	0.171	11.3	1.23
.00720	.256	13.5	1.84
.00720	.256	17.5	1.84
.00720	.341	16.3	2.46
.00720	.426	25.2	3.07
.00720	.426	18.8	3.07

$l = 5.8 \times 10^{-2}$

In Table XI are collected for each acid the values of α, the specific reactivity of the double molecules, l, the catalytic constant, and K_d, the electrolytic dissociation constant in aqueous solution. Unless a reference is given, the values of this last constant are taken from Landolt–Bornstein "Tabellen" (5th Auflage and Erster Ergänzungsband). The values of α marked * are only approximate, being taken from Table IX and equation (10).

TABLE XI

VALUES OF CONSTANTS

Acid	a	1	$\log_{10} l$	K_{dl}	$\log_{10} K_{dl}$.
Formic	8.0 X 10^{-3}*	1 6 X 10^{-3}	$\bar{3}$ 204	1.77 X 10^{-4}	$\bar{4}$ 248[30]
Iodoacetic	2 0 × 10^{-3}*	1 4 X 10^{-3}	$\bar{3}$ 146	7.5 X 10^{-4}	$\bar{4}$.875
a-Bromopropionic	1 58 × 10^{-3}	.....	...	1.08 × 10^{-3}	$\bar{3}$033
Monochloroacetic	1 20 X 10^{-2}	4 7 X 10^{-3}	$\bar{3}$.672	1.41 X 10^{-3}	$\bar{3}$ 149[31]
α,β-Dibromopropionic	2.35 X 10^{-2}	8 5 X 10^{-3}	$\bar{3}$.929	6.7 X 10^{-3}	$\bar{3}$.826
Nitroacetic	. ...	5.8 X 10^{-2}	$\bar{2}$.763	2.1 X 10^{-2}	$\bar{2}$.322[32]
Dichloroacetic	3 34	1.0 X 10^{-1}	$\bar{1}$.000	5 X 10^{-2}	$\bar{2}$.700
(Picric	....	8 4 X 10^{-4}	...	1.6 X 10^{-1})	.....

It appears from Fig. 10 that there is an approximate agreement with the reaction previously derived[33]

$$l = G_1K_d^x \qquad (11)$$

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[30] Harned and Owen, THIS JOURNAL, 52,5079 (1930).

[31] Grove, *ibid.*, 52, 1405 (1930).

[32] Pedersen, *Trans.* Faraday *Soc.*, 23, 316 (1927).

[33] Bronsted, Chem. *Rev.*, 5,312 (1928).

which has been shown to hold in aqueous solution in several cases.[34] In this case the exponent x has the value approximately unity. It must be remarked that while the catalytic constants refer to double acid molecules, the dissociation constants refer to single ones. This may explain why the catalytic value for picric acid (which exists as single molecules in benzene solutions) is very much lower than that predicted from equation (11), though we should expect the catalytic constants of the single carboxylic acid molecules to be still higher than those of the double ones. It is more probable that the abnormality of picric acid in this respect is connected with the fact that in a solvent of low dielectric constant the influence of the rest of the acid molecule will be much greater than in water, and thus equation (11) may only hold for acids of the same chemical type. It may be significant in this connection that for the carboxylic acids, the widest deviations are shown by formic and α,β-dibromopropionic acids, while the four substituted acetic acids show good mutual agreement.

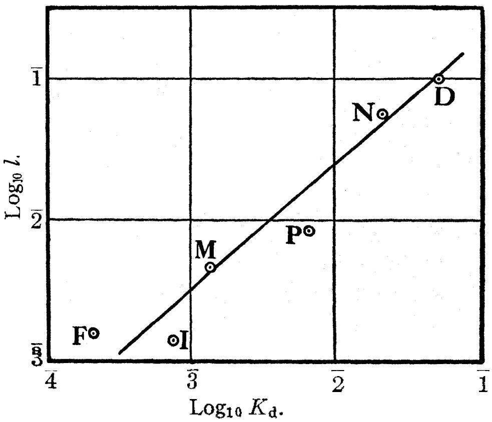

Fig. 10.—F, Formic; I, iodoacetic; M, monochloroacetic; P, α,β-dibromopropionic; N, nitroacetic; D, dichloroacetic.

According to modern views of the acid–base function, the cation of a weak base such as pyridine is also an acid, and we should anticipate that such ions would show catalysis in the reaction of phenol with diazoacetic ester. It was found, however, that a 0.0225 N solution of pyridinium trichloroacetate showed no measurable catalytic effect. It is possible that this represents an extreme case of the influence of electric type in solvents of low dielectric constant.

Summary

1. This paper contains a kinetic study of the reaction of diazoacetic ethyl ester with several substances in benzene solution. The reactions were followed by measuring the pressure of the nitrogen evolved.

2. In solutions of one or more carboxylic acids, the reaction consists of the replacement of the N_2 group by an acid molecule. The velocity of the reactions was found to be expressible by the equation

$$k_1 = \alpha c^2 + \beta c$$

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[34] Bronsted and Pedersen, *Z. physik. Chem.*, 108, 13 (1924); Rronsted and Duus, *ibid.*, **117**, 229 (1925); Bronsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927); Bronsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

c being the concentration of the acid, and α and β constants characteristic for the individual acids. The velocity increases with increasing acid strength.

This empirical equation is compatible with the assumption that the addition of an acid molecule is catalyzed by the presence of acid molecules of the same or different kind, taking into account the progressive dissociation of double acid molecules into single molecules as the dilution increases. The reaction can be considered as a case of general acid catalysis.

3. The velocity of addition of picric acid is directly proportional to its concentration.

4. The velocity of addition of phenol to diazoacetic ester is strongly catalyzed by the presence of carboxylic acids, the catalytic effect increasing with increasing acid strength. The equation

$$l = GK^x$$

which has previously been shown to hold true for general acid catalysis in aqueous solution also applies approximately in the presence case, the exponent x having the limiting value of unity. Picric acid is much less active than required by the above equation.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, HARVARD MEDICAL SCHOOL]

THE DETERMINATION OF CALCIUM BY ALKALIMETRIC TITRATION. I

BY CYRUS H. FISKE AND ELLIOTT T. ADAMS

RECEIVED MARCH 24, 1931 PUBLISHED JULY 8, 1931

Among the possible volumetric methods for the determination of small amounts of calcium, after precipitation as the oxalate, alkalimetric titration of the oxide should have certain definite advantages over oxidation with permanganate, which is now used almost exclusively for this purpose. The end-point in the titration of pure calcium oxide is so sharp that, if no errors are introduced in the precipitation and washing of the calcium oxalate or in its subsequent conversion to the oxide, a method based upon this principle should be accurate to 0.002 mg. of calcium. The permanganate titration method, on the other hand, according to the most extensive investigation so far published,[1] is subject to an error of 0.006–0.008 mg. in the analysis of samples containing between 0.2 and 0.5 mg. of calcium.

Of the various objections that have been raised against the determination of small amounts of calcium by permanganate oxidation of the oxalate precipitate, only two appear to be of much importance. These are (1) the fact that the precipitate must be washed with water (or dilute ammonia), in which its solubility is appreciable, and (2) the mechanical loss involved in centrifuging the calcium oxalate, which except perhaps in

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[1] Van Slyke and Sendroy, *J. Biol. Chem.*, 84, 217 (1929).

the case of fluids containing protein tends to float on the surface of the liquid. The necessity of washing with a liquid in which the precipitate is noticeably soluble has led to the introduction of a wide variety of empirical procedures which, whether by design or not, tend to compensate for the loss of calcium oxalate by leaving behind a little of the precipitating agent,[2] but methods in which the balancing of errors is so large a factor can hardly be expected to give identical results in the hands of every analyst. The mechanical loss of calcium oxalate can be avoided to a large extent by removing the supernatant fluid with a siphon, but apparently this device does not in practice lead to greater accuracy, probably because it is incompatible with the use of strictly uniform technique in washing the precipitate.

In the determination of calcium by titration of the oxide it is possible to avoid the weak points of the permanganate procedure and at the same time to retain the features of the standard gravimetric methods upon which their accuracy rests: *viz.*, (1) separation of the calcium oxalate by filtration, and (2) washing with ammonium oxalate solution, in which the solubility of the precipitate is practically nil. Jansen[3] has proposed a method of this kind for quantities of calcium in the neighborhood of 1 mg., but reports errors of at least 0.008 mg. in the analysis of known solutions. In other hands this method has given still less satisfactory results,[4] and is now rarely used. It is not in the ordinary sense a micro method, but a combination of standard textbook procedures designed for the analysis of samples containing 50 or 100 mg. of calcium and used without essential modification for the determination of much smaller quantities. The filter paper, for example, is out of all proportion to the size of the precipitate, and its presence materially complicates the subsequent steps of the analysis.[5]

Suction filtration on a small mat of paper pulp[6] is one way in which this defect might be overcome. Some risk of loss, however, is involved in the transfer of a very small precipitate from a filter of this type, by purely mechanical means, to the platinum dish in which it is to be ignited. The

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[2] For the literature see, for example, Bar, *Endokrinologie,* **1,** 90 (1928).

[3] Jansen, Z. *physiol. Chem.,* 101,176 (1917–1918).

[4] *Cf.* Heubner and Rona, *Biochem.* Z., 135,248 (1923).

[5] Ignition of the calcium oxalate to carbonate has likewise been suggested, as a means whereby the precipitate may be separated by centrifugation, and the ignition and titration subsequently carried out without transferring the material [Lebermann, *Munch. med. Wochenschrift,* 71, 1392 (1924); Trevan and Bainbridge, *Biochem.* **J.**, 20, 423 (1926)]. The objections to centrifugation, already mentioned, limit the usefulness of this procedure. Furthermore, the difficulty of dissolving the carbonate in hydrochloric acid is so great that Trevan and Bainbridge recommend phosphoric acid in its place, and hence are forced to use an end-point which is by no means sharp. Hendriks, who appears to have subjected this method to a much closer scrutiny than its originators, finds it far from accurate [*ibid.,* 23,1206 (1929)].

[6] See, for example, Fiske, J. *Biol. Chem.,* 46,288 (1921).

alternative procedure of transferring the precipitate dissolved in nitric acid has been tried repeatedly, but the results obtained by titrating the residue left after evaporating the nitric acid solution and igniting have not been satisfactory. Apparently the oxide formed by the decomposition of fused calcium nitrate is so compact that it will not dissolve readily in a moderate excess of standard acid, or else the product is not pure calcium oxide. In any event reconversion of the nitrate to oxalate before ignition is an effective remedy, which at the same time considerably diminishes the total time required for the analysis and brings the error regularly within the anticipated limit (Table I). If the dried calcium nitrate is evaporated with a few drops of a solution of oxalic acid, the oxide formed by ignition of the final residue is much less compact, and dissolves in the course of a few minutes even if the excess of acid added is not more than 0.1 cc. of 0.02 N. The undissolved particles of oxide are, moreover, intensely stained by the indicator (methyl red), so that no difficulty is experienced in deciding when solution is complete.

Experimental

Solutions of calcium nitrate were prepared by dissolving calcium carbonate (Kahlbaum's "zur Analyse") in a slight excess of nitric acid. Accurately measured samples of these solutions were evaporated to dryness on the water-bath in a small platinum dish. The dry calcium nitrate residue was treated with 0.5 cc. of *2.5%* oxalic acid (base-free), and the contents of the dish were again evaporated to dryness and then carefully ignited over a micro-burner. The cooled residue in each instance was dissolved in an excess of standard hydrochloric acid (0.02 or 0.1 *N*, according to the amount of calcium present), added 1 cc. at a time from a calibrated Ostwald pipet, and the solution was titrated back to the turning point of methyl red with 0.02 N sodium hydroxide (free from carbonate and silicate) from a calibrated micro-buret of 5 cc. capacity with 0.02 cc. graduations. Toward the end of the titration the alkali was added in 0.005 cc. portions.

TABLE I

TITRATION OF CALCIUM OXIDE

0.5 cc. of 2.5% **oxalic acid was used to convert the calcium nitrate to the** oxalate **before ignition.**

Calcium present, mg.	Calcium found, mg.	Error, %	Calcium present, mg.	Calcium found, mg.	Error, %
0.200	0.202	+1.0	1.000	1.000	0
0.200	0.198	−1.0	1.000	1.002	+0 2
0.200	0.198	−1.0	1.990	1.986	−0.2
1.000	1.000	0	1.990	1.990	0

Summary

A method is described for converting calcium nitrate to the oxide in a form which can be readily analyzed by alkalimetric titration. Since small

calcium oxalate precipitates, which have been separated by filtration and washed with ammonium oxalate solution, can thus be transferred to a platinum dish with the aid of nitric acid before conversion to the oxide, certain defects inherent in the customary perrnanganate oxidation methods can be avoided.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

ADSORPTION BY SILICA FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE

BY F. E. BARTELL, G. H. SCHEFFLER AND C. K. SLOAN[1]

RECEIVED APRIL 2, 1931 PUBLISHED JULY 8, 1931

An interferometric method for measurement of adsorption by carbon from binary organic liquid systems was described in earlier papers from this Laboratory.[2] It was shown that, in every case investigated, the curve representing adsorption over the entire concentration range was S-shaped. The component having the higher adhesion tension against carbon was adsorbed to the greater extent. The component of lower adhesion tension was, however, preferentially adsorbed if present in sufficiently low concentration. An equation was derived which was based on the assumption that adsorption of each component of a binary liquid system follows the Freundlich equation. The equation $H\Delta x/m = ax^n(1 - x) - b(1 - x)^d x$ thus obtained was used to calculate the preferential adsorption over the concentration range.[3]

It is quite well known that carbon adsorbs better from aqueous solutions than from organic liquids, while silica adsorbs better from organic liquids.[4] Carbon has been shown to have a high adhesion tension against non-polar organic liquids and a relatively low adhesion tension against certain polar organic liquids and water;[5] the converse is true for silica.[6] From

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[1] Du Pont Fellow in Chemistry, 1927–1928.

[2] Bartell and Sloan, THIS JOURNAL, 51, 1637 (1929); 51, 1643 (1929).

[3] The symbols used in this paper are the same as those of earlier papers

H = total number of millimoles in the solution
x = mole fraction solute at equilibrium
Δx = mole fraction change due to adsorption
m = weight of adsorbent
c_0 = initial concentration
c = final concentration
Δc = change in concentration due to adsorption
N = total weight (in grams) of solution
a, n, d and b are constants

[4] Patrick and Jones, *J. Phys. Chem.*, 29, 1 (1925).

[5] Bartell and Osterhof, *Ind. Eng. Chem.*, 19, 1277 (1927).

[6] Bartell and Miller, *ibid.*, 20, 738 (1928).

previous investigations in this Laboratory it has been shown that, other factors being equal, adsorption should be greatest from that liquid which has the lowest adhesion tension against a given solid adsorbent. This explains why adsorption by carbon should be greater from an aqueous solution, and why adsorption by silica should be greater from organic liquids. In the present work the interferometric method was used to determine concentration changes which occurred during the process of adsorption. Binary organic liquid systems were used with silica as the adsorbent. The results obtained are compared with those previously obtained with carbon. The experimental procedure employed was that described by Bartell and Sloan.[2]

Preparation of Silica.—The silica used was prepared by a method similar to that which had previously been used in this Laboratory.[7] A sodium silicate solution of 1.02 specific gravity was treated with concentrated hydrochloric acid in the presence of nickel nitrate. The silica gel thus formed was allowed to synerize slowly. The resulting brownish-black material was digested in conductivity water to remove nickel nitrate. This gel was then heated to 260° for two hours and again digested in conductivity water. After the nickel salt had been removed in this manner, the "silica gel" (about 15 g. per batch) was heated at 1000° for four minutes in order further to dehydrate it. At this stage the "silica" was perfectly white. It was next allowed to cool in dry nitrogen and then transferred to flasks also filled with dry nitrogen. A sufficient quantity of the "silica" was prepared to insure that uniform samples might be used throughout the course of the work.

Purification of Liquids.—Standard methods were employed for the purification of the liquids. Each liquid, after preliminary treatment, was distilled through a tall fractionating column with a large area of cooling surface. The middle fractions only were used. The liquid systems investigated were: (1) ethyl carbonate–benzene, (2) ethyl alcohol–benzene, (3) ethyl carbonate–dimethylaniline, and (4) ethyl carbonate–methyl benzoate.

Results

Adsorption from the System Ethyl Carbonate–Benzene.—The adsorption data obtained for this system when plotted give an S-shaped curve. This curve is shown in Fig. 1. Ethyl carbonate was preferentially adsorbed until a concentration of 0.68 mole fraction of it was reached. Beyond this concentration benzene was preferentially adsorbed. The values of the constants were determined by the method used by Bartell and Sloan.[2] The equation representing the adsorption over the entire concentration range for the above system is

$$H\Delta x/m = 7.603\,(x)^{0.574}(1 - x) - 8.1798(1 - x)^{0.982}\,(x)$$

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[7] Bartell and Fu, "Colloid Symposium Monograph," Vol. VII, 1930.

The agreement between the values calculated from the equation and the values determined experimentally is shown in Table I.

TABLE I

ADSORPTION OF ETHYL CARBONATE FROM BENZENE

c_0	m, g.	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H\Delta x}{m}$ obs.	$\frac{H\Delta x}{m}$ calcd.	Difference
0.0100	0.20	0.00837	0.03587	0.00556	0.31919	0.31725	−0.00194
.0500	.20	.04635	.08054	.02962	.69526	.69026	− .00500
.1000	.20	.09515	.10780	.06274	.94686	.93245	− .01441
.2000	.20	.19478	.11725	.13264	1.07050	1.06020	− .01010
.3000	.20	.29543	.10379	.20954	0.98678	0.98534	− .00144
.7483	.20	.74808	.00555	.66250	.06303	.04617	− ,01691
.8883	.20	.88862	− .00804	.84062	− .09750	− .11301	+ .01551
.9500	.20	.95031	− .00747	.92359	− .09738	− .09692	− .00046
.9850	.20	.98512	− .00299	.98668	− .03925	− 03930	+ .00050

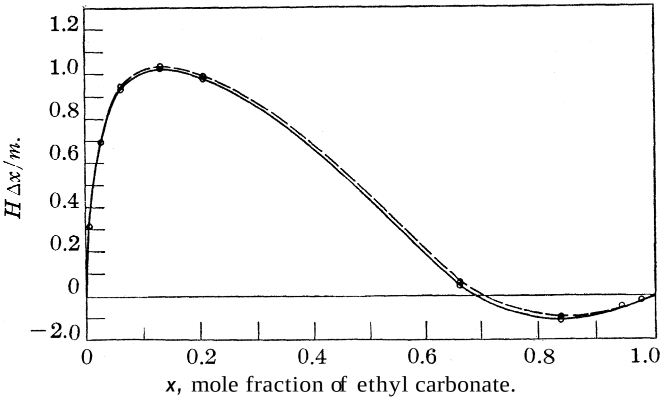

Fig. 1.—Experimental points, — — — — —; 7.603 $(x)^{0.574}$ $(1 - x) - 8.1798\,(1 - x)^{0.982}\,(x)$, ————. Adsorption of ethyl carbonate from benzene.

Adsorption from the System Ethyl Alcohol–Benzene.—The results obtained with the system ethyl alcohol–benzene give an S-shaped curve, as shown in Fig. 2. Ethyl alcohol in this system is highly adsorbed at a low concentration of this component. Preferential adsorption of benzene is indicated at high alcohol concentrations.

The data obtained for the system alcohol–benzene are given in Table II. The equation representing the adsorption of this system is

$$H\Delta x/m = 8.8105\,(x)^{0.227}\,(1 - x) - 4.664\,(1 - x)^{0.615}\,(x)$$

For purposes of comparison, data obtained with carbon as an adsorbent[2] are plotted also in Fig. 2.

Adsorption from the System Ethyl Carbonate–Dimethylaniline.—In the system ethyl carbonate–dimethylaniline, preferential adsorption of each component is noted over some part of the concentration range.

TABLE II

ADSORPTION OF ETHYL ALCOHOL FROM BENZENE

c_0	m	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H\,\Delta x}{m}$
0.01436	0.2622	0.00601	0.1388	0.01014	3.0108
.02745	.2503	.01720	.1783	.02882	3.8299
.04217	.2608	.03001	.1952	.04984	4.1564
.13070	.2534	.12810	.2071	.19928	4.1312
.29195	.2186	.28320	.1656	.40021	3.0001
.74883	.2540	.74810	+ .0112	.83430	0.1596
.90157	.2675	.90288	− .0200	.94035	− .2676
.96640	.2577	.96745	− .0160	.98053	− .2083

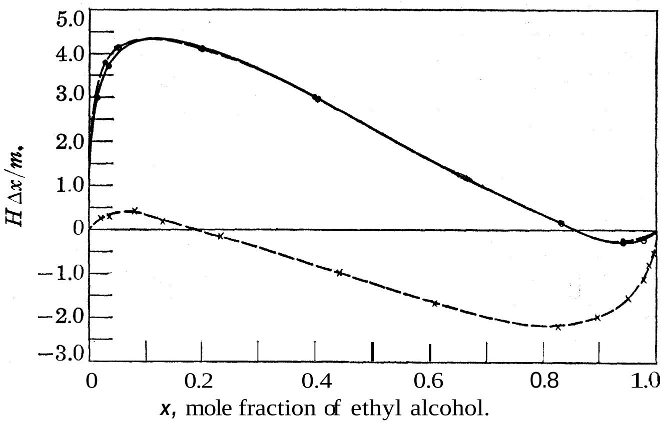

Fig. 2.—Silica (experimental), — — — —; carbon (experimental), X — — — —; 8.8105 $(x)^{0.227}$ $(1 - x)$ − 4.664 $(1 - x)^{0.615}$ (x), O ———. Adsorption of ethyl alcohol from benzene.

Data for this system are given in Table III, and the corresponding adsorption curve in Fig. 3. The equation representing the results obtained is

$$H\Delta x/m = 1.0448\,(x)^{0.658}\,(1 - x) - 0.645\,(1 - x)^{0.784}\,(x)$$

TABLE III

ADSORPTION OF ETHYL CARBONATE FROM DIMETHYLANILINE

c_0	m	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H\,\Delta x}{m}$
0.01194	0.2708	0.01129	0.00835	0.01158	0.07074
.07870	.3230	.07736	.01604	.07923	.13566
.1703	.3802	.16802	.02129	.17168	.17964
.3442	.2983	.34252	.02176	.34838	.18276
.6748	.2930	.67409	.00920	.67975	.07661
.9300	.3125	.93004	.00046	.93171	− .00378
.9894	.2419	.98948	.00119	.98974	− .00985
.9958	.2581	.99585	.00067	.99600	− .00550

Adsorption from the System Ethyl Carbonate–Methyl Benzoate.—In this system, as in the others, preferential adsorption of each of the two components occurred over some portion of the concentration range. The adsorption curve for this system is shown in Fig. 4 and the data are given

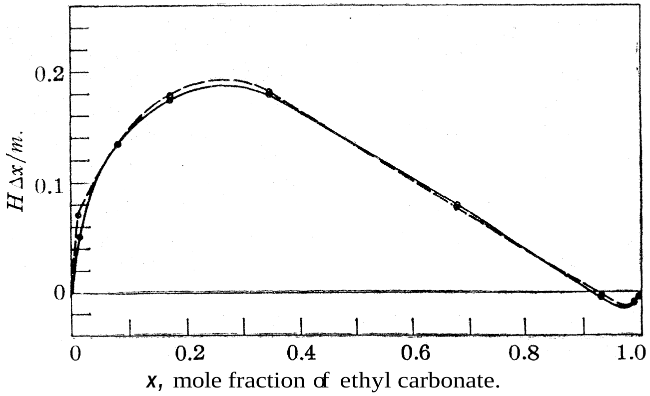

Fig. 3.—Experimental points, — — — — —; $1.0448(x)^{0.658}(1-x) - 0.645(1-x)^{0.784}(x)$, ————. Adsorption of ethyl carbonate from dimethylaniline.

in Table IV. The adsorption data obtained for this system are represented by the equation

$$H\Delta x/m = 0.8479(x)^{0.591}(1-x) - 0.1619(1-x)^{0.246}(x)$$

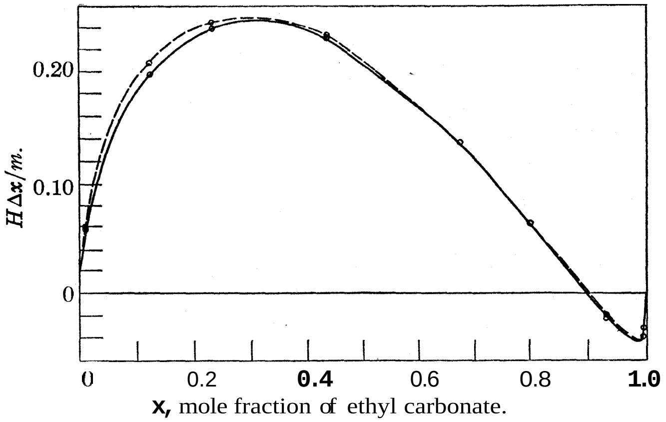

Fig. 4.—Experimental points, — — — — —; $0.8479(x)^{0.591}(1-x) - 0.1619(1-x)^{0.2462}(x)$, ————. Adsorption of ethyl carbonate from methyl benzoate.

Discussion

The interferometric method had previously been used for the determination of the extent of preferential adsorption by carbon, of the components of binary non-aqueous systems over the entire range of concentration.[2] In each case investigated an S-shaped adsorption curve was obtained.

TABLE IV

ADSORPTION OF ETHYL CARBONATE FROM METHYL BENZOATE

c_0	m	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H\Delta x}{m}$
0.0106	0.2450	0.01017	0.00717	0.01172	0.06071
.1111	.2724	.10942	.02494	.12417	.20807
.2032	.2424	.20129	.03229	.23336	.27521
.4042	.2010	.40249	.03337	.43723	.26651
.6425	.3141	.64065	.02381	.67295	.13683
.7727	.2618	.77216	.00844	.79629	.06399
.9220	.2657	.92203	− .00042	.93169	− .00313
.9914	.2843	.99180	− .00520	.99516	− .03838
.9951	.2715	.99539	− .00406	.99701	− .03000

It was noted that the component having the higher adhesion tension against the carbon was preferentially adsorbed over the greater portion of the concentration range.

In the present investigation the same method was employed for the measurement of concentration changes during adsorption, but in this work silica was used as the adsorbent. It was found, as in the earlier investigation, that the component having the higher adhesion tension against the solid was preferentially adsorbed over the greater portion of the concentration range.

In general, it may be stated that the order of increasing adhesion tension values of a series of liquids against carbon is the reverse of the order of increasing values against silica. It must accordingly follow that the order of decreasing interfacial tension values of a series of liquids against carbon is the reverse of the decreasing interfacial tension values of this series of liquids against silica. One would be justified in expecting that the adsorption effects obtained with carbon would be different, in fact, practically the reverse, of the effects obtained with silica. Our results indicate that if one obtains adsorption values for a binary liquid system over the concentration range for carbon, one can by means of the adsorption curve predict with a fair degree of accuracy the degree of preferential adsorption to be expected at the different concentrations, when silica is used as adsorbent. Each adsorbent will tend to give an S-shaped adsorption curve. The one curve will tend to be the inverted and reverse form of the other. In Fig. 2 are plotted curves showing preferential adsorption values for benzene and for ethyl alcohol adsorbed with carbon and with silica. When carbon was used as the adsorbent, the non-polar liquid benzene was much more highly adsorbed than was the polar liquid alcohol; also, benzene was preferentially adsorbed over the greater portion of the concentration range.[2] With silica as adsorbent, the alcohol was more highly adsorbed than was benzene and it was also preferentially adsorbed over a greater portion of the concentration range.

Zero preferential adsorption with carbon comes at a concentration of approximately 0.2 mole fraction of alcohol, and with silica at a concentration of approximately 0.82 mole fraction of alcohol. At zero preferential adsorption both components are adsorbed, but they are adsorbed in the same proportions as represented by the concentration of the bulk of the solution.

Summary

1. In a study of the adsorption by silica from non-aqueous binary systems over the entire concentration range the interferometric method was used to measure changes in concentration of solutions.
2. In each system investigated an S-shaped adsorption curve was obtained. Over some portion of the concentration range each of the components was preferentially adsorbed.
3. The adsorption curve obtained with silica as adsorbent is very nearly the inverted and reverse form of that obtained with carbon for the same binary liquid system.
4. That component having the higher adhesion tension against the solid is preferentially adsorbed over the greater portion of the concentration range.
5. The Freundlich equation when so modified as to express the measure of adsorption in terms of change in concentration, as

$$H\Delta x/m = ax^{*}(1 - x) - b(1 - x)^{d}x$$

was found to express the adsorption as determined over the entire range of concentration.

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

ADSORPTION BY SILICA AND CARBON FROM BINARY ORGANIC LIQUID MIXTURES OVER THE ENTIRE CONCENTRATION RANGE

BY F. E. BARTELL AND GEORGE H. SCHEFFLER[1]

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Several different investigators have used different adsorbates, constituting an homologous series, in their studies of adsorption with silica.[2] A variety of solvents have been used in such work, but measurements

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[1] The material presented in this paper is from a dissertation submitted by George H. Scheffler to the Graduate School of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930. This paper was presented at a meeting of the Colloid Division of the American Chemical Society at Cincinnati, September, 1930.

[2] Bartell and Fu, *J. Phys. Chem.*, 33, 680 (1929); Holmes and McKelvey, *ibid.*, **32,** 1522 (1928); Th. Sabolitschka, *Pharm. Z.*, **74,** 382 (1929).

have been carried out only over a limited range of concentration. The adsorbate components have usually been the fatty acids, since for these the change in concentration due to adsorption can be determined by ordinary analytical methods.

In general the results have shown that, in the different homologous series studied, adsorption from an organic solvent is positive. This is to be expected as it is known that, other factors being equal, the greater adsorption is obtained of that component which has the higher adhesion tension against the adsorbent. The adhesion tension values of the fatty acids against silica are greater than are those of the solvents used. The fatty acids, accordingly, should be preferentially adsorbed. It has been found that for the fatty acid series the adsorption is decreased as the molecular weight of the fatty acid adsorbate is increased. Since the adhesion tension values of the different fatty acids against silica are similar, the difference in degrees of adsorption is probably due to the increasing solubility tendency of the adsorbate as its hydrocarbon chain is increased.

Because of the similarity in chemical constitution of the saturated monobasic alcohols and the fatty acids it seems reasonable to expect that the order of adsorption of an homologous series of the saturated monobasic alcohols by silica from benzene should be similar to that obtained for the fatty acids from benzene. The solubility tendencies of the alcohols in benzene should increase as their molecular weights increase. This tendency then should result in a lower adsorption of the higher alcohols from benzene.

If carbon be employed as the adsorbent for the alcohol systems instead of silica, the amount of adsorption of the alcohols should be much less, for the adhesion tension values of the alcohols against carbon are lower than the adhesion tension values against silica and, also, the adhesion tension values of the alcohols against carbon are lower than the adhesion tension of benzene against carbon. In fact, it should be expected that the preferential adsorption tendency with carbon, when considered for different concentrations extending over the entire concentration range, would be just about opposite to that with silica.

Neither volumetric nor gravimetric methods are suitable for measuring the changes in concentration of alcohols due to adsorption. Such changes were therefore measured by interferometric analysis. This method was found to be satisfactory for the determination of the slight concentration changes involved in the adsorption from the systems studied.[3] The accuracy of the method is high for the entire range of concentration.

Preparation of Materials.—The silica was prepared as described in a previous paper.[4] A large quantity was prepared in order that all the samples used should have identical properties.

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[3] Bartell and Sloan, THIS JOURNAL, 51, 1637 (1929).

[4] Bartell, Scheffler and Sloan, *ibid.*, 53,2501 (1931).

The carbon was a purified ash-free blood charcoal.[5] It was activated by heating for twenty minutes in a muffle furnace at a temperature of 1000°. It was cooled in dry air and was transferred directly to the adsorption flasks.

Standard methods were employed in the purification of the liquids. The middle fractions only were used in this work.

Results

The results obtained are indicated in the curves presented herewith. In order to conserve space, tables of data are not given. In Fig. 1 are given curves for the different alcohol–benzene systems with silica. In Fig. 2 are given the curves for the different alcohol–benzene systems with carbon. The modified Freundlich equation $H\Delta x/m = ax^n(1 - x) - b(1 - x)^d x$ was found to apply to all of these systems. The equations applicable to each system are:

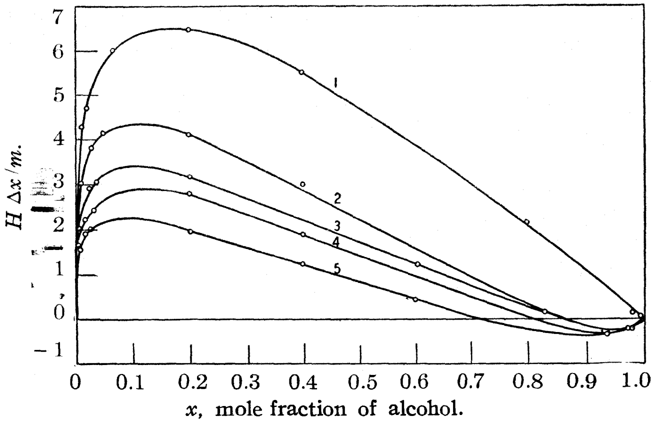

Fig. 1.—Adsorption by silica, alcohols from benzene: 1, methyl alcohol; 2, ethyl alcohol; 3, *n*-propyl alcohol; 4, n-butyl alcohol; 5, isoamyl alcohol.

Methyl alcohol–benzene–silica

$$H\Delta x/m = 11.429\ (x)^{0.215}\ (1 - x)$$

Ethyl alcohol–benzene–silica

$$H\Delta x/m = 8.840\ (x)^{0.227}\ (1 - x) - 4.664\ (1 - x)^{0.615}\ (x)$$

n-Propyl alcohol–benzene–silica

$$H\Delta x/m = 6.807\ (x)^{0.222}\ (1 - x) - 3.733\ (1 - x)^{0.684}\ (x)$$

n-Butyl alcohol–benzene–silica

$$H\Delta x/m = 7.261\ (x)^{0.222}\ (1 - x) - 4.808\ (1 - x)^{0.643}\ (x)$$

Isoamyl alcohol–benzene–silica

$$H\Delta x/m = 4.529\ (x)^{0.216}\ (1 - x) - 3.491\ (1 - x)^{0.600}\ (x)$$

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[5] This charcoal was furnished by E. J. Miller of the Michigan Agricultural Experiment Station.

Methyl alcohol–benzene-carbon

$$H\Delta x/m = 5.327\,(x)^{0.222}\,(1 - x) - 12.218\,(1 - x)^{0.465}\,(x)$$

n-Propyl alcohol–benzene–carbon

$$H\Delta x/m = 1.496\,(x)^{0.616}\,(1 - x) - 3.819\,(1 - x)^{0.323}\,(x)$$

n-Butyl alcohol–benzene–carbon

$$H\Delta x/m = 1.738\,(x)^{0.704}\,(1 - x) - 3.475\,(1 - x)^{0.324}\,(x)$$

Isoamyl alcohol–benzene–carbon

$$H\Delta x/m = 2.716\,(1 - x)^{0.270}\,(x)$$

As indicated in Fig. 1, the preferential adsorption of the alcohols by silica from an organic solvent (benzene) having a lower adhesion tension against silica than have the alcohols, decreases as the molecular weight of the alcohols increases. Figure 2 indicates that the preferential adsorption of the series of alcohols from the same solvent by carbon is in the same order, although much less, than with silica. This is because the solvent has a higher adhesion tension against the carbon than have the alcohols. This same solvent has a relatively low adhesion tension against silica and accordingly adsorption by this adsorbent must be high.

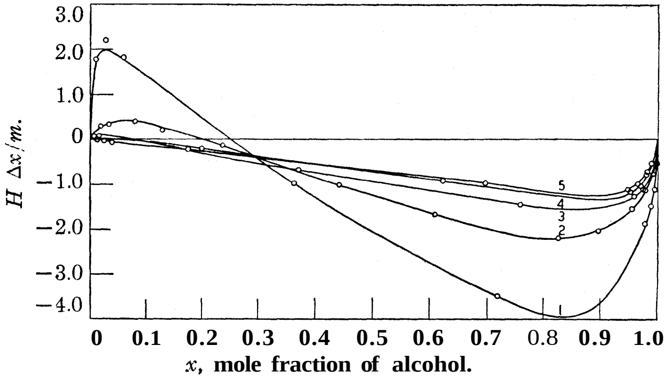

Fig. 2.—Adsorption by carbon, alcohols from benzene: 1, methyl alcohol; 2, ethyl alcohol; 3, n-propyl alcohol; 4, *n*-butyl alcohol; 5, isoamyl alcohol.

The results obtained are consistent and are in general what were to be expected from the energy relationships of the different systems.

Two sets of results only are not as might have been predicted. The results are those obtained with the methyl alcohol–benzene system with silica and the isoamyl alcohol–benzene system with carbon. All other binary organic liquid systems which have been studied have given S-shaped adsorption curves; that is, preferential adsorption of each of the components occurred over some portion of the concentration range. With the methyl alcohol–benzene–silica system no preferential adsorption of benzene could be detected with silica as adsorbent and with the isoamyl alcohol-benzene–carbon system no preferential adsorption of isoamyl alcohol was detected. These systems were checked repeatedly since at least a slight preferential adsorption was expected over the range indicated. Special precautions were taken to insure that perfectly dry (water-free) alcohol was used, but in no case were we able to obtain evidence of negative preferential adsorption over the range indicated.

After the completion of this work and after the paper had been written (June, 1930), a paper by Jones and Outridge[6] appeared on "Adsorption by Silicic Acid Gel in the System n-Butyl Alcohol–Benzene." Adsorption of the liquid components was studied over the entire concentration range. From their results they conclude, "No region occurs, in the high equilibrium concentrations of alcohol, where there is a negative selective adsorption of the alcohol . . . ." The solutions were analyzed by the "critical solution temperature" method of Jones.[7] Their adsorption curve for the n-butyl alcohol–benzene system was not S-shaped. This does not agree with the results presented in this paper for this system. While we shall not at this time attempt to account for the difference in the results obtained in these two researches we have no reasons to believe that our own results covering this system are in appreciable error.

Summary

1. The monobasic alcohols of the saturated hydrocarbon series **are** preferentially adsorbed by silica from benzene over the greater portion of the concentration range and in an order decreasing as the molecular weight increases. The preferential adsorption by carbon from similar systems is in the same order, is of much less magnitude, and occurs over but a limited portion of the concentration range.

2. The modified Freundlich equation which has been used in other investigations recently reported from this Laboratory was found to apply to the preferential adsorption effects for both the silica and the carbon adsorbents.

3. The degree of adsorption of one component, the adsorbate, from a binary organic liquid system is dependent upon the adhesion tension of that component against the adsorbent as compared to the adhesion tension of the solvent against the adsorbent, and also upon the solubility of the adsorbate in the solvent. The effect of solubility is noted when a series of compounds of similar adhesion tensions against an adsorbent are adsorbed from a given solvent, such as benzene. The greater the solubility of the adsorbate, the less will be its tendency to be adsorbed.

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[6] Jones and Outridge, *J. Chem. Soc.*, 1513 (1930).

[7] Jones, *ibid.*, **123,** 1392 (1923).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PURDUE UNIVERSITY]

EXTRACTION OF KRYPTON AND XENON FROM LIQUID AIR RESIDUES[1,2,3]

BY F. J. ALLEN AND R. B. MOORE

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Introduction

On account of the difficulty and expense of obtaining any considerable quantities of krypton and xenon, there has been little experimental work done with these elements except such as required only small amounts of the gases. Much credit is due to the pioneers in this field, who, in many instances, made up for scarcity of material with what might well be called a microtechnique.

Early in the study of the extraction of krypton and xenon from air it became evident that the evaporation of liquid air brought about an increased concentration of krypton and xenon in the residual liquid and this suggested that liquid air residues might well be the best source of these gases. Experience has confirmed this idea; hence the opportunity to obtain liquid air residues from a plant which carried on fractionation of liquid air on a large scale was welcomed in the hope that sufficient quantities of krypton and xenon might be obtained to permit of a more careful determination of some of their properties.

Source of Raw Material.—The Air Reduction Sales Company of New York kindly supplied cylinders of compressed gas. The bulk of gas in each cylinder was oxygen, but nitrogen, carbon dioxide, argon, krypton and xenon were also present, the latter two in proportions much greater than in ordinary air.

In the fractionation of liquid air the higher vapor pressure of nitrogen allows the liquid air in the still to become mainly oxygen, but with continuous operation there collect in this liquid oxygen the less volatile krypton and xenon.

It has been the custom at certain plants to discard periodically this liquid from the still. Arrangements, however, were made with the company referred to above to transfer liquid so withdrawn to large vacuum-walled vessels and to permit it to reduce its volume by evaporation and thus increase its proportion of krypton and xenon. When the volume had

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[1] A preliminary note in regard to this work has already been published, THIS JOURNAL, 52,4173 (1930).

[2] This paper represents part of a thesis submitted by F. J. Allen to the Graduate School of Purdue University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[3] Since the completion of this research, Dean R. B. Moore has died. This paper has not, therefore, had the benefit of his criticism. The thesis of which this is a part was, however, carefully gone over by Dr. Moore.

diminished sufficiently, the remaining liquid was poured into a metal cylinder of the type used for marketing compressed oxygen. The cylinder had been previously cooled with liquid oxygen. The valve was screwed in and the pressure checked after the cylinder and contents had come to room temperature. This cylinder was then sent to our laboratory.

Unfortunately, only the briefest sort of record was kept at the plant in regard to this procedure. Knowledge as to the quantity of liquid oxygen from the still, the fraction of this allowed to evaporate and kindred information would have been of much interest.

F. J. Metzger of the Air Reduction Company states that, "Each cylinder of gas represents the rare gases which we have been able to collect from about fifteen million cubic feet of air." It will be seen later that only a small proportion of the krypton and xenon actually in that volume of air got into the cylinders. Rabinowitsch[4] has concluded from a study of all the available data that the most reliable values that can be assigned for the percentages of krypton and xenon in the air are, respectively, 0.0001 and 0.00001. Six cylinders in all were received and the inert gases were extracted in a manner later to be described.

Experimental

Separation of Inert Gases from Liquid Air Residues.—The following workers have reported on the extraction and purification of krypton and xenon: Ramsay and Travers,[5] Ladenburg and Krügel,[6] Moore,[7] Dewar,[8] Valentiner and Schmidt,[9] Aston,[10] Claude[11] and Le Pape.[12]

A number of patents[13] dealing with the extraction of krypton and xenon have been granted.

The extraction of krypton and xenon for the present work had been completed before the papers of Claude and Le Pape were noted, the methods used following in general the principles established by earlier investigators.

The gas from the cylinder was freed from carbon dioxide by bubbling through a concentrated solution of potassium hydroxide and was next dried by calcium chloride and

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[4] Rabinowitsch, *Z. angew. Chem.*, 39, 737 (1926).

[5] Ramsay and Travers, *Trans. Roy. Soc. London*, **A197**, 47 (1901).

[6] Ladenburg and Krügel, *Sitzb. preuss. Akad. Wiss.*, 727 (1900).

[7] Moore, *Proc. Roy. Soc.* (London), **A81**, 195 (1908).

[8] Dewar, *ibid.*, 68, 362 (1901).

[9] Valcntiner and Schmidt, *Sitzb. preuss. Akad. Wiss.*, 38, 806 (1905)

[10] Aston, *Proc. Roy. Soc.* (London), **A103**, 462 (1923).

[11] Claude, *Compt. rend.*, 187, 581 (1928).

[12] Le Pape, *ibid.*, 187, 231 (1928).

[13] British Patent 226,783, Dec. 26, 1923, and British Patent 218,266, June 29, 1923, both assigned to Soc. anon. d'eclairage et d'applications électriques; British Patent 227,800, Jan. 19, 1924, and British Patent 236,217, June 25, 1924, both assigned to Soc. l'air liquide, and Soc. anon. pour l'étude et l'exploitation des procédés G. Claude.

passed through charcoal at the temperature of liquid air. At first the gas was metered out through a small gas meter, but experience soon showed that the rate could be adjusted suitably by the bubbling in the solution of potassium hydroxide and the total quantity of gas taken out in a given run could be calculated with sufficient accuracy from the initial and final pressures of the gage and the size of the cylinder.

The apparatus was in process of evolution throughout the entire investigation, but a few trials brought it to a fairly satisfactory stage. Figure 1 shows the plan of operation. It represents the set-up as used in the later runs. The various units were joined by means of heavy pressure tubing, but these connections are not shown in the figure.

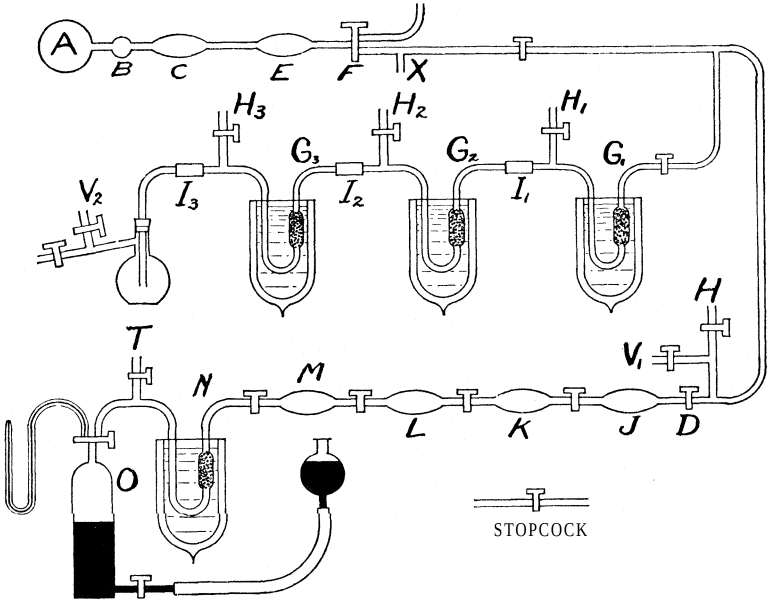

Fig. 1.—Diagram illustrating apparatus used to extract krypton and xenon from liquid air residues.

Gas from the cylinder A was passed through the gage B, the carbon dioxide adsorbers C, the drying agent E and through the two-way stopcock F. The two-way stopcock was put in as a safety unit to permit release of pressure in the event of the line becoming plugged. From F the gas flowed past a connection to a manometer X and on to the charcoal tubes G_1, G_2, G_3, which were cooled in liquid air.

It was not found practicable to prevent the formation of liquid oxygen in the charcoal tubes though reduced pressure was tried in the hope of doing so. The assumption was that krypton and xenon would be taken out by the cooled charcoal while the bulk of the oxygen passed on through. The results partly confirm this idea.

An average run consisted of passing about 300 liters of gas from the cylinder through the liquid-air cooled charcoal. The average rate of flow varied from one-half liter to one liter per minute.

When the gas from the cylinder was shut off, the charcoal tubes were clamped off and kept cooled by liquid air. G_1 was then permitted to deliver its gas through what is called, for want of a better name, the "inerting" line. By a suitable adjustment of stopcocks and of the clamps between the charcoal tubes, the gas could be sent from G_1,

G_2 or G_3 through D and through the soda lime J, the copper K, the drying agent L, the calcium M and could be taken into the charcoal tube N. This process of delivering from G_1 a large volume of gas, which, in the inerting line, is reduced to a small volume of inert gas capable of being collected over mercury in the reservoir O, is believed to be a new procedure. It obviates the use of large reservoirs for the collection and storage of the gases from G_1. Some care was required in the manipulation, such as a slow rate of addition of the oxygen-rich gas from G_1 to prevent over-heating in the copper filled tube.

Previous to use all charcoal tubes were baked out for about two hours under a vacuum of about 0.001 mm. and at a temperature of about 400°. The charcoal used was "Adsorbite," supplied by the Barnebey–Cheney Engineering Company of Columbus, Ohio.

Calcium was obtained in finely divided form by various methods, all of which were tedious. It would be a great advantage if this element were marketed in larger and more coherent lumps. With fair sized pieces good shavings were obtained on the lathe or shaper. Some shavings were drilled out but this is wasteful unless the honeycomb pieces remaining can be utilized. By far the most efficient results were obtained with a milling machine using a slow speed, spiral-grooved, cylindrical cutting tool. With larger lumps of calcium this method would be almost ideal.

The copper was prepared by reducing four mesh copper oxide with hydrogen. Care was taken to bring about the reduction at the lowest possible temperature and thus to obtain the copper in a condition of maximum porosity. The reduction can be carried out in an iron pipe but in the line the copper was contained in a large tube of Pyrex glass. This permits observation but is otherwise subject to criticism. Temperatures higher than the glass can safely stand are easily obtained by the action of the oxygen on the copper.

The "inerting" line, with the exception of the tube N which was baked out separately, was pumped out and the pumping maintained for about four hours while the calcium and copper tubes were strongly heated with bunsen burners. It was usually possible to attend to this part of the work while the run was going on; then as soon as the gas from the cylinder was shut off the gas from a G tube could be admitted through D and the soda lime to the copper by suitable clamp adjustment at I_1, I_2, etc.

The rate of flow of gas from G_1 could be controlled by regulation of the outlet stopcock and the depth of immersion in the liquid air. The line was kept open to the manometer and in all the work a reduced pressure was maintained whenever possible. This meant that in the event of a leak, gas would not be lost but only contaminated by having some air leak into it.

The copper had to be hot to start its action with the oxygen, but once started the burner could be removed, the action being so strongly exothermal as to cause a red glow to travel down inside the tube marking the zone of reaction. It was easy to overheat to the extent of having the glass soft enough to be pressed in against the tube contents. If this occurred only slightly it was usually possible to complete the run, especially if the defective place was kept hot, for on cooling such places often cracked.

As gas collected in the copper tube it was gradually let on through the drying agent to the calcium, which was kept as hot as the Pyrex tube in which it was contained would permit, and thence to the charcoal tube N.

When no more gas came from G_1 by removal of its liquid air bath, its temperature was gradually increased to about 450" with the line open all the way to N, which was cooled in liquid air. The manometer would soon show a fair vacuum. Tube N could then be closed to the line and allowed to deliver its gas to the mercury-filled reservoir O. On heating N to 450° practically all the remaining gas could be pumped off through the T connection to the Topler pump and added to the gas in O.

H could be put in connection with H_2, or H_3 when the gas was to be sent from G_2 or G_3, respectively, to the inerting line. V_1 and V_2 are for connection to the vacuum pump. T could be put in connection with the vacuum pump or the Töpler pump.

At any time during operation the gas from the line could be drawn back into G_1 or N. This was very convenient for example when a copper or a calcium tube needed to be replaced.

The gas from O was subsequently "re-inerted," that is, subjected to the action of fresh calcium. As a rule this "re-inerting" was carried out by passing the gas from O through an appropriate line to another reservoir and thence back to O, this process being repeated until no further diminution in volume was observed. The line contained copper, copper oxide, soda-lime and a drying agent in addition to calcium. This was considered necessary because of the possibility of some moisture getting to the calcium or to the calcium nitride and forming hydrogen or ammonia. Soddy[14] and more recently, Leatherman and Bartlett[15] have shown that under the proper conditions calcium is very efficient in removing all but the inert gases, but in this work a tube was sometimes used overlong with consequent loss of efficiency, hence the "re-inerting."

In the early trials only one 25-g. charcoal tube was used but later a second and third were added. In the last runs three tubes were used, each containing about 50 g. of charcoal. Inert gas was obtained from each one. Whether this gas was carried from one tube to the next by the action of liquid oxygen or whether too large a volume of gas was taken from the cylinder for the total capacity of the charcoal used or whether some other factor was operating remains to be investigated.

The average time for a run was twelve to fifteen hours, and several times as long was usually required between runs in getting the line in shape for use again. Unusual good fortune favored the work in that the accidents which occurred were not at critical times.

About 1100 ml. of inert gas was obtained from the six cylinders. A test run was made on a portion of the gas from the last cylinder received. A volume of 16 liters of gas from this cylinder was freed from all but the inert gases by passing it directly into the inerting line. The 16 liters reduced to 30 ml. of inert gas. This corresponds to about 0.2% inert gas in the gas from the cylinder. Since the cylinder contained 260 liters of gas from which 173 ml: of inert gas was obtained by the charcoal separation it appears that in this case the efficiency of extraction was about 35%.

The inert gas was made up largely of argon, not more than one-third of its volume being krypton and xenon.

Separation of Krypton and Xenon from Mixtures of Inert Gases and Preparation of Samples of Krypton and of Xenon of High Purity

The mixtures dealt with were made up of argon, krypton and xenon. The separation of these was checked by density determinations, the apparatus and method being that of Ramsay and Travers.[5]

The general scheme of purification starting with a sample of the inert gas mixture as it came from the "re-inerting" line will be first considered. The gas was condensed to a liquid or solid by making connection between the reservoir and an evacuated bulb dipping into liquid air. The bulb contents were next allowed to evaporate by reducing the pressure and several fractions thus obtained. The fraction coming off most readily would be mostly argon and that least readily, mostly xenon. The inter-

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[14] Soddy, *Proc. Roy. Soc.* (London), **A78,** 429 **(1906).**

[15] Leatherman and Bartlett, Ind. *Eng. Chem., Anal.* **Ed., 1, 223 (1929).**

mediate fractions ranged in composition from krypton in argon to krypton in xenon. This general method is that used by Moore[7] in his work. In any given series the fractions in numerical order are in order of increasing density.

In the preliminary work no attempt was made to check up on the density of the various fractions. When, however, several series of fractions had been obtained in the same way, combinations were made of the corresponding fractions in the several series and density determinations made for these composite samples.

The a, b and d series were thus grouped into the e series for which some data are given in Table I.

TABLE I

DATA FOR SERIES E FRACTIONATIONS

Sample number	Vol. of sample, ml.	Density of sample, g./l.
1	85	2.85
2	52	2.90
3	68	3.04
4	40	3.51
5	50	3.76
6	20	4.13
7	22	5.07
8	22	5.44

Since krypton and xenon have rather slight vapor pressures at the temperature of liquid air, some attempts to separate them were carried out at about −150°.

To obtain and hold this temperature a method was employed which will be referred to again later and which will be called "cold-air-stream cooling." The stream of cold air was obtained by forcing air through a copper coil immersed in liquid air. By careful regulation of the rate of flow of air through the coil and the depth of immersion of the coil in the liquid air a fair regulation of temperature could be obtained in an unsilvered "Dewar" tube into which the cold air was passed. By this method various temperatures from −170 to −100° were obtained. With extreme painstaking a temperature could be maintained within 1° for as long as fifteen to twenty minutes but for the fractionation work it was not felt necessary to maintain such careful control.

The fractionation of the samples richer in krypton and xenon was carried out in a manner somewhat different from that used with the first inert gas samples. Figure 2 will help make this clear.

Sample 1 is divided according to the best judgment of the worker into a a more volatile fraction 7 and a less volatile fraction 8. Sample 8 is added to sample 2 which is the next less volatile than 1 in the starting series used here (numbers 1–6) and fractions 9 and 10 obtained. The less volatile 10 with 3 gives 11 and 12, etc.

Samples 7, 9, 11, 13, 15, 17, 18 thus obtained are used as the starting series for repeating the process and obtaining eight new samples. A large number of fractionations of this sort were carried out and most of the argon was separated from the krypton and xenon.

Reference has been made to studies which showed differences in the adsorptive power of charcoal for argon, krypton and xenon at certain temperatures. These deal in the main with the idea of allowing a mixture of the gases to be adsorbed by charcoal and then obtaining a degree of separation by either slowly raising the temperature of the charcoal and collecting the gas first set free as mainly argon, the next as mainly krypton and that held most firmly and hence last to be given off as mainly xenon; or by a temperature difference between the gas containing charcoal and a fresh tube of charcoal free from any gas. In the latter case, for example, connection might be made between a charcoal tube containing the three gases at say −140° and a gas-free charcoal tube at the temperature of liquid air. With this temperature difference maintained for a period of one, two, or more hours the gas held least firmly would to a large degree migrate to the cooler tube.

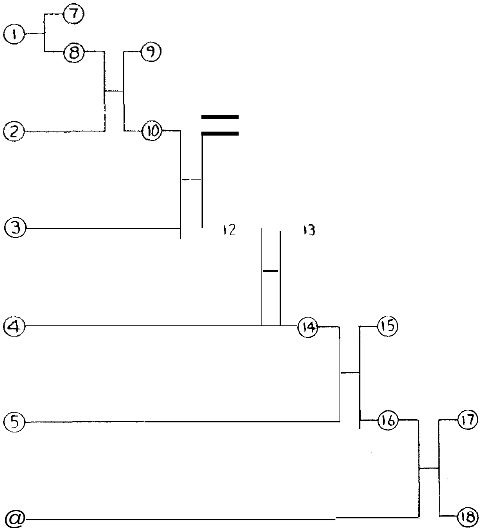

Fig. 2.—Diagram to explain fractionation of inert gas mixture.

A number of experiments were performed making use of the above method but it was soon apparent that a line was required which could be maintained "vacuum-tight" for hours at a time. The use of even the best obtainable vacuum tubing permitted some air to leak in. About fifteen trials were made, however, and the general indications were very favorable. A typical trial is described in the following paragraph.

A sample of gas of density 3.0 g./l. was taken into a five-gram charcoal tube (A) at the temperature of liquid air. Tube A was then allowed to warm up to −120° and was then placed in connection with a similar tube (B) which was at the temperature of liquid air. After three hours the connection between the tubes was closed and B was freed from gas by the usual process of baking and pumping out. The gas from B had a density of 1.7 g./l. Tube A was now brought to −80° and left for one hour in connection with B at liquid-air temperature. This time the gas obtained from B had a density of 3.2 g./l. The operation was repeated with **A** at 20° and B in liquid air again. This time fifteen minutes were allowed for gas to go from A to B and the gas from B had a density of 3.8 g./l. On baking out A a gas of density 4.7 g./l. was obtained. As stated before this method is not new but a density check on the separation as given above has not been previously reported.

The same general results were obtained in the other trials and as a result of these experiments considerable progress was made toward getting pure samples of krypton and xenon.

An inventory of inert gas samples on hand at this time gave results as shown in Table II.

TABLE II

DATA ON FRACTIONS OBTAINED IN PRELIMINARY PURIFICATION

Sample number	Density, g./l.	Approx. vol., ml.
I	1.8 ± 0.1	404
II	2.0 ± 0.1	114
III	2.3 ± 0.1	142
IV	2.7 ± 0.1	95
V	3.4 ± 0.1	63
VI	3.6 ± 0.1	154
VII	4.7 ± 0.1	53
VIII	6.4 * 0.1	29

The accepted densities for argon, krypton and xenon in grams per liter are, respectively, 1.78, 3.708 and 5.851.

Samples V–VIII show by their densities that they consist mainly of krypton and xenon. Accordingly steps were taken toward final purification. The method now employed was that which Ramsay[6] used in his final purifications, namely, the sparking of gas over moist potassium hydroxide after pure oxygen had been added to the inert gas. When further sparking gave no reduction in volume, the excess oxygen was removed by phosphorus, the usual precautions being taken to produce vigorous combustion.

Sample VI so treated increased its density from 3.6 to 3.9 g./l. It should be kept in mind that in all this work the gases were handled over mercury and every precaution was taken to avoid contamination of the samples, but even so traces of air got in, especially when samples had been transferred many times from tube to tube and from tube to reservoir or to pump and thence to other tubes as was necessary in carrying out the various steps in the purification. As higher grade samples were obtained, greater care was used to avoid contamination; in fact, "seasoned" tubes were used; that is to say, a krypton sample if transferred to the pump or fractionating bulb was returned to the tube which had contained it rather than to a tube in which the air had just been displaced by mercury.

Samples V, VII and VIII were also treated in the manner that has just been described for sample VI.

The next step in purification was fractionation and in the case of krypton this was a tedious process, since this gas, having a vapor pressure intermediate between argon and xenon, is hard to separate from them. Enough krypton must be allowed to distil away to carry out all the argon so that the process is far from economical. Better efficiency obtains in getting krypton from xenon but even in such a case some samples must be set aside which, though very largely krypton, contain traces of xenon. Repeated reworking of these "border line" samples permitted getting more and more of the krypton from them. The general scheme involved in fractionation has been explained already.

Sample VI after its purification by sparking yielded on fractionation a sample judged to be mostly krypton, since its density was 3.81 g./l. This fraction, about 90 ml. in volume, was refractionated to give five samples. Of these the first was set aside as possibly containing argon, although in these higher density samples the chance for argon to be present was rather slight. The second and third samples totaling about 60 ml. were fairly pure krypton, but the fourth and fifth were set aside as possibly containing xenon.

The 60 ml. of krypton referred to in the preceding paragraph was divided into three fractions and the middle one of about 30 ml. volume was used. Its density was found to be 3.733 g./l. The temperature of its triple point agreed closely with that of the sample of which it was the middle fraction and with that of another sample of high purity krypton the preparation of which will next be reported.

All second best samples of krypton which had been accumulated in the process of getting out the most nearly pure sample just referred to above were mixed together and repeatedly passed over strongly heated copper, copper oxide and then over calcium and were then dried by standing over phosphoric anhydride. This process was assumed to remove any gases not inert that might have got in as impurities. The treatment with oxygen followed by sparking in contact with potassium hydroxide was omitted. An all-glass apparatus was used which gave no evidence of leakage over a period of twenty-four hours.

The inert gas thus obtained was fractionated from a bulb which was connected to a manometer. There was small evidence of impurities more volatile than krypton; nevertheless, the first 10 or 12 ml. was pumped off and set aside. The next fraction, about 30 ml. in volume, was high grade krypton and its density was found to be 3.728 g./l. It is significant that the vapor pressure remained constant during the entire time that this second fraction was being pumped out. In fact no change was observed in the vapor pressure while the third and most of the fourth fractions were being pumped out. The pumping was stopped from time to time to check up on this by allowing time for equilibrium to be established. Toward the last the vapor pressure diminished, which was taken to indicate the presence of a small trace of xenon.

After the two samples of krypton of respective densities 3.733 and 3.728 g./l. had been used in vapor pressure studies, they were combined into one sample, and this was fractionated into five samples of which the first and last were very small (2–3 ml. each). The density of fraction 2 was found to be 3.737 g./l. and that of fraction 4 was 3.725 g./l., the difference being not greater than the probable experimental error and in the wrong direction to indicate the presence of xenon. The density bulb used held 21.92 ml. and the weight of krypton contained usually varied from 0.0500 to 0.0700 g. depending on the pressure at which the gas was supplied when the bulb was filled. **An** Ainsworth analytical balance was used and the weighings were not in error by more than ±0.0001 g.

The average of all density determinations on the high grade krypton gave a value of 3.733 g./l. and this gives a value for the atomic weight of krypton about 1% higher than that which is now accepted. Aston[16] states that his recent mass spectrograph studies indicate that the present atomic weight assigned to krypton is too low. He also states that there is good reason to believe that much of the information in the literature concerning krypton and xenon is subject to revision.

The atomic weight of krypton calculated from the 3.733 g./l. value and using Watson's[17] value for the compressibility of krypton comes out 83.6.

The xenon was purified by taking the highest density gas into a bulb at the temperature of liquid air and pumping out several fractions through the Tdpler pump. **A** middle fraction of about 50 ml. was fairly pure xenon. From this 50 cc. a middle fraction was taken later which was xenon of high purity. Its vapor pressure checked closely with a sample of xenon which Dr. R. B. Moore kindly loaned and which was known to be of high purity since it had been very carefully purified in order to determine the density of xenon. The present atomic weight of xenon was established from this sample of xenon. Also Aston had tested this sample and found it to show no evidence of krypton.

The density of xenon was found to be 5.887 ± 0.007 g./l. From this value the atomic weight of xenon would be 131.4 using Watson's[17] value for the compressibility of xenon.

Summary

A new method of handling liquid air residues from compressed gas cylinders has been used. This method permits obtaining the bulk of the inert gases present in the liquid air residues without the use of large gasometers and otherwise affords many advantages in manipulation.

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[16] Aston, Proc. *Roy. Soc.* (London), **A126,** 511 *(1929).*

[17] Watson, *J. Chem. Soc., 97,* **833** (1910).

Krypton and xenon of high purity have been extracted from liquid air residues.

Preliminary density determinations on the most carefully purified krypton and xenon indicate that the atomic weights assigned to these elements are too low.

New quantitative data on the partial separation of argon, krypton and xenon by means of suitably cooled charcoal have been reported.

Fractionations were carried out with a manometer in connection, thus permitting a check on the degree of separation by the change in vapor pressure.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PURDUE UNIVERSITY]

DETERMINATION OF CERTAIN PHYSICAL CONSTANTS OF KRYPTON AND XENON[1]

BY F. J. ALLEN AND R. B. MOORE

RECEIVED APRIL 15, 1931 PUBLISHED JULY 8, 1931

The preparation of samples of krypton and xenon has been reported by the authors in a previous paper.[2] On account of the small amount of experimental work that has been done with these elements it seemed desirable to recheck some of the physical constants. Accordingly plans were made to redetermine the triple point temperatures and pressures as well as the vapor pressures of the krypton and xenon in the range from the temperature of liquid air up to the boiling points of these gases.

The apparatus for the vapor pressure studies was of simple design and in part was patterned after that of Ramsay and Travers.[3] It consists, as shown in Fig. 1, of a siphon pipet (A) through which the gas may be introduced, a trap (B) to stop mercury, the bulb (C) which in operation dipped into an unsilvered Dewar tube into which also extended the copper tube supplying cold air and the platinum resistance thermometer and the open arm manometer (F) which was clamped to a glass scale ruled on a mirror. It should be noted that bulb C is offset, thus permitting more easy adjustment of the cooling assembly. Hair felt was packed snugly about the tubes leading into the Dewar so as to plug the neck and also

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[1] This paper represents part of a thesis submitted by F. J. Allen to the Graduate School of Purdue University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

Since the completion of this research, Peters and Weil have reported work on purification and properties of krypton and xenon: Z. *physik.* Chem., [A] 148, 1–35 (1930); Z. *angew.* Chem., 43, 608 (1930). The results reported in this paper in general agree very well with those reported by Peters and Weil.

[2] Allen and Moore, THIS JOURNAL, 53,2512 (1931).

[3] Ramsay and Travers, *Trans.* Roy. *Soc.* London, **A197,** 47 (1901).

extend some 5 cm. above the vessel itself. The copper tube supplying the cold air was insulated by a hair felt wrapping throughout the major part of the length from its liquid air bath to the neck of the Dewar tube.

After the work on vapor pressure was once in progress, no gas was admitted to the line except the samples of krypton and xenon and since the less pure samples were used in the first trials it would seem reasonable to think that these served to "wash out" the apparatus. On several occasions the apparatus was left standing under vacuum for more than a week with no perceptible inleak of gas.

The apparatus once exhausted was supplied with the krypton or xenon through A, and C was cooled to the desired temperature. The temperature was then allowed to rise very slowly, thus causing a gradual increase of the vapor pressure. At intervals readings were taken on the manometer, barometer and resistance box. These readings were not quite simultaneous since for the most part they were all made by one observer, but it was possible to adjust the resistance box to the proper reading to get the temperature from the platinum resistance thermometer and then very quickly to read the manometer. The barometer reading could then be obtained with some leisure since its change was not likely to be rapid enough to matter even if the reading were taken several minutes later.

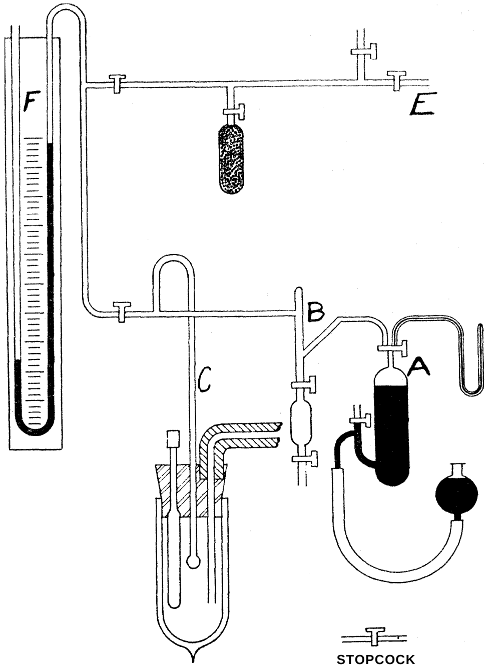

Fig. 1.—Apparatus for finding melting points, boiling points and vapor pressures of krypton and xenon.

Experience showed that on cooling, the vapor pressure was slow to diminish to a minimum value for a given temperature, hence the idea of taking the readings while the temperature was slowly increasing. If, for example, the equilibrium pressure at -150° was desired, the gas would be cooled several degrees below that temperature and allowed to increase slowly to -150°. The temperature change was at the rate of about 0.05" per minute.

Table I shows the vapor pressures found for krypton. Sample A is the one of density 3.728 g./l. and sample B is the one of density **3.733** g./l.

The error in the temperature reading was probably of the order of 0.1" and of the vapor pressure +20 mm., except for the equilibrium pressure at the triple point of krypton, which is not in error by more than ±3 mm. The results indicate that Ramsay and Travers'[3] value on the melting point is far from correct. They give −169.1° for krypton as compared with the −156.6° found in this investigation.

TABLE I

VAPOR PRESSURES OF KRYPTON

Sample A		Sample B	
Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm
−158.3	524	−159.0	476
−158.0	530	−158.0	503
−157.4	539	−157.1	528
−157.1	549	−156.6"	556
−156.7"	558	−156.3	599
−156.6"	558	−154.8	653
−156.3	609	−154.7	679
−155.5	634	−154.4	681
−155.2	649	−154.1	705
−154.4	707	−154.0	716
−154.3	705	−153.6	726
−153.6	750	−153.4	739
−152.9	787	−153.1	749
−132.7	790	−152.9	764
−152.3	816	−152.7	775
−152.0	824	−152.2	803

[a] **Values for the triple point.**

The results also show that the accepted value of −151.8° for the boiling point of krypton is too high, a better value being −153.1°, although the results here reported are not so satisfactory for the boiling point as for the triple point.

The triple point was best observed by getting the solid krypton or xenon in the bulb in as fluffy and snow-like a form as possible and watching for it to melt as the temperature rose. The snow-like form could be produced by cooling the element in the liquid form to the temperature where it was about to solidify and then quickly reducing the pressure for an instant, e. *g.*, by opening momentarily to a low pressure space in A. This usually resulted in a sort of "explosion" of the liquid into solid. The temperature was next kept slightly below the temperature of the triple point found on previous trials until time had been allowed for attainment of equilibrium and then was permitted to rise slowly. With krypton the vapor pressure rose as the temperature rose, up to the triple point, where the pressure held constant until most of the solid had melted. The earlier trials served to develop a technique which permitted more careful work in later ones.

Dr. R. B. Moore and Mr. G. C. Finger assisted in checking the triple point for the krypton from which the sample of density 3.733 grams per liter was later taken as a middle fraction. The average of five trials gave −156.5°, the lowest temperature being −156.8° and the highest −156.3°.

Xenon was less satisfactory to deal with than krypton. The change from solid to liquid was not nearly so sharply defined nor was the corresponding pressure. The quantity of xenon which had been most carefully purified was insufficient to fill the apparatus at the pressure of the triple point and was accordingly supplemented by the high purity xenon loaned by Dr. Moore. Results are shown in Table II.

TABLE II

VAPOR PRESSURES OF XENON

Sample of density 5 887 g /l.

Trial 1		Trial 2	
Temp., °C.	Pressure, mm	Temp. °C.	Pressure, mm.
−117 2	465	−119 1	454
−116 2	491	−116 2	482
−115 3	501	−114 4	523
−114 4	525	−113 5	544
−113 4	560	−112 2	571
−113.2	583	−112 0	581
−113.0	586	−111.7	581
−112 9	588	−111 6	585
−112.7	590	−110 7	602
−112 6	594	−107 6	750
−112 2	600	−107.2	755
−112.0	604	−107 0	760
−111.7	618		
−109.2	723		
−109.0	717		
−108.0	756		
−107 1	760		
−106.9	771		
−104 3	846		

The erratic behavior of xenon in the vicinity of its triple point suggests the possibility of a transition point of the solid xenon to a different solid form just below the triple point. The results show the triple point of xenon to be between −111.0" and −112.0" and the boiling point to be between −106.9" and −107.4". The only other value that has been reported for the triple point is that of Ramsay and Travers, namely, approximately −140°. The above investigators gave −109.1" for the boiling point of xenon. Patterson, Cripps and Whytlaw-Gray, using some of the xenon purified by Moore,[4] reported a boiling point of −106.9°, but since this was based on extrapolated values they considered it of doubtful accuracy.

In this connection it may be pointed out that the literature shows rather a small range of temperature between the melting and boiling points

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[4] Moore, *Proc. Roy. Soc.* (London), **A81,** 195 (1908).

of the other rare gases. This work indicates the range for krypton and xenon to be more in keeping with other members of the family.

A summary of the values which this work indicated to be most reliable is found in Table III.

TABLE III

SUMMARY OF RESULTS

	Krypton	**Xenon**
Density in grams per liter	3.733 ± 0.007	5.887 ± 0.009
Atomic weight	83.6 ± 0.2	131.4 ± 0.3
Boiling point, °C.	−152.9 ± 0.3	−107.1 ± 0.3
Triple point temperature, °C.	−156.6 ± 0.1	−111.5 ± 0.5
Triple point pressure, mm.	557 ± 3	600 ± 20

The temperatures were determined by the use of a platinum resistance thermometer, a Wheatstone box bridge set-up being used to measure the resistances.

The galvanometer was of the cylindrical type manufactured by the Leeds and Northrup Company of Philadelphia. It was mounted on a wall shelf and fitted with a telescope and scale. It far exceeded the need as to sensitivity since a difference in resistance corresponding to 0.01° could be detected easily and temperatures are given in this report to 0.1".

The accuracy of the box bridge was checked by connecting a resistance box calibrated by the Bureau of Standards, in place of the platinum resistance thermometer. The bridge was not in error over the range used with krypton and xenon by an amount sufficient to affect the temperature values given as stated above to 0.1".

The platinum resistance thermometer was also a Leeds and Northrup instrument of the type designed especially for low temperature work. Constants for the Van Dusen[5] equation were supplied by a calibration made by the Bureau of Standards and this equation was used to calculate a set of data relating temperature and resistance. From the data so obtained a curve was plotted so that if a value were known for the resistance of the platinum, the corresponding temperature could be read from the curve. The scale used made one mm. equal 0.2° and one mm. equal 0.02 ohm.

Grateful acknowledgment is made to colleagues in the Chemistry Department of Purdue University for helpful suggestions as well as occasional assistance with the experimental work.

Mr. W. E. Fish, department mechanician, often worked after regular hours and on holidays preparing the liquid air which was needed for the work, sometimes in amounts up to fifteen or twenty liters per day. His helpful cooperation has been greatly appreciated.

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[5] Van Dusen, THIS JOURNAL, 47,326 (1925).

Summary

New values are reported for temperatures and pressures for the triple points of krypton and xenon.

Studies of the vapor pressures of krypton and xenon have been made, principally in the range of temperature just including the triple points and boiling points. The results indicate the accepted values for the boiling points to be in error and new values are reported.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE PHOTO-POLYMERIZATION OF STYRENE AND VINYL ACETATE

BY HUGH S. TAYLOR AND ARTHUR A. VERNON

RECEIVED APRIL 17, 1931 PUBLISHED JULY 8, 1931

In a number of oxidation processes sensitive to light the chain reaction theory has been shown to account satisfactorily for the phenomenon of inhibition of oxidation in such systems. An examination of the quantum yield of these photo-reactions shows that a large number of molecules react per light quantum absorbed, that the light absorbed, therefore, starts a chain of secondary oxidation processes. It has been known now for some time that many polymerization processes are light sensitive and also show the phenomenon of inhibition by added agents. Thus far, however, quantitative studies similar to those with oxidation reactions have been lacking. An additional interest attaches to such studies with processes of polymerization. It has been shown by Alyea and Bäckström,[1] in certain reactions, that the inhibitor in oxidation processes is oxidized in the process of breaking the reaction chains. Such a fate for the inhibitor molecule is impossible in polymerization processes carried out in the absence of oxygen. The question suggests itself, therefore, as to the nature of the inhibitory act in a polymerization reaction. It was to gain some insight into the quantitative aspects of the photo-polymerization that the following studies were made.

Only recently has any attention been given to the quantitative side of the question although references to qualitative experiments and reaction products are frequent. The theoretical side of the polymerization has drawn attention more recently as is indicated by the work of Carothers,[2] Staudinger[3] and Moureu and Dufraisse.[4]

[1] Alyea and Backstrom, THIS JOURNAL, 51, 90–109 (1929).

[2] Carothers, *ibid.*, 51, 2548 (1929).

[3] Staudinger, *Ber.*, 62, 2893 (1929); 62, 2933 (1929).

[4] Moureu and Dufraisse, *Bull. soc. chim. France*, [4] 35, 1564 (1924). Since the completion of this work an article has appeared by Starkweather and G. B. Taylor [THIS JOURNAL, 52, 4708 (1930)] describing experiments made to determine the kinetics of the thermal polymerization of vinyl acetate.

In order to broaden the scope of the investigation, two compounds—styrene and vinyl acetate—were used to study the photochemical polymerization process. Both of these compounds contain an ethylenic bond but oxygen is present in only one,

Experimental Details

Apparatus.—In most of the experimental work, the source of illumination was a vertical mercury arc of the Cooper–Hewitt type operating at about **175** watts. The liquids were illuminated in Pyrex reaction vessels made from tubing **2** cm. in diameter and **15** cm. long. By means of a ground-glass joint at the top, an inlet tube was immersed in the liquid to within **1 cm.** of the bottom. An outlet was provided by a tube in the Pyrex vessel **2** cm. below the ground-glass joint. Both inlet and outlet tubes were provided with stopcocks. The liquid under study could be thoroughly flushed out by allowing a stream of oxygen-free hydrogen to pass in the inlet tube and out at the outlet tube. By closing the stopcocks the liquid could be sealed in an atmosphere of hydrogen and the reaction carried out under these conditions. This procedure was necessary since oxygen was found to influence the reactions and their velocities.

To obtain several checks on each experiment as rapidly as possible, a round copper vessel **10** cm. in diameter and **15** cm. high was used. Through the center of this was fastened by means of a water-tight joint a quartz tube about **2.5** cm. in diameter. The vertical mercury arc was supported in this tube. Water was circulated in and out of the copper vessel and, by means of a heater, any desired temperature up to 100° could be maintained.

Measurement **of** Reaction **Rate.—A** method was used which was suggested by Dr. G. B. Kistiakowsky. One cubic centimeter of the original solution was dissolved in a given amount of benzene and the freezing point of the benzene determined by the usual Beckmann method. After illumination, the same procedure was followed. In this case, the depression was less due to polymerization. Since the molecular weight of the polymer is at least of the order of 3000–4000,[5,6] it can safely be assumed that the effect of the polymeric molecules upon the freezing point of the benzene is negligible as compared with that of the rest of the molecules present. From the differences in the depression of the freezing point of benzene before and after illumination, the amount polymerized could be calculated. These measurements were supplemented by viscosity determinations on the same solutions.

Materials Employed.—In the experiments with styrene, a commercial preparation consisting of a 46% solution of styrene in ethylbenzene, supplied by the U. S. Rubber Company. was employed. To prepare the solution for illumination, the mixture was steam distilled in a partial atmosphere of hydrogen after the system had been freed of oxygen. The distillate was separated from the water, dried over oxygen-free calcium chloride and stored over hydrogen in a ground-glass stoppered bottle. The final styrene content of the purified solutions was determined by polymerizing the styrene with stannic chloride, precipitating the polymer in ethyl alcohol, filtering, drying and weighing.

For the experiments with vinyl acetate, a 30% solution by volume of vinyl acetate in ethyl acetate was employed. The vinyl acetate was kindly supplied by the Union Carbide and Carbon Chemical Corporation and the ethyl acetate was of high grade. In preparing these solutions for illumination, each constituent was distilled in hydrogen separately, the two were mixed in an atmosphere of hydrogen and stored over hydrogen.

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[5] Stobbe and Posnjak, **Ann., 371, 259 (1909).**

[6] Staudinger, **Ber., 59, 3019 (1926).**

Experimental Results

Influence of Oxygen on Polymerization.—This was determined by separating a solution of styrene into two parts. One part was stored over hydrogen and the other part over oxygen. Samples were removed at various intervals and allowed to undergo photo-polymerization at 100° under identical conditions. No correction for thermal polymerization was made in these tests, the results of which are given in Table I.

TABLE I

EFFECT OF OXYGEN ABSORPTION ON PHOTO-POLYMERIZATION OF STYRENE

Time of storage, hours	Contact with H_2 % polymerized per hr	Contact with O_2 % polymerized prr hr
0	**ti 39**	6 39
48	6 50	9.14
96	6.20	9 15
144	5.85	10 25

This summary shows the acceleration due to absorbed oxygen and also the degree of constancy of result obtained when the mixture stands in contact with hydrogen. In all succeeding experiments, values within 10% of those indicated above for contact with hydrogen were recorded.

A further check upon this point was made by testing a solution which had been distilled in vacuum after having been steam-distilled in oxygen-free hydrogen. The results of this experiment indicated a polymerization rate which was within 10% of those given in Table I for contact with hydrogen.

The conclusion from these results is evident. Light alone may cause polymerization of styrene and the true rate of the photo-process is obtained with the hydrogen-distilled samples. That oxidation of styrene, whether thermal or photochemical, is also accompanied by polymerization is evident and, hence, the results of the polymerization of solutions stored over oxygen indicate a sum total of both of these effects. Table I shows that the increase due to complete oxygen saturation is about 50%; but the polymerization due to a very small percentage of oxygen in the hydrogen-prepared solution would be negligible as compared with that due to the ultraviolet light.

TABLE II

EFFECT OF OXYGEN ABSORPTION ON PHOTO-POLYMERIZATION OF VINYL ACETATE

Time of storage, hours	Contact with H_2, % polymerized per hour	Contact with On, % polymerized per hour
0	29.0	29.0
18		20.0
24	29.0	
48		**12.0**
90	29.5	
114		2.0
138	32 0	

The effect of oxygen upon the polymerization of vinyl acetate is different. Here oxygen inhibits the polymerization. The tests upon vinyl acetate solutions were made in the same way as were those with styrene. The results of these tests are embodied in Table II.

Effect of Temperature on Polymerization Velocity.—Using the method as outlined previously, photo-polymerizations were made at temperatures of 30, 70 and 100° in the case of styrene and at 40 and 70" in the case of vinyl acetate solutions. The curves for Fig. 1 and Fig. 2 are plotted from the results of two typical experiments. The straight lines were obtained from freezing point depression measurements while the curves record viscosity changes. The viscosity curve brings out the impossibility of using viscosity measurements to determine the rate of polymerization unless a viscosity–concentration curve has first been made.

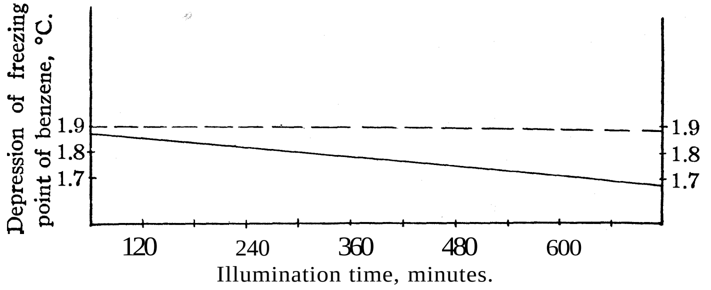

Fig. 1.—Polymerization of styrene–ethylbenzene solution: — — —, thermal, 70°; —, photochemical. 70°.

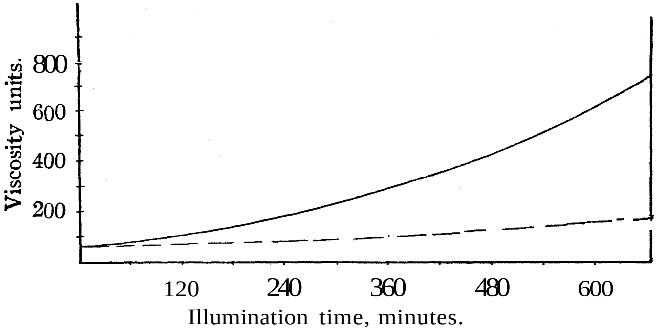

Fig. 2.—Polymerization of styrene-ethylbenzene solution: — — —, thermal, 70°; —, photochemical, 70°.

There is a measurable thermal polymerization of styrene at 70 and 100° which must be taken into consideration when temperature coefficients are determined. At 30° no correction was necessary with styrene and at neither 40 nor 70° was a thermal correction necessary for vinyl acetate. From the freezing point depression curves, rates of reaction can be measured and from these temperature coefficients determined. The results are given in Table III. They have been corrected for thermal effect where necessary.

TABLE III

TEMPERATURE COEFFICIENT OF PHOTOCHEMICAL POLYMERIZATION

Solution	Temperature interval, °C.	Temp coefficient per 10° rise
Styrene	30–100	1 30
Styrene	30–70	1 33
Styrene	70–100	1.27
Vinyl acetate	40–70	1 26

To interpret these results it is necessary to know whether the absorption of the solution changes with temperature, since the wave lengths involved are near the absorption limits of the solutions. To determine this, a monochromator was set up with a mercury arc as the source of light. The emitted light from the monochromator was focused upon a potassium hydride photo-electric cell. The recorder was a sensitive Moll galvanometer connected in series with the cell. No change in light absorption with temperature could be observed within the accuracy of the measurements, which was about 5%.

Effect of Concentration on Polymerization Velocity.—Solutions of several different concentrations were made and these were illuminated for the same length of time. The freezing point depression changes were determined and each polymerized solution was then diluted with ethylbenzene or ethyl acetate to a concentration of 10% by volume. The viscosities of these diluted solutions were thus determined at comparable concentrations. The results of these experiments are incorporated in Tables IV and V.

TABLE IV

CONCENTRATION–VELOCITY DATA FOR STYRENE IN ETHYLBENZENE

Concentration, %	Viscosity change, units	Change in dep. of f. p. of benzene, °C.
10	50	0.03
30	84	.16
65	150	.20
100	149	.305

TABLE V

CONCENTRATION–VELOCITY DATA FOR VINYL ACETATE IN ETHYL ACETATE

Concentration, %	Viscosity change, units	Change in dep. of f. p. of benzene, °C.
13	20	0.10
65	44	.14
100	230	.45

To determine whether these results were due to concentration variations, to light absorption variations, or to both, monochromatic light was used with an arrangement as described previously. A quartz vessel was used for the absorption cell and the loss due to reflection was obtained by measurement on the vessel filled with ethyl acetate and ethyl benzene, respectively. Measurements were made with solutions of three different concentrations and from these the absorption coefficients were calculated using the equation

$$I_{\text{abs.}} = I_{\text{ent.}}\ (1 - e^{-\alpha c})$$

where I_{abs} is the intensity of the absorbed light, $I_{\text{ent.}}$ is the intensity of the entering light, α is the absorption coefficient and c is the concentration of the absorbing constituent. The values of the coefficients are necessary to calculate the absorption for the lowest concentration of solution, since the absorption in this case was too low to measure accurately. In the following table these data are incorporated.

TABLE VI

ABSORPTION DATA FOR VINYL ACETATE IN ETHYL ACETATE

Concentration, %	3100 Å. Measured abs., %	3100 Å. Corrected abs., %	Coefficients	3600 Å. Meas. abs., %
0	10	..	....	..
13	..	6	0.00434	0
30	22.5	14	.0050	0
60	30.0	23	.00430	0
100	38.0	31	.00372	0
		Average	.00434	

TABLE VII

ABSORPTION DATA FOR STYRENE IN ETHYLBENZENE

Concentration, %	3100 Å. Measured abs., %	3100 Å. Corrected abs., %	Coefficient	3600 Å. Meas. abs., %
0	20	..	....	..
10	..	12	0.0125	2
30	44	30	.0119	9
60	66	57.5	.0140	17
100	75	69.0	.0115	20
		Average	.0125	

The above tables give all the data necessary to interpret the experiments which have been summarized in Tables IV and V.

Effect of Inhibitors.—Hydroquinone was selected as the inhibitor to be studied since it was found to have a large effect and, therefore, could be used in small concentrations. The experiments were made with 40% styrene solution at 100° and 30% vinyl acetate solution at 70°. Table VIII gives a summary of these results.

As shown by Anderson and Taylor,[7] an inhibitor may act in either or both of two ways. In one case it may cause a decrease in reaction rate by

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[7] Anderson and Taylor, THIS JOURNAL, 45, 650 (1923).

TABLE VIII

INHIBITORY EFFECT OF HYDROQUINONE

Styrene in ethylbenzene		Vinyl acetate in ethyl acetate	
Concentration of hydroquinone	% of normal polymerization rate	Concentration of hydroquinone	% of normal polymerization rate
1 mole in 160	2	1 mole in 150	2
1 mole in 400	24	1 mole in 300	10 8
1 mole in 800	49.1	1 mole in 1500	27 0
1 mole in 4000	86	1 mole in 3000	50.0

absorbing light which would otherwise be used to produce a reaction. In the other case it may cause a decrease in reaction rate by some inhibitor mechanism. Ratios of absorption of styrene or vinyl acetate to that of hydroquinone under the conditions of the experiments were not determined but the fact that hydroquinone does absorb[8] seems to explain the relationship between concentrations of inhibitor and reaction rate. This will be discussed later.

Quantum Yields in the Polymerization.—A series of experiments was made to find the variation of quantum yield with wave length of absorbed light. The first measurements were made with the line of wave length **2300** Å. The source of the energy was a high voltage interrupted spark discharge across cadmium electrodes in air, constructed by Dr. G. B. Kistiakowsky. In order to determine the quanta which fell upon the system, it was desired to use the decomposition of oxalic acid sensitized with uranyl ions. This has been shown by Bowen and Watts[9] to have a quantum yield of one and a temperature coefficient of unity in the near ultraviolet.[10] Experiments made in light of wave length **2300** to 2500 Å. indicated that for our purpose the value of Bowen and Watts could be employed.

Quantum yield measurements were made at $\lambda = 2536$ Å. with both vinyl acetate and styrene. For this a hot mercury arc and chlorine–bromine filter were used. A correction was made for the visible light which passed through the filter and the decomposition of oxalic acid–uranyl acetate solutions was used to determine the number of quanta falling on the system. The absorption of the **2536 Å.** line was measured by means of a thermopile.

Finally the quantum yield was determined when exposed to the mercury arc as in the original experiments. This is designated as the quantum yield at wave lengths between $\lambda = 3000$ Å. and $\lambda = 4000$ Å. Pure styrene and pure vinyl acetate were exposed in a quartz reaction cell. This cell was immersed in a Pyrex water-bath and thus the conditions of the original

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[8] "International Critical Tables," Vol. V, p. 361.

[9] Bowen and Watts, J. Chem. *Soc.*, 129, 1607 (1926).

[10] Recently Leighton and Forbes [THIS JOURNAL, $2,3139 (1930)] have found that a more careful determination indicates a quantum yield of 0.49 to 0.60 in ultraviolet light. However, since the polymerization quantum yields here presented are only orders of magnitude, the value of Bowen and Watts is sufficiently accurate.

experiments were reproduced. The results of these experiments are summarized in Table **IX.**

TABLE IX

POLYMERIZATION QUANTUM YIELDS

	Vinyl acetate			Styrene		
Wave length, A.	Yield, molecules/$h\nu$	Temp., °C.	Remarks	Yield, molecules/$h\nu$	Temp., °C.	Remarks
2300	1.7	50	Pure liquid	...	..	......
2536	1.2	50	Pure liquid	7.4	70	40% solution
3000–4000, inc.	935	65	Pure liquid	4.0	90	Pure liquid

Discussion

Effect of Oxygen.—Moureu and Dufraisse[4] pointed out the effect of oxygen upon the photo-polymerization of acrolein and found that small amounts of this gas caused a very great increase in rate of polymerization. Since then there has been a tendency to attribute photo-polymerization to peroxide formation. No objection, theoretically, can be advanced against assuming that polymerization can occur as a consequence of molecules initially activated by light. The experiments described in this paper represent the distinct separation of these two methods of polymerization. **It** seems well established that polymerization may be induced by light which is absorbed by the molecules in question and that all the data of this paper represent the various phases of such a process.

Effect of Temperature.—The curves of Fig. 1 and Fig. 2 are typical of those from which the values of Table II were calculated. Calculations were made from the viscosity curves to find how the viscosity of the solution changed with temperature for the same percentage polymerization as shown by freezing point depression measurements. The results of the calculations are given in Tables X and **XI.** The values for the percentages

TABLE X

CHANGE IN SIZE OF POLYMER WITH TEMPERATURE FOR STYRENE SOLUTION

Total % polymer	Viscosity change at		
	30°, units	70°, units	100°, units
1 35	5	8	20
3 37	15	26	60
6 75	40	72	135
10 6	80	130	200
16 9	245	290	480
21 2	320	450	760

TABLE XI

CHANGE IN SIZE OF POLYMER WITH TEMPERATURE FOR VINYL ACETATE SOLUTION

Total % polymerized	Viscosity change at	
	40°, units	70°, units
14.3	220	220
42.9	2000	1440
57.2	4000	2800

where the viscosity change is less than 50 units are subject to a large error of reading. The other values represent reliable data.

An examination of these tables would seem to indicate that the aggregates of styrene are of a much larger size at high than at low temperatures. This would be different from the thermal polymerization as studied by Staudinger.[6] However, any more definite conclusions from these tables must wait for more experiments to determine completely this viscosity relationship. It would seem that, for styrene, the photochemical effect is stronger than the thermal, while for vinyl acetate the thermal effect somewhat overbalances the photochemical. It is evident, in any case, that the temperature effect is much different in the case of styrene than in the case of vinyl acetate.

Effect of Concentration on Reaction Velocity.—The change in reaction rate with concentration is due entirely to the change in absorption of light with concentration. This is evident by comparing Tables VI and VII with Tables IV and V.

A calculation of per cent. polymerized at the various concentrations shows a practically constant value. This lends further proof to the explanation given previously.

Effect of Inhibitor.—Inhibition which was due to deactivation by collision with the foreign molecules would be inversely proportional to the inhibitor concentration. If the inhibitor also acted in some other way as, for example, by screening, the decrease in reaction rate would be correspondingly greater. Table VIII shows that for styrene solutions a change of inhibitor concentration from 1 molecule in 160 to 1 molecule in 400 produced over a ten-fold change in reaction velocity. A similar effect is evident for vinyl acetate.

Since the only factors present in our case were deactivation by collision and screening by absorption of the active light, it seems clear that the inhibiting effect was due to both of these causes. The belief that hydroquinone could deactivate by collision was further substantiated by the results of some thermal experiments. In these tests it was found that hydroquinone was effective in preventing the thermal polymerization when present in concentrations of the order of magnitude of 1 molecule in 1000.

Quantum Yields.—The quantum yields given in Table IX represent the number of molecules which gather together as a result of the absorption of one quantum of light energy. The values of Table IX are in all cases upper limits of the quantum yields. The low quantum yield of vinyl acetate in light of wave lengths shorter than 3000 Å. was probably due to decomposition.

An example of the quantum yield calculations is given below.

Quantum Yield of Vinyl Acetate Polymerization at λ = 3000–4000 Å.—1. Quanta absorbed by vinyl acetate in one hour as determined from oxalic acid–uranyl acetate experiment and measurements of the relative absorption of vinyl acetate and oxalic acid solution were 1.07×10^{19}.

2. (a) Initial depression of freezing point of benzene due to 1 cc. of vinyl acetate in 25 cc. of benzene = 2.095°.

(b) Change in depression after illumination for one-half hour = 0.11°.

(c) Temperature = 65".

(d) Grams of vinyl acetate exposed = 13.5 *g*.

Therefore the number of molecules of vinyl acetate polymerized in one hour

$$2 \times \frac{0.11}{2.095} \times \frac{13.5}{86.06} \times 6.06 \times 10^{23} = 1.0 \times 10^{22}$$

$$\text{Hence, the quantum yield at } 65° = \frac{1.00 \times 10^{22}}{1.07 \times 10^{19}} = 935 \frac{\text{molecules}}{h\nu}$$

Conclusions

The photochemical polymerization results which have been presented indicate that the polymerization process has many of the characteristics of a chain mechanism. The initially activated molecule initiates the reaction by combining with another molecule. This process is exothermic and as a result these two are energy-rich and can add a third to their aggregate. This addition process continues until the energy of the group is insufficient to cause the addition of another member. This loss of energy may be caused by collision with foreign molecules of the solvent, by collision with the walls or by distribution over the whole aggregate to such an extent that further reaction is impossible.

The authors wish to express their thanks to Dr. G. B Kistiakowsky for his aid in developing the experimental procedure and interpreting the results.

Summary

1. Several phases of the photochemical polymerization of styrene and vinyl acetate have been investigated. A method of studying photochemical polymerizations has been developed which gives reproducible results and avoids all effects due to oxygen absorption.

2. Oxygen aids but is not necessary for the photo-polymerization of styrene.

3. Oxygen inhibits the photo-polymerization of vinyl acetate.

4. Both reactions have temperature coefficients markedly greater than unity.

5. The effect on the reaction velocity of a change in concentration of polymerizing constituent depends upon the change of light absorption with concentration of that constituent.

6. The orders of magnitude of the quantum yields have also been determined for several wave lengths. They indicate clearly that the polymerization process involves a chain mechanism.

PRINCETON, NEW JERSEY

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

THE ENERGY OF ACTIVATION FOR BIMOLECULAR REACTIONS INVOLVING HYDROGEN AND THE HALOGENS, ACCORDING TO THE QUANTUM MECHANICS

BY HENRY EYRING[1]

RECEIVED APRIL 23, 1931 PUBLISHED JULY 8, 1931

Experiment shows that in homogeneous bimolecular reactions the specific reaction rate constant, k, is approximately

$$k = Se^{-A/RT} \tag{1}$$

A is the energy of activation and the proportionality factor, *S*, is equal to the number of collisions at unit concentration of the colliding substances. An *a priori* method of determining *A*, therefore, would make possible the prediction of rates of reactions.

Heitler and London,[2] using the quantum theory, were able to account satisfactorily for the binding of two hydrogen atoms. The so-called zeroth approximation as evaluated by Sugiura[3] gave a binding energy equal to three-fourths of the experimental value. The term "binding energy" will be used to indicate the energy which must be supplied to break the bonds in question. It is, therefore, the negative of the potential energy of the system referred to the dissociated state as the state of zero energy.

The perturbation theory yields expressions for the binding energy of three and four atoms. Agreement between theory and experiment for some typical cases involving three atoms has been reported elsewhere by Polanyi and the author.[4] They made the calculations for the reactions $H_{2para} + H = H_{2ortho} + H$; $Br + H_2 = HBr + H$ and $Br_2 + H = HBr + Br$ and have also considered the dynamics of such reactions. Many details of calculation were also given which it has not been deemed necessary to repeat here. Certain bimolecular reactions involving three and four atoms are considered below.

London[5] gives for the binding energy, E, holding three monovalent atoms together the expression

$$E = Q + \left[\frac{1}{2}\left((\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2\right)\right]^{1/2} \tag{2}$$

The limitations on this formula will be discussed later. In equation (2) Q is the coulombic binding between three atoms, *i. e.*, the binding energy that one would calculate using classical electrodynamics if one assumed the

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[1] Presented March 31, 1931, as part of the Symposium on "Applications of Quantum Theory to Chemistry," Indianapolis Meeting of the American Chemical Society.

[2] W. Heitler and F. London, Z. *Physik*, 44, 455 (1927).

[3] V. Sugiura, *ibid.*, 45, 484 (1927).

[4] Eyring and Polanyi, *Z. physik Chem.*, [B] *12, 279* (1931).

[5] (a) London, *Z. Electrochem.*, 35, 552 (1929); (b) Sommerfeld Festschrift, S. Hirzel, p. 104.

electrons to be the diffuse clouds of quantum mechanics. The coulombic energy is really the sum of three terms: $Q = A' + B + C$. The A is primed to distinguish it from the activation energy. To define these quantities further, consider the three atoms W, X, Y, which form the triangle of Fig. 1. The energy required to make the distances r_1, r_2, r_3 simultaneously very large is E of Equation 2. The binding between the atoms W and X when Y is far away is $E_1 = A' + a$, and depends only on the distance r_1. Similarly the binding between X and Y with W far away is $E_2 = B + \beta$ and depends only on r_2; and between W and Y with X far away, the energy is $E_3 = C + \gamma$. The energy $E_1 = A' + a$ plotted as a function of r_1 is just the familiar Franck curve for the diatomic molecule, WX. Such curves may be readily constructed using spectroscopic data; it is thus possible to calculate E of Equation 2 if either the coulombic or the interchange binding is known.[6]

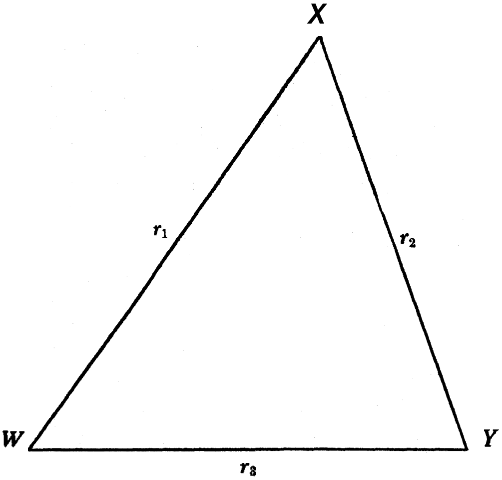

Fig. 1.

Morse[7] has obtained a convenient function which gives the dependence of the binding energy, E, on the distance, r, between the atoms for a diatomic molecule. In this equation

$$E = D'(2e^{-a(r-r_0)} - e^{-2a(r-r_0)}) \qquad (3)$$

a is defined by the equality $a = 0.1227\, \omega_0(M/D')^{1/2}$. D' is the heat of dissociation of the molecule plus the half quantum of vibrational energy it has in the lowest level. ω_0 is the vibration frequency in the lowest level and M, the reduced mass, is defined by the expression

$$M = \frac{M_1 \cdot M_2}{M_1 + M_2}$$

where M_1 and M_2 are the atomic weights of the two elements. D' and ω_0 are to be taken in wave numbers.

E_1 can thus be obtained from optical data and A', the coulombic part of the potential energy, can be calculated from the approximate wave functions of Zener[8] and Slater? The interchange binding a is then given by

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[6] H. Eyring, *Naturwissen.*, 44, 915 (1930).

[7] Morse, *Phys. Rev.*, 34, 57 (1929).

[8] Clarence Zener, ibid., 36, 51 (1930).

[9] J. C. Slater, *ibid.*, 36, 67 (1930).

the relationship $\alpha = E_1 - A'$ with similar expressions for β and γ. The direct calculation of the interchange binding is not feasible both because of the difficulty of such a calculation and because of the approximate nature of the eigenfunctions.

In what follows, however, the coulombic binding will be taken as 10% of the total binding for all values of r, *i. e.*, the theoretical value for H_2. It was shown in a previous paper[4] that in the case of H_2, for all values of r important in determining the energy of activation, the theoretical coulombic binding energy is about 10% of the total theoretical binding energy and about 8% of the empirically found binding energy. This assumption for other gases, while not strictly correct, will make possible a comparison of the theory with experiment and leads to some striking qualitative predictions which depend only on the coulombic binding being approximately 10% of the total.

Consider the reaction

$$WX + Y = W + XY \tag{3a}$$

To begin with, the distance r_1 may be supposed to have the normal value r_0 for the molecule WX while r_2 and r_3 are very large. The total binding energy is thus equal to $A' + \alpha$. If the atom Y is made to approach the molecule WX in such a way as to keep $\beta = \gamma$, the radical in Equation 2 will decrease continuously, becoming zero when $\alpha = \beta = \gamma$; *i. e.*, three identical monovalent atoms at the corner of an equilateral triangle have no interchange binding.

Examination of Equation 2 shows that Y may approach WX with the smallest increase of potential energy of the system if all the atoms remain on a straight line. In this case two distances, say r_1 and r_2, will fix the third, r_3, and so determine the energy of the configuration. If r_1 and r_2 be plotted at right angles to each other and lines of equal energy be drawn, a contour map results which gives the potential energy of the system. Such a map for three hydrogen atoms is given (Fig. 2).

In Fig. 2 the course of the reaction $H_{2\text{para}} + H = H_{2\text{ortho}} + H$ is indicated by the broken line and the arrows. To begin with, r_2 is very large and $r_1 = 0.76$ Angstrom ($A' + \alpha = 107.6$ Calories, *i. e.*, the heat of dissociation plus a half quantum of vibration), then as the H atom approaches the para hydrogen molecule the potential energy increases adiabatically until the distance $r_1 = r_2 = 0.93$ Ångström when 11.4 Calories of potential energy have been stored up. This is the activation energy for the reaction. The reaction can now go to completion or the system may return to its former configuration. If r_1 increases the reaction goes to completion. The 11.4 Calories is the minimum value of the energy along the line $r_1 = r_2$, *i. e.*, $\alpha = \beta$, but it is the maximum value along the line with arrows which represents the course of the system during the reaction. It is thus a saddle value and may be calculated from Equation 2 by setting

$\alpha = \beta$, finding the minimum, and subtracting this value from the heat of dissociation of the hydrogen molecule. For reactions with unlike atoms the saddle value will not occur along the line $r_1 = r_2$ but will still be along the curve $\alpha = \beta$. Thus the energy of activation, A, for the reaction

$$WX + Y = W + XY \tag{3a}$$

is $A = D - (Q + \alpha - \gamma)_{\text{min.}}$. Here D is the heat of dissociation of the molecule WX and $(Q + \alpha - \gamma)_{\text{min.}}$ is the minimum value for this quantity

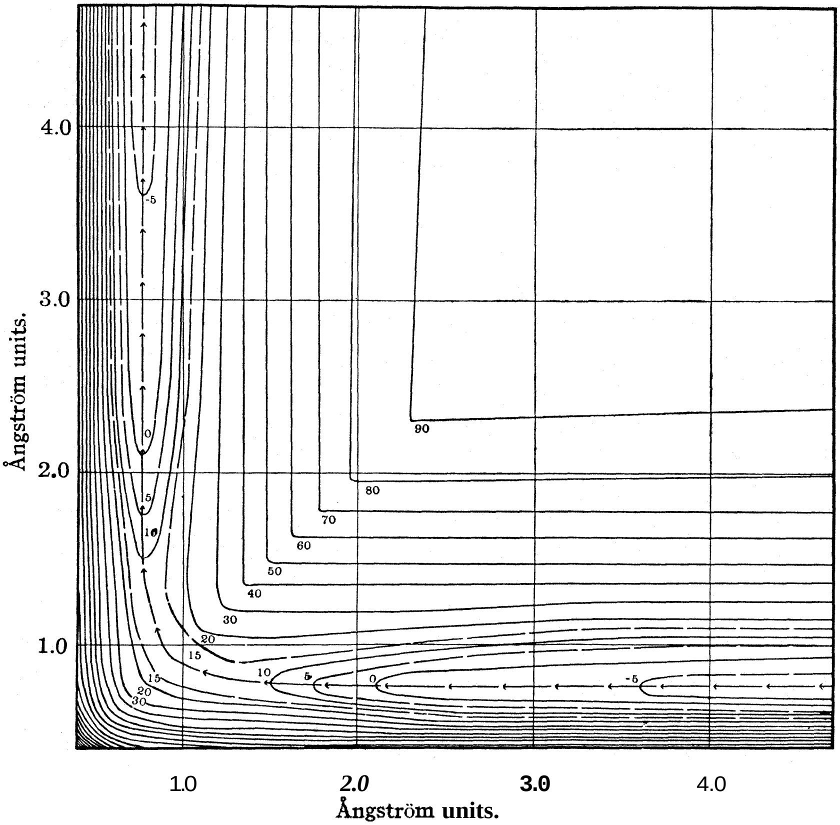

Fig. 2.

along the curve $\alpha = \beta$. It is important to remember that all binding energies are taken, like the heat of dissociation itself, as the negative of the potential energy, referred to complete dissociation as the zero of energy.

This reaction may thus be visualized as the motion of a mass point under the impetus of its kinetic energy moving up a valley until the lowest place in the divide between this valley and a neighboring valley is reached. Here the point may either return or pass over into the adjoining valley. The quantum mechanics provides still another alternative. The point may pass through the energy mountain without bothering to go over the divide. Langer[10] discusses this possibility for chemical reactions. The chance of this happening falls off exponentially with the square root of the area enclosed between the line through the mountain and the one over the divide. This process becomes very improbable for the gentle slopes met in this type of reactions. The probability of going over the top of the mountain falls off exponentially with the height and does not depend on the slope.

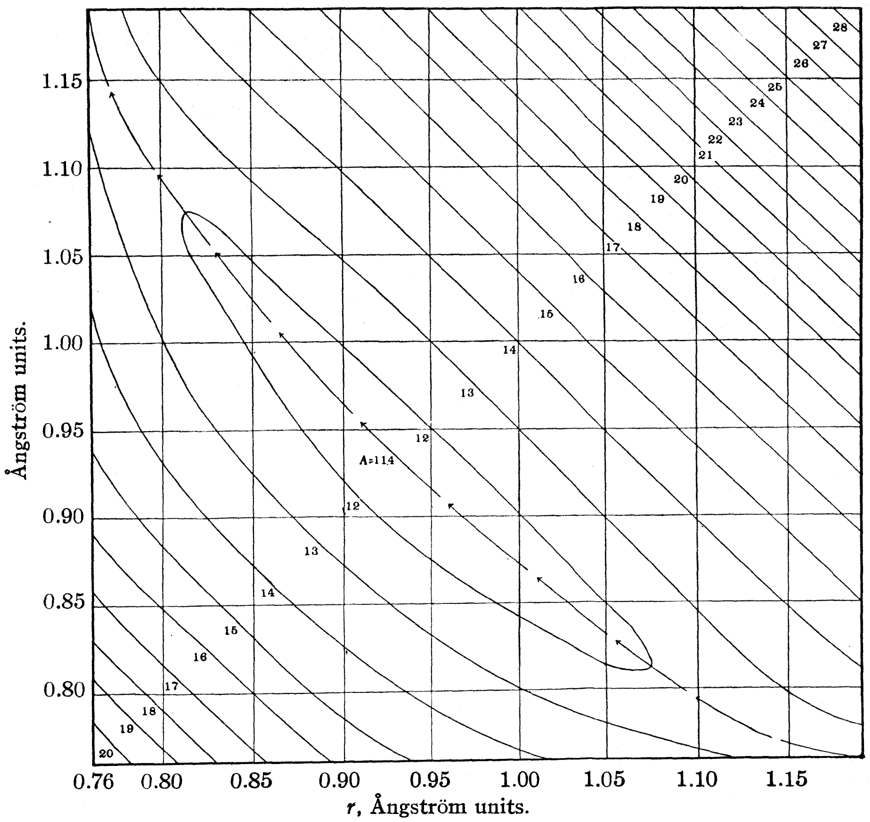

Fig. 3.

It is this exponential dependence on kinetic energy which makes it improbable that the mass point will arrive at the top of the divide with much excess kinetic energy. Thus the height of the divide measured from the bottom of the first valley can be identified with the energy of activation for the forward reaction, whereas for the reverse reaction the height of the divide must be measured from the second valley. The difference in the height of the two valleys is the heat of reaction. Having reached the top

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[10] R. M. Langer, *Phys. Rev.*, **34**, 92 (1929).

of the divide, if P_1 represents the chance that the mass point will return to the first valley and P_2 the chance that it will continue on into the second, the entropy of the reaction is $\Delta S = R \ln (P_2/P_1)$.

A closer examination of the potential energy surface for three hydrogen atoms as shown in Fig. 3 reveals a slightly more complex surface than Fig. 2 would lead one to suspect. The configuration of lowest potential energy for which both of the outer hydrogen atoms are symmetrically placed with respect to the central atom is 11.4 Calories higher than the configuration in which the hydrogen atom is far away from the hydrogen molecule but this symmetrical configuration, instead of corresponding to a saddle value, is really the floor of a shallow basin with a rim 1.6 Calories higher in the direction of the two valleys. However, since it is rather difficult to calculate the exact position and height of the rim of the basin and since in the reactions with which we are concerned the difference between the height of the rim and the floor of the basin will be about a Calorie and a half the values included in Table II are for the floor of the basin.

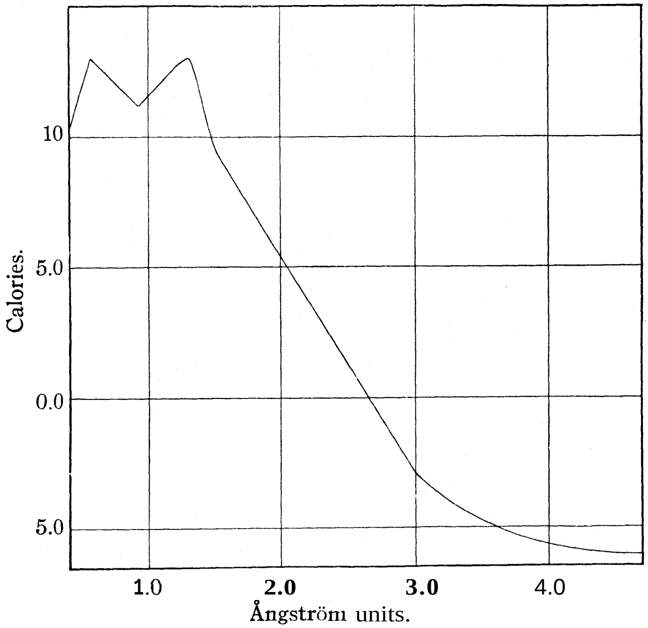

Fig. 4.

In Fig. 4 one simply sees in elevation the section through the contour map 2 traversed by the arrows. Because of the complete symmetry the section is only carried a little way beyond the symmetrical basin.

In Fig. 4 the smallest possible potential energy of the three atoms in a straight line is plotted as ordinate while as abscissa the distance between the nearest atom in the molecule and the approaching free atom is plotted until the symmetrical position is reached at 0.93 Angstrom. From here on the distance between the receding atom and the nearest atom of the new molecule is plotted as abscissa. The profile shows that an H_3 molecule is so unstable (heat of dissociation 1.6 Calories) that even if the heat of formation were carried away it would survive only a very few collisions and consequently has no existence in the ordinary chemical sense.

For reactions involving more atoms the potential energy surface will depend on more than two positional coordinates but with this single exception the discussion just given applies without essential change.

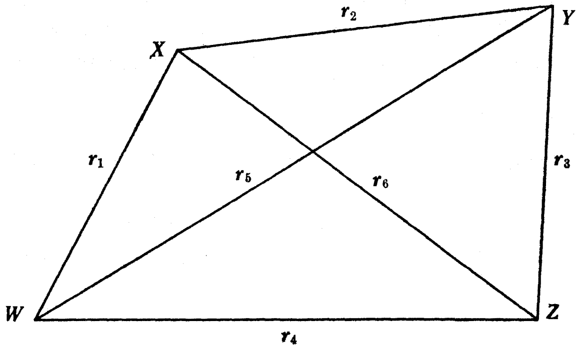

Fig. 5.

For the binding energy, E, of four atoms London[6]'' has given the value

$$E = Q + \sqrt{\frac{1}{2}((\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2)} \tag{4}$$

The coulombic energy, Q, has the value Q $= A_1 + A_2 + B_1 + B_2 + C_1 + C_2$. In this equation, α_1 and A_1 depend only on r_1 of Fig. 5; and the dependence of the other quantities may be indicated by writing $\alpha_2(r_3)$, $\beta_1(r_2)$, $B_1(r_2)$, $B_3(r_4)$, $B_2(r_4)$, $\gamma_1(r_5)$, $C_1(r_5)$, $\gamma_2(r_6)$, $C_2(r_6)$. Each of these quantities has the same meaning as in the three atom case and may be determined in the same way from the binding of diatomic molecules.

The reaction may be written

$$WX + YZ = WZ + XY \tag{5}$$

Reaction 5 consists in passing from a configuration in which only r_1 and r_3 are small to a final one in which only r_2 and r_4 are small. The system will necessarily pass through an intermediate configuration for which $\alpha_1 + \alpha_2 = \beta_1 + \beta_2$. A simple argument shows that this is the smallest value E is forced to take in the reaction (*i. e.*, the largest potential energy the system must take) and so is the one to use in calculating the activation energy.

First it may be shown that the reaction will take place with the four atoms in a plane. For suppose any configuration in a plane has been reached, such, for example, as that shown in Fig. 5. Keep all distances except r_5 fixed and make it smaller. Since $(\gamma_1 + \gamma_2) < (\alpha_1 + \alpha_2)$ and also $(\gamma_1 + \gamma_2) < (\beta_1 + \beta_2)$, this change in r_5 which increases γ_5 will decrease the radical in Equation 4. Q will increase but by a smaller amount so that the total binding will be diminished. Since changes occurring in reaction can all take place in a plane and since every departure from a plane decreases the binding energy, it follows that in the activated state all the atoms will lie in a plane. Four identical atoms at the corners of a symmetrical tetrahedron have no interchange binding.

Next consider the change in E for $(\alpha_1 + \alpha_2) = (\beta_1 + \beta_2)$ and $\delta(\alpha_1 + \alpha_2) = -\delta(\beta_1 + \beta_2)$. Then the change in $(\gamma_1 + \gamma_2)$, *i. e.*, $\delta(\gamma_1 + \gamma_2)$ will be negative since this change can be carried out in such a way as to increase the length of r_5 and r_6, and the change in the total binding energy, E, is

$$\delta E = \delta Q + \frac{1}{2}\frac{(\alpha_1+\alpha_2-\gamma_1-\gamma_2)(\delta(\alpha_1+\alpha_2)-\delta(\gamma_1+\gamma_2))+(\beta_1+\beta_2-\gamma_1-\gamma_2)(\delta(\beta_1+\beta_2)-\delta(\gamma_1+\gamma_2))}{\sqrt{\frac{1}{2}((\alpha_1+\alpha_2-\beta_1-\beta_2)^2+(\alpha_1+\alpha_2-\gamma_1-\gamma_2)^2+(\beta_1+\beta_2-\gamma_1-\gamma_2)^2)}}$$

$$= \delta Q - \frac{(\alpha_1+\alpha_2-\gamma_1-\gamma_2)\delta(\gamma_1+\gamma_2)}{\sqrt{\frac{1}{2}((\alpha_1+\alpha_2-\beta_1-\beta_2)^2+(\alpha_1+\alpha_2-\gamma_1-\gamma_2)^2+(\beta_1+\beta_2-\gamma_1-\gamma_2)^2)}}$$

but $(\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2) > 0$ and $\delta(\gamma_1 + \gamma_2) < 0$ so that for δQ small, which is true for reactions with large activation energies, δE is positive, or becomes positive after emerging from the very shallow coulombic basin (depth of the order of a Calorie and a half), which we can ignore as in the case of three atoms. This shows that the reaction WX + YZ = WZ + XY reaches a configuration when $\alpha_1 + \alpha_2 = \beta_1 + \beta_2$ such that the reaction can proceed in either direction with a decrease in the potential energy. Thus to find the activation energy one finds the minimum value of Equation 4 subject to the condition

$$\alpha_1 + \alpha_2 = \beta_1 + \beta_2 \tag{6}$$

which is just the minimum value of $E' = Q + \alpha_1 + \alpha_2 - \gamma_1 - \gamma_2$. This quantity subtracted from the sum of the heats of dissociation of WX and YZ gives the energy of activation.

The following scheme was used in calculating the activation energies given below. First, potential energy curves were constructed for all molecules entering into the reactions. The necessary constants were taken for the most part from the "International Critical Tables" and from Landolt–Bornstein.

r_0 for bromine was calculated from Morse's relation $r_0^3\omega_0 = 3000$. The constants in Table I for hydrogen, bromine and hydrogen bromide are slightly different than those used by Eyring and Polanyi.[4] The difference arises from taking the constants from different sources, and represents a slight uncertainty rather than an improvement. The effects on the calcu-

TABLE I

CONSTANTS USED IN DETERMINING THE MORSE EQUATION

Gas	D	D'	r_0	a	ω_0
H_2	101.5	107.6	0.76	1.85	4262
F_2	63.5	65	1.4	2.39	1071.5
Cl_2	58	58.8	1.74	2.22	570
Br_2	45.7	46.2	2.09	2.00	326.6
I_2	34 5	34.8	2.66	1.50	213.9
HI	69	72.2	1.62	2.28	2272
HBr	82.1	85.8	1.42	1.83	2603
HCl	101.5	105.7	1.28	1.77	2940.8
HF	146.5	152.2	0.023	2 00	3987
ICl	50.7	51.2	1.99	1.84	382

lated activation energies are very small, as a comparison of the results shows.

D in the table is the heat of dissociation in large calories and D' is the heat of dissociation plus a half quantum of vibrational energy. The other quantities have been defined. Consider for example the reaction

$$I + H_2 = HI + I$$

The maximum value of $(A + B + C + \alpha - y)$ was calculated for the case of the three atoms on a line where in addition $\alpha = \beta$. This maximum value was then subtracted from the heat of dissociation of hydrogen, giving the energy of activation.

Two series of activation energies were calculated: one in which A, B and C were taken as 10% of the corresponding bonds, and the second for which they were taken as 3.5%.

For reactions of the type

$$H_2 + I_2 = 2HI$$

the maximum value of

$$(A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \alpha_1 + \alpha_2 - \gamma_1 - \gamma_2) \tag{7}$$

was calculated subject to the conditions $(\mathrm{cur} + \alpha_2) = (\beta_1 + \beta_2)$. By considering (4) it can be shown that for the saddle value $r_2 = r_4$ and $r_5 = r_6$. Using these conditions, the maximum value of (7) is soon found. This maximum value is subtracted from the sum of the heats of dissociation of hydrogen and iodine to give the energy of activation. In Table II the results of the calculations are tabulated.

The first column in Table II gives the letter which will be used in referring to the reaction in the second column. The third to sixth columns give the distances between the atoms in the activated state. For three atom reactions the distances to which the r values refer will be clear from considering the general expression (3a) for a reaction in connection with Fig. 1. For four atom reactions the same information is obtained by considering equation (5) in conjunction with Fig. 5. Columns 7 and 8 give the calculated energy of activation when the coulombic binding

TABLE II

ENERGIES OF ACTIVATION IN K. CAL.

	Reaction	r_1	$r_2 = r_4$	r_3	$r_5 = r_6$	A_{10}	$A_{3.5}$	$A_{\text{exp.}}$	References
a	$H_2 + I_2 = 2HI$	0.86	1.78	3.17	2.43	28	40	40	11, 12
b	$H + I_2 = HI + I$					0	0		
c	$H_2 + I = HI + H$	1.23	1.67		2.90	29	41	>23	
d	$H_2 + Cl_2 = 2HCl$	0.93	1.70	1.87	2.15	54	75	>39	
e	$H + Cl_2 = HCl + Cl$					0	0	<10	13
f	$H_2 + Cl = HCl + H$	0.93	1.43		2.36	14	25	>10	14, 15, 16, 20
g	$H_2 + Br_2 = 2HBr$	0.94	1.72	2.28	2.26	45	62	>43	
h	$H + Br_2 = HBr + Br$					0	0	<10	13
i	$H_2 + Br = HBr + H$	1.13	1.53		2.66	26	32	19 to 30	13
j	$H_2 + F_2 = 2HF$	0.93	1.50	1.50	1.90	50	71	>25	17
k	$H + F_2 = HF + H$					0	0		
l	$H_2 + F = HF + H$	0.84	1.33		2.17	5	15	> 0	17
m	$I_2 + Cl_2 = 2ICl$	2.83	2.25	1.85	3.20	12	20	>15	18
n	$Cl_2 + I = ICl + Cl$	1.96	2.10		4.05	5	7		
o	$I_2 + Cl = ICl + I$					0	0		
p	$2H_{2\text{para}} = 2H_{2\text{ortho}}$	1.20	1.20	1.20	1.70	96	115	>55	
q	$H_{2\text{para}} + H = H_{2\text{ortho}} + H$	0.93	0.93		1.86	11	21	4 to 11	19

is taken as 10 and 3.5%, respectively. Column 9 gives the available experimental information on energies of activations. Activation energies are in kilocalories and distances in Ångströms.

To the theoretical activation energy of a reaction of the type $H_2 + I = H + HI$ must be added half the heat of dissociation of I_2 in order to obtain the apparent activation energy for the thermal combination of hydrogen and iodine by way of the atoms. This follows from thermodynamic considerations. Thus the theory shows the combination of hydrogen and iodine will not involve the atoms since this would require an activation energy greater by $41 + 17 - 40 = 18$ Calories than if the reaction involved only molecules. This value is arrived at using the figures in Column 9; exactly the same conclusion is reached using Column 8. Column 8 indicates that bromine will react with hydrogen without dissociating into atoms. Column 9 indicates it will involve atoms. Experimentally it is known to go through the atoms. On the other hand, all the other halogens

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

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

[13] E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119,** 285 (1926).

[14] Coehn and Jung, *ibid.*, **110,** 705 (1924).

[15] Bodenstein and Dux, *ibid.*, 85, 297 (1913).

[16] R. G. W. Norrish, *ibid.*, **120,** 205 (1926).

[17] H. N. Wartenberg and J. Taylor, *Nachr. Ges. Wiss. Gottingen. Geschaft. Mitt. Math.-physik. Klasse,* **1,** 119 (1930).

[18] Gibson and Liebhafsky, unpublished.

[19] L. Farkas, *Z. physik. Chem.*, [B] **10,** 419 (1930).

[20] H. v. Hartel, *ibid.*, [B] **11,** *96* (1930).

will react with hydrogen by way of the atoms. This is in agreement with experiment. The theory also shows that the change of para to ortho hydrogen will proceed by way of the atoms. This too is correct, as Farkas'[19] experiments show.

This evidence is particularly cogent since with the exception of bromine it is independent of the fraction of the binding energy taken to be coulombic and so is direct evidence for the correctness of the adiabatic theory of reactions. Another interesting bit of evidence for the theory may be given.

The energy of activation for a three-atom reaction is $A = D - Q - \alpha + \gamma$. The three atoms in the activated state lie on a line thus: WXY and α is the interchange binding which would exist between W and X and also between X and Y if in each case the third atom were removed. γ is the interchange binding which would exist between W and Y if X were removed without altering the distance between W and Y. Since γ falls off with the distance between W and Y, a lower activation energy is to be expected for reactions in which the central atom is large, *i. e.*, for the halogens the activation energy should decrease progressively as the central atom changes through the series from fluorine to iodine. This fact is suggested and beautifully illustrated by some recent experiments of v. Hartel and Polanyi.[21]

Reactions	Activation energy
$CH_3F + Na = CH_3 + NaF$	25
$CH_3Cl + Na = CH_3 + NaCl$	8.8
$CH_3Br + Na = CH_3 + NaBr$	3.2
$CH_3I + Na = CH_3 + NaI$	0

They suggest that a proportionately greater coulombic binding, Q, for the heavier halogens, together with weaker binding, D, may partly account for this trend. There is, however, no indication in Table II that the coulombic part of the binding is greater for the heavier atoms.

Experimental values are not given in Table II for the reaction of hydrogen atoms with the halogens. However, the experiments of Boehm and Bonhoeffer[13] show that the mean life of hydrogen atoms in the presence of Cl_2 and Br_2 is less than a hundredth of a second and Polanyi shows that the ratio of the rates is as seven to one. These facts are at least consistent with the theoretical activation energy of zero Calories for both reactions.

The heat of dissociation of 63.5 kilocalories for fluorine estimated by Wartenberg and Taylor[1'] is rather uncertain. If, however, even a value as high as 82.6 kilocalories be assumed, the activation energies for (j) are, respectively, 56 and 79 kilocalories; for (k) they are zero and zero and for (l) are 6 and 13 kilocalories for Columns 8 and 9, respectively. These changes would affect none of our conclusions and the intermediate value of

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[21] H. v. Hartel and Polanyi, *Z. physik. Chem.*, [B] **11**, 97 (1930).

72 kilocalories for D estimated by Mullikan[22] would give intermediate values of the activation energies.

The numerical agreement between the calculated and experimental activation energies in Table II is as good as could be hoped for and indicates the essential correctness of the theory. Better checks must await more accurate experiments as well as the theoretical evaluation of the ratio of coulombic to total binding. The latter, though difficult, is by no means impossible. The above theoretical calculations suffice, however, to decide whether bimolecular reactions will involve single atoms or not and give the actual activation energies as accurately as they are known experimentally in a majority of the cases considered. Taking explicit account of the fact that the valence electron on the halogens is a p-electron would not change the activation energy for three atom reactions but would increase it for four atom reactions. This is in a direction to give better agreement with experiment in every case and to insure that the reaction between bromine and hydrogen will go by way of the atoms. Equations 2 and 4 were first obtained by group theory methods but may be very readily obtained by the method of Slater.[23] The details will not be given here. These equations in the form written are only strictly valid when the atoms are rather far apart. At closer ranges normalizing factors should be introduced. This correction has been approximately achieved in the above calculations by substituting for the quantities $A + a$, etc., the experimental values for diatomic molecules which are automatically normalized.

Certain general remarks can be made regarding the applicability of the method of calculating activation energies that has been used here. It has been assumed that the atoms behave as they would classically in the potential energy fields calculated from quantum mechanics. This is possible because it is permissible to assume eigenfunctions for the atoms which have much greater curvature than the curvature of the potential energy fields in which the atoms move.

Even in reactions where the three and four atoms of the previous calculations are replaced by radicals or even by surfaces, the calculation should give a good approximation for the activation energy provided the bonds made and broken involve only the spins of three or four S electrons. This will include many reactions. The group theory can be used to obtain the potential energy in more complicated cases.

As the fraction of the binding which is coulombic increases, the activation energy decreases, becoming zero, for example, in strong electrolytes.

I have had the advantage of many helpful discussions with Dr. Clarence C. Zener, Professor G. E. Gibson and other members of the Departments of Chemistry and Physics, in the preparation of this paper.

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[22] R. S. Mullikan, *Phys. Rev.*, **32**, 186 (1930).

[23] J. C. Slater, *ibid.*, **34**, 1293 (1929).

Summary

The adiabatic (London) theory of reaction rates has been applied, for the first time, to reactions involving four atoms. It shows, unambiguously, that the thermal reaction of hydrogen with iodine will involve only iodine molecules, while the other halogens will react with hydrogen by way of the atoms. It shows further that the conversion of para to ortho hydrogen will involve an atom and a molecule rather than two molecules. It explains the well-known greater reactivity of the heavy halogen compounds over the lighter ones. These checks with experiment are independent of the ratio of coulombic to total binding except in the case of bromine. If the known theoretical ratio of coulombic to total binding for hydrogen is assumed to hold for the other atoms, approximate agreement with experiment is obtained. To obtain exact agreement in the reaction $H_2 + I_2 = 2HI$ the coulombic binding must be assumed to be only three and a half per cent. of the total binding. The theoretical evaluation of the coulombic binding is possible, but difficult, using the approximate eigenfunctions of Zener and Slater.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 283]

THE VAPOR DENSITY OF SELENIUM TETRABROMIDE AND THE EXISTENCE OF SELENIUM DIBROMIDE

BY DON M. YOST AND JOHN B. HATCHER

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Introduction

The results of the few qualitative observations that have been made on selenium tetrabromide[1] show definitely that it decomposes to some extent at room temperature and much more so at higher temperatures, the products of the decomposition being bromine and a lower bromide or bromides of selenium. Since no information of a quantitative nature seems to exist on the chemistry involved in the decomposition, the experiments described in this paper were undertaken.

Experimental Procedure and Preparation of the Materials.—The experiments consisted essentially in determining by the Dumas method the vapor densities of mixtures of selenium and bromine over the temperature range from 250 to 500°. Carefully weighed portions of bromine and elementary selenium were introduced into a cylindrical Pyrex tube

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[1] *Cf.* Abegg, Auerbach and Koppel, "Handbuch der anorganischen Chemie," Leipzig, 1927, IV Band, 1 abt., I halfte, p. 724; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, London, 1930, V. X, p. 899; J. Meyer and V. Wurm, *Z. anorg. Chem.*, **190**, 90 (1930).

of known volume, the bromine being contained in a small glass capsule with an easily breakable tip. The end of the tube was provided with a heavy-walled capillary whose end was drawn down to a thin tip and sealed off. After filling the tube, it was carefully evacuated, and then sealed off. A vigorous shake sufficed to break the tip of the bromine capsule, permitting the bromine to react with the selenium. The tube with the capillary was weighed and then placed in an electric furnace. After temperature equilibrium had been attained, the tip of the capillary was heated until the pressure inside the tube forced an opening through the softened glass and allowed the excess of gas to escape. The tip was not resealed until it was judged that the contents of the tube had again reached the temperature of the furnace, some cooling having resulted from the adiabatic expansion of the gas. The tube was then removed from the furnace, cooled and again weighed. The difference in the weights was the amount of material that had escaped; and this amount, subtracted from the original amount present, yielded the quantity remaining in the tube. The same tube was used for a series of experiments at increasingly higher temperatures.

The method of purifying the selenium was the same as that used in a former investigation.[2] The bromine was prepared by heating C. P. cupric bromide in a vacuum and subsequently drying and redistilling the bromine from pure potassium bromide.

Results of the Experiments

In Table I are presented results of representative vapor density measurements, of which thirty were made in all. It was assumed in making the calculations that the vapor obeyed the perfect gas law, and in the table are given the values of the apparent molecular weight M of the vapors as calculated directly from the equation, $M = 82.07(t + 273.1)m/pv$, p being expressed in atmospheres and v in cubic centimeters. The initial amount of bromine used varied from 0.37 g. to 0.53 g.

In order to determine qualitatively whether or not bromine was present in the hot vapors, their absorption spectra were observed and compared with that of an equal thickness of pure bromine at 200 mm. pressure, a visual spectrometer being used. When the atomic ratio Br:Se was four, the absorption bands of bromine were present with an intensity comparable to that observed in the comparison tube. In experiments where the composition of the mixture corresponded to selenium monobromide, no bromine bands could be seen, indicating that little or none of it was present. With a Br:Se ratio of two the bromine bands were very faint when the tube was hot and increased in intensity when, on cooling, condensation took place. This showed qualitatively that little or no bromine was

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[2] Yost and Kircher, THIS JOURNAL, 52, 4680 (1930).

TABLE I

RESULTS OF THE VAPOR DENSITY EXPERIMENTS

Formula weights: $SeBr_4$ = 398.86; Se_2Br_2 = 318.23; $SeBr_2$ = 239.03

Initial atomic ratio of Br:Se	Temp. (t), °C.	Bar., mm.	Vol. (v), cc.	Material (m) left in tube, g.	Molal weight M (calcd.)
4	250	743.9	41.4	0.1932	204.7
4	300	739.0	41.7	.1714	198.7
4	300	739.0	40.7	.1663	197.6
4	326	747.5	41.4	.1660	200.7
4	326	747.5	41.4	.1655	199.9
4	350	739.0	40.7	.1529	197.6
4	351	739.0	41.7	.1578	199.2
4	399	739.0	41.1	.1433	197.7
4	400	739.0	40.7	.1420	198.2
4	450	739.0	41.7	.1359	198.8
4	500	739.0	41.7	.1265	197.8
2	355	742.8	40.8	.1843	238.2
2	422	742.8	40.8	.1666	238.3
2	470	742.8	40.8	.1556	238.0
1	310	739.0	41.4	.4463	[a]
1	440	739.0	41.2	.3683	[a]
1	470	742.8	41.4	.2981	

[a] Considerable black unvaporized liquid residue was present in these experiments, so that the values for the molecular weight would have no significance.

present until the vapor in the tube began to alter its composition as a result of condensation.

When the atomic ratio was unity, corresponding to Se_2Br_2, complete vaporization of the material was never attained even at 500°. The unvaporized residue was a black liquid, whose appearance was that of molten selenium, but which might have contained some dissolved monobromide. With a Br:Se ratio of two or four the material vaporized completely without difficulty and in the former case gave rise to a molecular weight whose significance will appear later. Clear solutions containing no free bromine always resulted when the tetrabromide tubes were opened under water after the vapor density experiments had been made.

Discussion of Results

Since Table I shows that the molecular weight calculated from the measurements with mixtures having the composition of selenium tetrabromide is almost exactly one-half the formula weight of this substance, it follows that the tetrabromide does not exist as such under the conditions of the experiments, but decomposes completely in such a way that two molecules result from one of the tetrabromide. That this dissociation is complete is shown by the fact that the molal weight remains the same throughout the whole range of temperatures investigated (250–500°).

Such a decomposition might occur in the following ways

$$SeBr_4 = Se(s) \text{ or } (l) + 2Br_2(g) \qquad (1)$$
$$2SeBr_4 = Se_2Br_2(g) + 3Br_2(g) \qquad (2)$$
$$SeBr_4 = SeBr_2(g) + Br_2(g) \qquad (3)$$

The decomposition according to equation (1) is, however, excluded since no solid or liquid selenium (whose vapor pressure[3] is 4 mm. at 400°) was ever present in the tubes having a Br:Se ratio of four.

If the decomposition of the tetrabromide took place according to reaction (2), normal values for the molecular weight of the monobromide[4] would have resulted in the experiments with it alone, and no unvaporizable residue should have remained, providing it were not decomposed. Yet, as may be seen from the last three results in the table, the monobromide experiments do not yield a normal molecular weight and considerable unvaporizable residue remained even at the highest temperature.

The possibility of the monobromide decomposing into the tetrabromide and selenium according to the reaction

$$2Se_2Br_2 = SeBr_4(g) + 3Se(l) \qquad (4)$$

is excluded by the fact that the tetrabromide as such does not exist even in the presence of bromine, as already shown. That decomposition of the monobromide into bromine and selenium did not occur is shown by the fact that no absorption bands of bromine were found when the Br:Se ratio was unity and that the escaping vapor showed itself, on testing, to be rich in selenium. Moreover, no residue of selenium was ever found in the tetrabromide experiments even at 220° where the vapor pressure of liquid selenium is only 0.005 mm.[5] It appears then that the decomposition of the tetrabromide does not take place according to reaction (2).

There remains therefore only the possibility that the decomposition of the tetrabromide takes place in accordance with reaction (3). If this be the case, complete vaporization of the mixtures used should occur when the Br:Se ratio is two, and this was in fact found to be true. Moreover, if the existence of selenium dibromide is assumed, the results of the experiments on the selenium monobromide are easily explained by assuming that the monobromide decomposes according to the reaction

$$Se_2Br_2 = Se(l) + SeBr_2(g) \qquad (5)$$

One must conclude, therefore, that selenium monobromide does not exist to any appreciable extent in the vapor phase at the temperatures of 250–500°; but that the hitherto unknown compound selenium dibromide does so exist. The dibromide vapor, however, seems not to condense as

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[3] Preuner and Brockmoller, *Z. physik. Chem.*, 81, 129 (1913).

[4] The vapor pressure of the monobromide, if it existed as such, would have exceeded one atmosphere since at the lowest temperatures the total initial pressures in tubes containing the tetrabromide were about four atmospheres, and one-half of this would be due to the monobromide.

[5] L. E. Dodd, THIS JOURNAL, 42, 1579 (1920).

such to a solid or liquid phase, but to break up into the familiar liquid monobromide and solid tetrabromide.

It is of interest to point out that the equilibrium relations of a system composed of selenium and bromine are very similar to those of one composed of selenium and chlorine.[2,6]

Solid Selenium Tetrabromide.—The appearance, on cooling, of the substance in the tubes containing selenium tetrabromide was observed. The vapor itself has a dark red color (as does also selenium dibromide). The first solid material that appears is black in color and forms small hexagonal plates. As the temperature becomes lower still, the crystals that form possess a red color but are not, under a pocket lens, hexagonal in shape. If the temperature is suddenly lowered from about 50° to room temperature by holding the tube under the water tap, the clear portions of the tube are covered with very small lemon-yellow crystals. These differently colored substances may all be different modifications of solid selenium tetrabromide; no attempt was made to study them further.

Summary

The vapor density of mixtures corresponding in composition to selenium tetrabromide has been determined over the temperature range from 250 to 500°. The results show that it is completely decomposed at these temperatures into bromine and the previously unknown selenium dibromide.

Experiments with selenium monobromide showed that it decomposes, to a considerable extent at least, into selenium and selenium dibromide on vaporization. Mixtures of the composition of selenium dibromide vaporize completely, and in the vapor phase consist principally of selenium dibromide itself.

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[6] Simons, THIS JOURNAL, **52,** 3483 (1930)

[CONTRIBUTION FROM THE NUTRITION LABORATORY, UNIVERSITY OF ADELAIDE, S. AUSTRALIA]

THE FIRST DISSOCIATION OF PHOSPHORIC ACID IN AQUEOUS SALT SOLUTIONS AT 18°

BY JOSEPH W. H. LUGG

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In a previous paper[1] the author has employed conductivity data of pure phosphoric acid solutions in recalculations of the first dissociation constant. The present paper deals with an investigation of this important dissociation in aqueous solutions containing certain inorganic salts.

It is at present impossible to interpret correctly electrical conductivity measurements of solutions of high ionic concentration, and on this account the conductivity method is inapplicable to a study of the first dissociation of phosphoric acid in salt solutions. The method discussed in this paper has been used to determine the stoichiometric dissociation constant in solutions of sodium chloride, potassium chloride, magnesium chloride, and calcium chloride, of varying concentration. From what follows it will be seen that the method presented herein is somewhat similar to that evolved by Harned and Robinson[2] for studying the dissociations of weak electrolytes, but it seems to possess certain advantages over their method. Thus the assumption of complete dissociation of hydrochloric acid (which is later checked and proved experimentally) does not involve a possible error in the e. m. f. of a "chloride" as well as a "hydrogen" electrode, and there is no delay waiting for a "chloride" electrode to reach equilibrium. Furthermore, by replacing the hydrochloric acid with nitric acid the method could be extended to solutions containing nitrates, and corrections might be made if the nitric acid proved to dissociate incompletely.

Outline of the Method and the Principles Involved

Electrometric measurement of hydrogen-ion activity is ordinarily subject to junction potential and standardization errors, and these may influence the second decimal place so seriously that the result can safely be called "PH value" only. A chain consisting of two half-cells in which are solutions of the same concentration with respect to some neutral foreign metal chloride, but of different concentration with respect to very small quantities of hydrochloric acid, has a negligible liquid junction potential, and may be used to find the relative hydrogen-ion activities in the two solutions with great exactitude. If the hydrochloric acid in one half-cell is replaced by a small quantity of phosphoric acid, the junction potential will still be negligibly small and the relative hydrogen-ion activities can

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[1] Lugg, THIS JOURNAL, 53, 1 (1931).

[2] Harned and Robinson, *ibid.*, 50, 3157 (1928).

again be measured with accuracy. Secondary and tertiary dissociations of phosphoric acid are negligible under these acid conditions, and were the actual concentration of hydrogen ions in the hydrochloric acid solution known, the first stoichiometric dissociation constant, K_1, of phosphoric acid could then be calculated, because the activity coefficients of hydrogen ions are the same in solutions whose thermodynamic environments are kept sensibly constant by a relatively high concentration of foreign salt.

Although it is an experimental fact that the measured hydrogen-ion activity is directly proportional to the small hydrochloric acid concentration when the ionic environment is kept sensibly constant, it cannot be concluded therefrom that the hydrochloric acid is completely dissociated, because it may be shown from the mass law that the same behavior would be observed even if hydrochloric acid were a typically weak acid. But if the provisional assumption of complete dissociation for the hydrochloric acid is made, and the phosphoric acid dissociation constant calculated on it, the validity of this assumption may be tested by repeating the measurement in the presence of a different quantity of phosphoric acid. Theory and experiment show that the activity coefficients of ions and un-ionized solutes in the presence of a preponderating amount of foreign salt are constant. The second determination of K_1 could be the same as the first only if the provisional assumption were valid. Such double determinations of K_1 in sodium, potassium, magnesium and calcium chloride solutions are recorded herein, and from their close agreement provide excellent confirmation for the Complete Dissociation Theory in the case of hydrochloric acid, a typical strong electrolyte.

Instead of employing a chain such as that described above, one might measure the e. m. f. between a calomel electrode and a quinhydrone electrode in the hydrochloric acid solution, and repeat the measurement with phosphoric acid replacing the hydrochloric acid. Provided that precautions are taken to ensure the junction potential being the same in both measurements, the difference in e. m. f. will be the same as that of the chain described earlier, and as the quinhydrone salt error will be the same in both cases, the difference in e. m. f. will be subject to no errors other than experimental ones.

This procedure was actually followed in obtaining the present data, in the hope that the hydrogen-ion activity coefficient could be obtained with fair accuracy in each case, after correcting for the quinhydrone salt error. Junction potentials were of such magnitude, however, and so variable, that this could not be done with any expectation that the results would have physical significance. To ensure that the changes in junction potential would not vitiate the measured difference in e. m. f. between phosphoric acid and hydrochloric acid solutions, the 0.1 N potassium chloride calomel electrode was connected by the same saturated agar bridge successively with the two solutions; the order was then reversed and a mean value of the differences was taken. It was found that the difference could be reproduced by this method to within a few tenths of a millivolt. Stock solutions were standardized to within 0.1%. All measurements were made at 18.0°.

Where ΔE is the e. m. f. difference in volts, (H_3PO_4 solution)-(HCl solution), α_{H^+} represents hydrogen-ion activity, and p signifies negative common logarithm, we have

$$-\frac{\Delta E}{0.05773} = \Delta p\alpha_{H^+} = p\alpha_{H^+(H_3PO_4)} - p\alpha_{H^+(HCl)} \qquad (1)$$

Since γ_{H^+}, the hydrogen-ion activity coefficient, is the same in both solutions

$$\Delta p\alpha_{H^+} = p[H^+]_{(H_3PO_4)} - p[H^+]_{(HCl)} \qquad (2)$$

Assuming $[H^+](HCl) = [HCl]$, $[H^+]$ in the phosphoric acid solution is given by

$$p[H^+] = p[HCl] - \frac{\Delta E}{0.05773} \qquad (3)$$

$[H^+]$ must equal $[H_2PO_4^-]$ for electroneutrality, and where $[H_3PO_4]$ represents the initial phosphoric acid molarity, the mass law gives

$$K_1 = \frac{[H^+]^2}{[H_3PO_4] - [H^+]} \text{ or } pK_1 = 2p[H^+] - p([H_3PO_4] - [H^+]) \qquad (4)$$

Results

The data are given in Table I, which contains in the order of the columns, foreign salt molarity, hydrochloric acid molarity, phosphoric acid molarity, AE, $[H^+]$, pK_1, and $\sqrt{\mu}$. The ionic strength, μ, has been calculated for the phosphoric acid solutions from the definition, $\mu = {}^1/_2\Sigma(Cz^2)$, where C is the concentration of any ion in moles per liter, and z is its valence. In calculating μ, the metal chlorides were assumed to be completely dissociated.

TABLE I

EXPERIMENTAL DATA

[For. salt]	[HCl]	[H_3PO_4]	ΔE	[H^+]	pK_1	$\sqrt{\mu}$
			Sodium Chloride			
0.020	0.0015	0.002	4-0.00340	0.00172	1.977	0.147
.050	.0020	.002	− .00365	.00173	1.955	.227
.050	.0040	.005	− .00140	.00378	1.930	.232
.100	.0040	.005	− .00080	.00387	1.877	.322
.200	.0040	.005	− .00040	.00394	1.835	.452
.400	.0040	.005	− .00005	.00399	1.802	.636
.600	.0040	.005	+ .00055	.00409	1.735	.777
.800	.0040	.005	+ .00070	.00411	1.721	.897
1.600	.0040	.005	+ .00085	.00414	1.700	1.267
1.600	.0040	.010	+ .01505	.00729	1.707	1.268

TABLE I *(Concluded)*

[For. salt]	[HCl]	[H_2PO_4]	*AE*	[H^+]	pK_1	$\sqrt{\mu}$
			Potassium Chloride			
0.020	0.0015	0.002	+0 00330	0.00171	1.996	0.147
.050	.0020	002	− .00350	.00174	1.933	.227
.100	.0040	.005	− .00095	.00385	1.891	.322
.100	.0060	.010	+ .00235	.00659	1.895	.327
.200	.0040	.005	− .00080	.00387	1.877	.452
.400	.0040	.005	− 00025	.00396	1.821	.636
.600	.0040	.005	− .00010	.00398	1.809	.777
.800	.0040	.005	± 00000	.00400	1.796	.897
1.400	.0040	.005	+ .00045	.00407	1.748	1.185
1.400	.0040	.010	+ .01480	.00723	1.724	1.186
			Magnesium Chloride			
0.010	0.0020	0 002	−0.00360	0.00173	1.953	0.178
.025	.0040	.005	− .00080	.00387	1.877	.280
.050	.0040	.005	− .00045	00393	1.841	.392
.100	.0040	.005	+ .00045	.00407	1.748	.552
.250	.0040	.005	+ .00120	.00420	1.657	.869
.250	.0040	.010	+ .01590	.00757	1.628	.870
			Calcium Chloride			
0.010	0.0020	0.002	−0.00350	0.00174	1.935	0.178
.025	.0040	.005	− 00065	.00390	1.859	.280
.050	.0040	.005	− .00035	.00395	1.829	.392
.100	.0040	.005	+ .00035	.00406	1.757	.552
.200	.0040	.005	+ .00135	.00422	1.642	.778
.200	.0040	.010	+ .01600	.00757	1.628	.779
.350	.0060	.010	+ .00650	.00778	1.564	1.029

Discussion

By definition the stoichiometric constant, K_1, becomes the activity constant, K_1', at infinite dilution, where the activity coefficients of all ions and molecules concerned are unity. K_1' is a true constant, and its relation to K_1 is given in

$$pK_1 = pK_1' - p\gamma_{H^+} - p\gamma_{H_2PO_4^-} + p\gamma_{H_3PO_4} \tag{5}$$

The Hückel[3] equation connecting the activity coefficient of a univalent ion of the *r*th kind with the ionic strength in aqueous solutions at 18° may be expressed

$$p\gamma_r = \frac{0.5\sqrt{\mu}}{1 + r\sqrt{\mu}} - R\mu \tag{6}$$

where r and R are both positive, and constant for a particular type of ionic environment. *r* is proportional to the mean limit of approach of ions to ions of kind *r*.

The Debye–McAulay[4] equation connects the activity coefficient of an un-ionized molecule of the *s*th kind with the ionic strength

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[3] Hückel, *Physik. Z.*, **26**, 93 (1925).

[4] Debye and McAulay, *ibid.*, **26**, 22 (1925).

$$p\gamma_s = -\frac{S'}{\rho}\mu = -S\mu \tag{7}$$

where S' is constant for a particular un-ionized solute in a particular solvent and ρ is a mean diameter of the ions present. S is therefore constant for a particular type of ionic environment. The concentration of un-ionized molecules has been found experimentally to influence γ_s relatively little. S', and hence S, may be positive or negative.

Substituting (6) and (7) with appropriate coefficients in (5)

$$pK_1 = pK_1' - \frac{0.5\sqrt{\mu}}{1 + a\sqrt{\mu}} - \frac{0.5\sqrt{\mu}}{1 + b\sqrt{\mu}} - (S - A - B)\mu \tag{8}$$

the r and R of equation (6) being replaced by a and A for H^+ ions, and by b and B for $H_2PO_4^-$ ions. If a and b are equal, or, for practical purposes, when they are not too dissimilar, equation (8) may be simplified to

$$pK_1 = pK_1' - \frac{\sqrt{\mu}}{1 + a\sqrt{\mu}} - C\mu \tag{9}$$

where a now has some mean value, and $(S - A - B)$ is replaced by C.

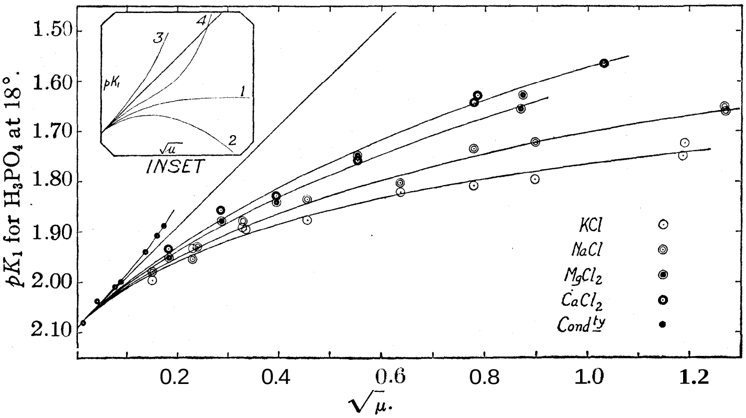

Fig. 1.

Whatever the values of the constants, equations (8) and (9) both reduce in the limit, as $\sqrt{\mu}$ approaches zero, to

$$pK_1 = pK_1' - \sqrt{\mu} \tag{10}$$

An examination of successive differential coefficients reveals that equations (8) and (9) both give similar curve types when plotted with decreasing pK_1 values as ordinates and $\sqrt{\mu}$ values as abscissas. These types are shown in the inset to Fig. 1. If C is zero, both equations give type 1, the curve being asymptotically parallel to the $\sqrt{\mu}$ axis. If C is negative, type 2 (concave downward) results from both equations. If C is positive and greater than $(a + b)/2$ in equation (8) (or greater than a in equation (9)), type **3** (concave upward) results. If C is negative and less than

$(a + b)/2$ in equation (8) (or less than a in equation (9)), type 4 is obtained. This curve is first concave downward to a point of inflection, and then proceeds concave upward. A limiting straight line, representing equation (10), is also shown.

The data in Table I were plotted as shown in Fig. 1, and curves were drawn through the points. As pK_1' has been obtained with sufficient accuracy from conductivity data, the extension of the curves to $\sqrt{\mu} = 0$, $pK_1 = 2.09$, was a matter of interpolation rather than extrapolation. Points from the author's recalculations of conductivity data are reproduced in Fig. 1 and the theoretical limiting straight line, $pK_1 = 2.09 - \sqrt{\mu}$, is also shown. Work done at higher $\sqrt{\mu}$ values might eventually show that the sodium chloride and potassium chloride curves rightly belong together or separately to type 2 or type 4, but at present they seem to satisfy the conditions for type 1 (*i. e.*, C = 0). The first few points on the magnesium chloride and calcium chloride curves suggest curves of type 4, but at higher $\sqrt{\mu}$ values there is no suggestion of this. It is possible that these salts dissociate incompletely, perhaps yielding compound ions, and, if so, the $\sqrt{\mu}$ values would be incorrect and the equation constants upset. Both curves drawn are of type 1. In passing, it should be mentioned that Onsager[6] has shown from conductivity data that salts such as sodium chloride, potassium chloride, magnesium chloride and calcium chloride, behave in dilute solution as if they were completely dissociated. Approximate equations of the form of (9) in which $C = 0$ may be applied to the four salt curves

$$\text{NaCl} \qquad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 1.60\sqrt{\mu}} \tag{11}$$

$$\text{KCl} \qquad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 2.12\sqrt{\mu}} \tag{12}$$

$$\text{MgCl}_2 \qquad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 1.14\sqrt{\mu}} \tag{13}$$

$$\text{CaCl}_2 \qquad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 0.93\sqrt{\mu}} \tag{14}$$

Since C is made zero here, it means that $S = A + B$ and is positive, but it is impossible to evaluate it. The smaller the value of a in equation (9), the smaller p should be in equation (7) and so S should be larger. The curve drawn from conductivity data belongs to type **3**, and the author's equation to it is $pK_1 = 2.09 - \sqrt{\mu}/(1 + 1.0\sqrt{\mu}) - 1.8$, S being positive and so large that A and B were assumed to be negligible in comparison and S was put equal to 1.8. The value 1.0 for a was assumed between discussed limits.

It will be observed in Table I that the higher the initial concentration of phosphoric acid in the presence of a fixed amount of salt, the lower, as a

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[6] Onsager, *Physik.* Z., 28,277 (1927).

rule, is the value found for pK_1. The reverse would be expected if hydrochloric acid were incompletely dissociated. It has been concluded therefore that small specific ion effects, and possibly those due to the small amounts of undissociated phosphoric acid, alone are responsible for the small decrease in pK_1, that hydrochloric acid is completely dissociated even in presence of very much metal chloride, and that the pK_1 values are quite reliable to within the experimental limits of accuracy. In the absence of detailed knowledge concerning the second dissociation of sulfuric acid, the method cannot be applied to sulfate solutions containing phosphoric acid.

In conclusion the author wishes to thank Professor J. A. Prescott and Mr. R. J. Best of the Waite Institute for provision of a constant temperature laboratory and a suitable potentiometer, the Council for Scientific and Industrial Research for materials used, Professor N. T. M. Wilsmore and Dr. G. A. Elliott of the University of Western Australia for criticism, and Dr. S. W. Pennycuick of the Adelaide University for suggested alterations and assistance in publication.

Summary

A method is discussed for studying weak acid dissociations in salt solutions, particularly the first dissociation of phosphoric acid in chloride solutions. Using a less delicate modification of it, experimental work has been done with phosphoric acid in the presence of sodium, potassium, magnesium and calcium chlorides, and the results are given and discussed.

Evidence is adduced to show that hydrochloric acid must be considered to be completely dissociated in solution, even in presence of much metal chloride.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE VOLUMETRIC DETERMINATION OF URANIUM. POTENTIOMETRIC TITRATION OF REDUCED URANIUM SOLUTIONS WITH CERIC SULFATE, OR WITH POTASSIUM PERMANGANATE. APPLICATION OF THE DIFFERENTIAL METHOD

BY N. HOWELL FURMAN AND IRL C. SCHOONOVER[1]

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Introduction

This investigation deals with the reduction of hexavalent uranium by amalgamated zinc, and with the potentiometric titration of the reduced solutions with standard permanganate or ceric sulfate solution. This study was found to be a necessary preliminary to the development of volumetric methods which are based upon the reactions of quadri- or hexavalent uranium with other substances as, for example, sodium, fluoride or phosphate ion.

The literature regarding the reduction of hexavalent uranium with zinc, or zinc amalgam, contains many contradictory statements. The chief point upon which disagreement has existed has been the extent to which reduction proceeds. A number of investigators have concluded that reduction proceeds quantitatively to the quadrivalent state.

Belohoubek[2] studied the reduction of uranyl sulfate, chloride, acetate, and nitrate with zinc. An attempt was made to exclude air while the solution cooled after the reduction. The solution was diluted "until the color disappeared," acid was added, and then the titration was made. Good results were reported for the sulfate and chloride solutions, poor ones in the case of the acetate and extremely poor ones for the nitrate solutions. No formation of trivalent uranium was observed.

Follenius[3] reduced uranyl acetate solutions with zinc and sulfuric acid; air was excluded. He found no reduction beyond the quadrivalent state; his results demonstrated clearly that the addition of hydrochloric acid before the titration caused too much permanganate to be consumed.

Zimmermann[4] treated 5 or 10 cc. portions of a uranium nitrate solution with 10 or 20 cc. of sulfuric acid of sp. gr. 1.23. After the mixture had been heated until sulfur trioxide was evolved, the solution was diluted and reduced with zinc in the absence of air. He found no evidence of the formation of trivalent uranium. In hydrochloric acid solutions, on the

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[1] Merck Fellow in Chemistry.

[2] Belohoubek, *J. prakt. Chem.*, 99, 231 (1866); *Z. anal.* Chem., 6, 120 (1867); application of the reaction to determination of phosphate, *ibid.*, 16, 104 (1877).

[3] Follenius, *ibid.*, 11, 179 (1872).

[4] Zimmermann, Ann., 213, 300 (1882).

contrary, trivalent uranium was formed. Zimmermann proved that the addition of manganous sulfate prevented the interaction between permanganate and hydrochloric acid, just as is the case with iron solutions.

Kern[5] reported that aluminum, magnesium, zinc, or zinc amalgam, reduce uranium quantitatively to the quadrivalent condition in sulfuric acid solution, whereas stannous chloride in hydrochloric acid solution forms some UCl_3 as well as UCl_4.

Of the more recent investigations in which no over-reduction (*i.* e., formation of U^{III}) was found, especial mention should be made of those of Gustavson and Knudson[6] and of Müller and Flath.[7] Although these investigators excluded air very carefully during the reduction, and performed the titrations potentiometrically, they found no evidence of reduction beyond the quadrivalent state in sulfuric acid solutions.

Failure to find over-reduction may have been due to incomplete exclusion of air in the earlier investigations, or to high acid concentration. The difficulty of reduction of U^{VI} solutions increases with the square of the hydrogen-ion concentration (or rather activity), as is shown by the e. m. f. relation, at 25°

$$E = E_0 + \frac{0.0591}{2} \log \frac{(UO_2^{++})(H^+)^4}{(U^{++++})} = E_0 + \frac{0.0591}{2} \log \frac{(UO_2^{++})}{(U^{++++})} + 0.0591 \log (H^+)^2$$

Luther and Mitchie[8] found that this expression, in terms of concentration, applied accurately over the range 0.1 N to 1 N sulfuric acid concentration.

The following investigators have all found evidence that the reduction proceeds partially to the trivalent stage in sulfuric acid solution with zinc or zinc amalgam as the reducing agent. Guyard[9] reported the formation of a mixture of salts of lower oxides upon reduction of acidified uranium solutions with zinc. He was unable to obtain accurate results with permanganate.

Pulman,[10] using a Jones reductor, found partial reduction of quadri- to trivalent uranium, and called attention to the rapidity with which the latter was reoxidized by air.

McCoy and Bunzel[11] found over-reduction with zinc, and proved that with a uranium solution which was 4 N in sulfuric acid, the trivalent form was rapidly converted to the quadrivalent, and the latter was only slowly oxidized by air at room temperature. The speed of oxidation of U^{IV} to U^{VI} was found to be approximately inversely proportional to the square root of the hydrogen-ion concentration.

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[5] Kern, THIS JOURNAL, 23, 685 (1901).

[6] Gustavson and Knudson, *ibid.*, 44, 2756 (1922).

[7] Muller and Flath, *Z. Elektrochem.*, 29, 500 (1923).

[8] Luther and Mitchie, *ibid.*, 14, 826 (1908).

[9] Guyard, *Bull. soc. chim.*, [2] *1*, 89 (1864), *cf.* especially pp. 94–95.

[10] Pulman, *Am. J. Sci.*, 16,229 (1903); *Z. anorg. allgem. Chem.*, *37*, 113 (1903)

[11] McCoy and Bunzel, THIS JOURNAL, 31,367 (1909).

Pierle[12] found over-reduction in the Jones reductor with sulfuric acid concentrations approximating one volume of acid in six volumes of solution.

Treadwell[13] and Ewing and Eldridge[14] found over-reduction with zinc or cadmium, or with zinc amalgam, respectively. Air was carefully excluded by a current of carbon dioxide. The potentiometric titrations with potassium permanganate gave a sharp inflection in the e. m. f.–cc. graph at the completion of the oxidation, $U^{III} \longrightarrow U^{IV}$, and a second sharp inflection at the end of the process $U^{IV} \longrightarrow U^{VI}$.

Lundell and Knowles[15] pointed out the advantages of reducing *cold* solutions of iron, uranium and other elements, in the Jones reductor. Over-reduction of uranium occurs in the cold solution to about the same extent as in hot solutions. These investigators[16] demonstrated by quantitative tests that in solutions containing 5% of concentrated sulfuric acid by volume, the trivalent uranium which is formed is oxidized rapidly by the action of a stream of air in one to five minutes; the quadrivalent uranium is relatively stable in air at room temperature (as long as four hours), but is oxidized very rapidly by air at 60–SO°.

The results of this investigation confirm the findings of Lundell and Knowles, Treadwell, Ewing and Eldridge, Pierle, McCoy and Bunzel and Pulman regarding the fact of over-reduction of uranium in solutions containing 2–5% of sulfuric acid of sp. gr. 1.84 by volume. Upon reduction of either hot or cold solutions in the Jones reductor the characteristic brownish color of a mixture of tri- and quadrivalent uranium salts was evident, and the potential (Pt vs. reference electrode) gave evidence of the presence of a more powerful reducing agent than U^{IV}. The amount of standard oxidizing agent which was consumed by the trivalent salt was extremely variable in duplicate determinations made under like conditions. In extreme cases more than 40% of the uranium was reduced to the trivalent state; generally from 25–40% of the uranium was in the trivalent condition.

Our results with regard to the ease of oxidation of U^{III} by air, and the relative stability of U^{IV} in air at room temperature confirm the findings of Lundell and Knowles.

A new method of determination, namely, titration of reduced uranium solutions with standard ceric sulfate, has been compared with the permanganate method; the potentiometric method was employed. The work of Treadwell and of Ewing and Eldridge has been confirmed with reference to the permanganate titration.

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[12] Pierle, *Knd. Eng. Chem.*, **12**, **60** (1920).

[13] W. D. Treadwell, *Helv. Chin?.Acta*, 5, 732 (1922).

[14] Ewing and Eldridge, THIS JOURNAL, 44, 1484 (1922).

[15] Lundell and Knowles, *Ind. Eng. Chem.*, **16**, 723 (1924).

[16] Lundell and Knowles, THIS JOURNAL, 47,2637 (1925).

A small quantity of iron (1 mg. per 25 cc.) is present in the 0.1 *N* ceric sulfate solutions which are prepared directly from commercial rare earth oxides.[17] The graph of the potentiometric titration data, therefore, shows three inflections (see Fig. 2), the first at the end of the oxidation of the trivalent uranium

$$U^{+++} + Ce^{++++} = U^{++++} + Ce^{+++}$$

the second at the end of the reaction

$$U^{++++} + 2Ce^{++++} + 2H_2O = UO_2^{++} + 2Ce^{+++} + 4H^+$$

and the third at the end of the reoxidation of the ferrous iron that is produced as the titration progresses. The amount of iron which is introduced up to the end of the oxidation of trivalent uranium is practically negligible. The experimental results show that the amount of ceric sulfate which is added between the first and the third inflections corresponds accurately to two equivalents of ceric ion per mole of U^{IV}. In other words, the ferrous iron is produced at the expense of an equivalent amount of quadrivalent uranium. It is more correct in principle to oxidize the trivalent uranium with air before starting the titration with ceric sulfate. It is at once evident that a crude ceric solution containing ferric iron should not be used in the simultaneous determination of uranium and iron.

It was found difficult or impossible to obtain concordant results when the side-arm of a saturated calomel half-cell dipped directly into the reduced solution. The use of a sulfate half-cell and bridge of saturated potassium sulfate eliminated the error. It was found that the differential titration method of MacInnes and Jones,[18] when used in the modified form which Clarke and Wooten[19] developed for work in an indifferent atmosphere, gave excellent results for all of the three inflections. This is apparently the first time that the possibility of the determination of a succession of oxidation–reduction end-points by the differential method has been demonstrated.

Experimental

Apparatus and Materials.—The titration vessel (a 250-cc. extraction flask) and its accessories are represented in Fig. 1. The simple expedient of inserting electrodes, buret, reductor and thermometer through tightly-fitting rubber tubes (F), mounted on the tops of glass tubes which were permanently mounted in the rubber stopper *(G)*, made it very easy to replace or modify parts of the apparatus.

A Leeds and Northrup students' type potentiometer and portable galvanometer (Type 2320d) and a Weston saturated standard cell were used. Various electrode assemblies were used: (1) Pt *vs.* saturated calomel; (2) Pt *vs.* saturated $K_2SO_4/Hg_2SO_4/$-Hg; (3) Pt *vs.* W; (4) Pt *vs.* sheltered Pt (differential method; see H, Fig. 1).

The calibration of the volumetric glassware used was checked carefully, and the necessary corrections were applied. The tip of the buret was drawn down so that one drop of liquid amounted to 0.025 cc.

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[17] Furman and Evans, THIS JOURNAL, 51, 1128 (1929).

[18] MacInnes and Jones, *ibid.*, 48, 2831 (1926).

[19] Clarke and Wooten, J. Phys. *Chem.*, 33, 1468 (1929).

Carbon dioxide from a cylinder was used.

Zinc of high purity was amalgamated with about 1% of mercury by a solution of mercuric nitrate prepared from the calculated amount of pure redistilled mercury. Frequent blank tests were made by passage of measured amounts of the sulfuric acid wash solution through the reductor. Potentiometric tests of the solutions showed that no blank correction was necessary with 0.1 *N* permanganate or ceric sulfate when the best available materials were selected.

Potassium permanganate and ceric sulfate solutions[20] were standardized potentiometrically against Bureau of Standards sodium oxalate.

Crystallized uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, of reagent grade was used. Careful qualitative tests proved the absence of vanadium, iron and the copper–tin group metals. A stock solution was prepared with 20.000 g. of the salt per liter of dilute sulfuric acid (2% of H_2SO_4 of sp. gr. 1.84 by volume). The uranium content of measured portions of the solution was determined either volumetrically with permanganate by the potentiometric method of Treadwell[13] and Ewing and Eldridge[14] with the $Pt-K_2SO_4/Hg_2SO_4/Hg$ electrode system, or gravimetrically as U_3O_8 after ammonia precipitation.[21]

This extended series of titrations fully confirmed the observations of Treadwell, Ewing and Eldridge and others on the character of this potentiometric titration. The reductions were made in cold solution as described later (under determinations with ceric sulfate). The graphs of the titration data were analogous to that of Fig. 2, except that there was no inflection due to iron. Titrations were made in a carbon dioxide atmos-

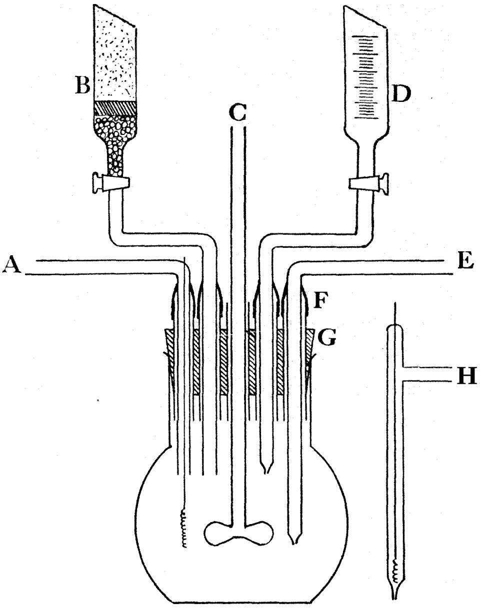

Fig. 1.—Titration vessel. A, Carbon dioxide inlet and electrode holder. A T-tube with adjustable platinum electrode was also used. B, Jones reductor. The top of the reductor was closed by a two-holed rubber stopper carrying a dropping funnel and a connection to the carbon dioxide line. C, Glass stirrer joined to a Cenco electric motor by a flexible shaft. D, Buret. E, Salt bridge to reference electrode. F, Rubber tubing. G, Rubber stopper. H, Sheltered platinum electrode which was substituted for E when the differential method was used. A T-tube, with a rubber bulb attached, was joined to the side tube of H; the T-tube was connected to the carbon dioxide supply by a tube carrying a stopcock. The stopper, G, was provided with an opening for a thermometer, not shown in the figure.

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[20] The ceric sulfate was prepared from rare earth oxides as described by Furman and Evans, THIS JOURNAL, 51, 1128 (1929). For standardization, *cf.* Willard and Young, *ibid.*, 50, 1322 (1928).

[21] Following the procedure given by Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1930, p. 368.

GRAVIMETRIC STANDARDIZATION

U^{VI} soln., cc.	20	30	25	25	10	10
U_3O_8 found, g.	0.2653	0.3977	0.3308	0.3310	0.1318	0.1320
U found, g.	.2250	.3373	.2805	.2807	.1118	.1119

Average 0.1123 g. U per 10 cc.

VOLUMETRIC STANDARDIZATION WITH 0.1147 N $KMnO_4$

U^{VI} soln., cc.	10	10	25	25	25	25[a]	50	50
$KMnO_4$, cc.	8.22	8.22	20.56	20.58	20 53	20.57	41.13	41.12
U found, g.	0.1125	0.1126	0.2808	0.2811	0.2804	0.2809	0.5617	0.5616

Average 0.1123 g. U per 10 cc.

[a] The acetate was expelled by repeated evaporations with excess of sulfuric acid before the solution was reduced.

phere, and the temperature was 80–90° at the second end-point (U^{IV} to U^{VI}). The initial volume ranged from 135–230 cc.

Preliminary Experiments.—Measured portions of uranyl solution at room temperature were passed through the reductor. In every case the characteristic color and low potential of a mixed solution of U^{III} and U^{IV} was obtained. It was proved that three to five minutes of stirring of the reduced solution with air reoxidized U^{III} to U^{IV}. The process was followed by potentiometer readings, and a sharp potential break (Pt *vs.* reference electrode) of over 0.1 volt was found at the end of the oxidation, thus confirming the conclusions of Lundell and Knowles.[16]

Several titrations of the U^{IV} solutions were made in air at 80–90°. Too little ceric sulfate was required. For example, portions of solution which required 9.04 cc. of 0.1043 N ceric sulfate under carbon dioxide, required 8.32, 8.77 and 8.90 cc. in the presence of air.

Many preliminary titrations were made potentiometrically with permanganate or ceric sulfate using a Pt–saturated calomel electrode system. Fairly concordant results could be obtained at any given initial volume with a carefully standardized procedure and with a constant amount of uranium. If double the amount of uranium was used, or if the working conditions were varied slightly, the consumption of oxidizing agent was not constant per unit volume of uranium solution, as is illustrated by the following results

Initial volume: 150–170 cc.

U^{VI} solution used, cc.	10	10	20	20	25	25
Ceric solution used, cc.	10.08	10.07	19.75	19.67	24.57	24.48
Ceric solution calcd., cc.	9.58	9.58	19.16	19.16	23.95	23.95

Different uranium and ceric solutions were used from those described under "standardization."

A careful study of the various possible variables: nature of electrodes, presence or absence of acetate, total acidity, etc., established the fact that the variability vanished when the saturated potassium chloride was not used. Too much oxidizing agent is consumed when chloride is present in appreciable amount. This observation confirms Follenius'[3] findings with regard to the error caused by the presence of hydrochloric acid. Others who have used the potentiometric method do not mention the error due to chloride; it is probable that the use of normal or 0.1 N potassium chloride would decrease the error.

The Pt–W electrode system failed to indicate the end of the oxidation of U^{III} to U^{IV}, but gave an excellent indication of the other end-points (U^{IV} to U^{VI} and Fe^{II} to Fe^{III}).

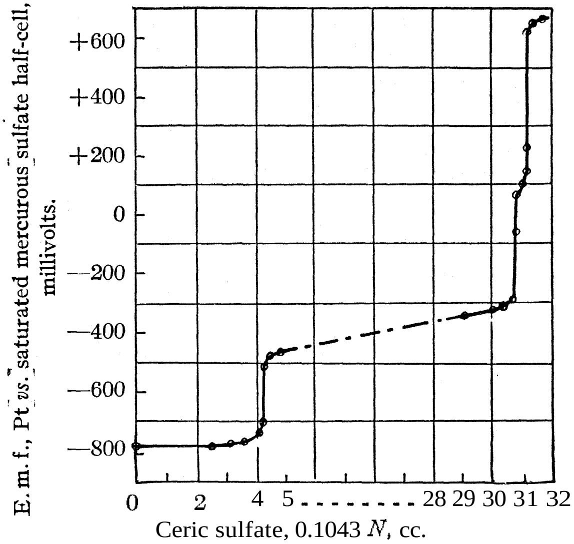

Fig. 2.—Graph representing potentiometric titration of 30 cc. of reduced uranyl solution with ceric sulfate (0.1043 N). The inflection at the left corresponds to the end of the oxidation of U^{III} to U^{IV}; the next to oxidation of U^{IV} to U^{VI} and the last to Fe^{II} to Fe^{III}.

Determinations with Ceric Sulfate Using the Pt vs. **K_2SO_4** (Satd.) **Hg_2SO_4–Hg** Electrode System.—The reductions prior to all determinations to be described subsequently were made by a procedure analogous to that given by Lundell and Knowles.[15,16]

Air was displaced from the receiving flask because it was desired to obtain data upon the extent of over-reduction. Measured portions of uranyl solution containing 2% by volume of concd. sulfuric acid were forced through the reductor by carbon dioxide pressure at room temperature; the reductor was washed with 25–50 cc. portions of 2% (volume) sulfuric acid, and finally with water, until the total volume of the solution was 130–240 cc.

The heating of the reduced solution was commenced, and the titration was started; the first inflection (Fig. 2) was found while the solution was warm, and the final inflections were found in hot solution (80–90°). The graph of the data of a typical titration is shown in Fig. 2. We attribute the third inflection to iron (ferric) that is present in the ceric solution, since the same inflection is found whether acetate is present or absent (see "acetate"). An entirely analogous form of graph was produced in permanganate titrations by adding a little ferric sulfate to the uranium solution after the first inflection had been passed. Quadrivalent uranium reduces ferric iron, and in so far as all of the ferrous iron is produced by oxidation of U^{IV} to U^{VI}, it is obvious that the distance from the first to the third inflection (Fig. 2) should be equivalent to the total uranium (process U^{IV} to U^{VI}). The amount of iron (ferric) that was introduced in the ceric solution up to the first inflection rarely exceeded 0.18 mg. and was generally less than half of this amount.[22] In principle it is preferable to oxidize the trivalent uranium with air before beginning the titration with ceric sulfate. The inflections were determined by the maxima of the Ae. m. f./Δcc. values. The results are summarized in Table I. In this series of determinations the initial volume ranged from 160–240 cc.

TABLE I

POTENTIOMETRIC TITRATION OF REDUCED URANIUM SOLUTIONS WITH CEKIC SULFATE (0.1053 *N*, Nos. 1–10; 0.1043 N, Nos. 11–14)

No.	U^{VI} soln., cc.	$Ce(SO_4)_2$ required for U^{IV}, cc.	U present, g.	U found, g.	Error, mg.	Over-reduction $Ce(SO_4)_2$ used for U^{III}, *cc.*	Over-reduction % of U^{IV} red. to U^{III}
1	10	9.00	0.1123	0.1128	+0.5	1.75	39.1
2	10	9.00	.1123	.1128	+ .5	1.55	34.6
3	10	8.96	.1123	.1123	± .0	1.46	32.6
4	10	8.97	.1123	.1124	+ .1	1.38	30.8
5	10	8.98	.1123	.1126	+ .3	1.47	32.8
6	20	17.97	.2246	.2253	+ .7	3.05	34.0
7	20	17.93	.2246	.2248	+ .2	3.14	35.0
8	20	17.96	.2246	.2252	+ .6	3.22	35.9
9	30	26.93	.3369	.3376	+ .7	4.22	31.4
10	30	26.92	.3369	.3375	+ .6	3.87	28.8
11	25	22.63	.2808	.2810	+ .2	3.15	27.9
12	50	45.16	.5615	.5608	− .7	4.05	17.9
13	50	45.22	.5615	.5616	+ .1	7.60	33.6
14	50	45.17	.5615	.5610	− .5	4.43	19.6

The last column of the table shows clearly the extreme variability in the extent of reduction beyond the quadrivalent stage.

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[22] The amount of iron was determined by passing measured volumes (50 cc.) of the ceric solution through a Jones reductor, followed by potentiometric titration with standard permanganate. Found 3.20 and 2.9 mg. Average 3.1 mg. per 50 cc. of ceric solution.

Acetate.—Belohoubek[2] stated that acetate caused erratic results if present during the reduction. The results present in Table I show that the error is non-existent, or within the experimental error of the ability of an operator to read an ordinary buret, when uranyl acetate is used. Titrations were also made in absence of acetate.

Portions of the uranyl solution were evaporated to dryness after adding an excess of sulfuric acid. Sulfuric acid was again added, and the acid heated to strong fuming. After cooling and diluting to about 2% sulfuric acid content, the solutions were reduced and titrated in the usual manner. The results are shown in Table II (Nos. 1–4). In other instances weighed portions of the U_3O_8, after the gravimetric determination, were dissolved in sulfuric acid, reduced and titrated (Table II, Nos. 5–6).

TABLE II

TITRATION OF REDUCED SOLUTIONS OF URANIUM IN ABSENCE OF ACETATE, WITH 0.1043 *N* CERIC SULFATE

No	U^{VI} soln., cc.	Ce(SO$_4$)$_2$ requirred for U^{IV}, cc.	U present, g.	U found, g.	Error, mg.	Over-reduction Ce(SO$_4$)$_2$ used for U^{III}, cc.	Over-reduction % of U^{IV} red. to U^{III}
1	10	9.05	0.1123	0.1124	+0.1	1.43	31.6
2	20	18.10	.2246	.2248	+ .2	3.23	35.7
3	10	9.07	.1123	.1126	+ .3	1.08	23.9
4	25	22.61	.2808	.2808	± .0	4.45	39.4
5	20	18.13	.2246[a]	.2252	+ .6	2.74	30.3
6	30	27.10	.3369[b]	.3366	− .3	5.85	43.1

[a] Found gravimetrically, 0.2250; [b] 0.3373 g. of uranium.

Practically the same range of error and percentage of over-reduction is found whether acetate is present or absent. In both series of determinations (Tables I and II) the results with ceric sulfate average slightly higher than those with permanganate, or by the gravimetric method. We believe that this slight discrepancy is in large part accounted for by the reduction of a small amount of iron by the trivalent uranium.

In other determinations 10 cc. of glacial acetic acid was added to the uranium solution before it was reduced. The other conditions were the same as in the previous determinations. The acetic acid (10 cc.) consumed a drop of ceric sulfate (0.05 cc.) in the absence of uranium, and this correction was applied to the volumes of ceric sulfate found. The results were as follows.

U^{VI} soln., cc.	Ce(SO$_4$)$_2$ required, cc.	U present, g.	U found, g.	Error, mg.	Ce(SO$_4$)$_2$ used for , .	Over-reduction, %
10	9.10	0.1123	0.1130	+0.7	0.85	19.8
10	9.08	.1123	.1128	+ .5	.45	9.96
10	9.04	.1123	.1128	+ .5	.65	14.3
20	18.15	.2246	.2254	+ .8	.55	6.1

The results appear to be consistently high in the presence of a large quantity of free acetic acid but, due to the uncertainty introduced by the correction, we are not convinced that pure acetic acid occasions any error. Errors of the same order of magnitude were observed in the absence of acetate (Table II). The percentage of over-reduction is markedly less in the solutions which contain acetic acid.

Application of the Differential Method.—In searching for the cause of the erratic results which were obtained when chloride was present (*cf.* preliminary experiments), the differential method of MacInnes and Jones[23] was applied satisfactorily to the determination of the three inflections of each titration. It was found to be necessary to exclude air from the tube (H, Fig. 1) which contained the sheltered platinum electrode; otherwise very rapid oxidation of the hot solution occurred. It was found to be advisable to attach a small rubber bulb to a T-tube in the carbon dioxide line which was joined to H (Fig. 1), as was suggested by Clarke and Wooten.[19] This bulb acts as a pressure regulator during slight changes in temperature, and serves as a means of expelling the liquid which surrounds the sheltered electrode. If the liquid is not changed after each addition of reagent near the end-point, the electrode, H, acts as a reference electrode, and the graph of the titration data resembles that of Fig. 2. If the liquid in the tube is changed after addition of each small increment of reagent, the succession of maxima is obtained

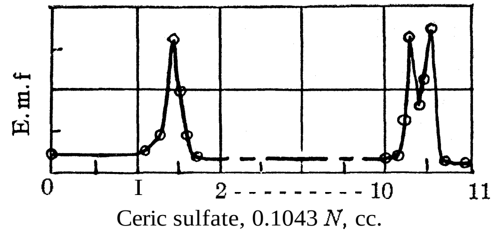

Fig. 3.—Differential titration of 10 cc. of reduced uranyl solution with ceric sulfate (0.1043 *N*). The maxima, left to right, correspond, respectively, to completion of oxidation of (1) U^{III}, (2) U^{IV}, (3) Fe^{III}.

TABLE III

DIFFERENTIAL TITRATION OF REDUCED URANIUM SOLUTIONS WITH CERIC SULFATE (0.1043 N)

No.	U^{VI} soln., cc.	$Ce(SO_4)_2$ required for U^{IV}, cc.	U present, g.	U found, g.	Error, mg.	Over-reduction $Ce(SO_4)_2$ used for U^{III}, cc.	Over-reduction, %
1	10	9.08	0.1123	0.1128	0.5	1.38	30.5
2	10	9.03	.1123	.1121	− .2	1.34	29.6
3	10	9.05	.1123	.1124	.1	1.15	25.4
4	10	9.07	.1123	.1126	.3	1.35	29.9
5	20	18.10	.2246	.2248	.2	3.40	37.6
6	20	18.10	.2246	.2248	.2	3.00	33.2

The general conditions of reduction and titration were the same as those which were described for the first series of determinations (Table I).

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[23] MacInnes and Jones, THIS JOURNAL, 48, 283 (1926).

as shown in Fig. 3, which is typical of a number of titrations. A summary of the results obtained is shown in Table III.

The distance between the second and third inflections was, in general, closely proportional to the amount of ceric solution used, and was close to but slightly greater than the value calculated from the amount of iron known to be present in the ceric solution. For example, with 10 cc. of ceric sulfate used, the value should have been 0.10 cc.; found, 0.11, 0.20, 0.13, 0.20. It is probable that a reliable correction could be made for the iron if the trivalent uranium were oxidized by air before the start of the titration.[24]

This investigation was made possible by the support of a fellowship in analytical chemistry, established by Merck and Company, Inc., of Rahway, N. J., and it is desired to express here our gratitude for this generous support.

Summary

This investigation has confirmed the fact that amalgamated zinc reduces hot or cold acidified uranyl solutions partially beyond the quadrivalent stage. Quantitative data are presented upon the extent of over-reduction. The ease of oxidation of trivalent uranium by air has been observed.

It has shown that a new method of oxidation of reduced uranium solutions, namely, by standard ceric sulfate, gives satisfactory results by the potentiometric method. Chloride interferes, causing erratic high results. The presence of small amounts of acetate causes no measurable interference.

The differential titration method has been applied to the determination of a succession of oxidation–reduction end-points in the titration of reduced uranium solutions with ceric sulfate.

PRINCETON, NEW JERSEY

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[24] During the correction of the proof of this work a communication along similar lines by D. T. Ewing and Mrs. M. Wilson appeared [THIS JOURNAL, 53, 2105 (1931)]. These investigators report interference of acetate, which we failed to find. We have subsequently applied the uranium titration with excellent results to the indirect determination of sodium in triple sodium magnesium uranyl acetate precipitates. We shall discuss the question of the interference or non-interference of acetate further in our report on the indirect determination of sodium by means of the uranium titration. Ewing and Wilson reduced boiling hot solutions, whereas the reductions reported in our work were made at room temperature; this difference in procedure may be significant.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 282]

THE ABSORPTION SPECTRA, STRUCTURE AND DISSOCIATION ENERGIES OF THE GASEOUS HALOGEN CYANIDES

BY RICHARD M. BADGER AND SHO-CHOW WOO

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Introduction

Spectroscopic investigations have yielded a great deal of interesting and useful information regarding the nature and strength of binding in diatomic molecules, and it is now desirable to extend studies of this sort to cases of molecules built up of several atoms. Several attempts have been made to do this, but in many instances the results obtained are difficult to interpret in an exact way, since the nature and energy states of the products into which more complicated molecules may dissociate are not known. In order to obtain quantitative information regarding the strength of individual molecular bonds, it seems advantageous to proceed gradually from very simple to more complicated cases, and in particular to choose for study those molecules about whose possible dissociation products we known as much as possible.

For this reason the cyanides seem to be very well suited for study, since the lower energy states of the cyanide radical are well known. Two cyanides have already been investigated: potassium cyanide by Villars,[1] and hydrogen cyanide by Badger and Binder.[2] As the subject of the investigation here described we have chosen the halogen cyanides, because there has been considerable discussion as to the structure of these compounds without any very definite conclusion being arrived at, and because certain inconsistencies in the literature make an independent determination of their heats of formation of interest.

Experimental Procedure

The substances used in the investigation were prepared as described below. In all cases chemically pure reagents were used.

Cyanogen Chloride.—In the preparation of this substance concentrated hydrochloric acid was dropped from a separatory funnel into an all-glass generator containing a solution of potassium chloride, potassium chlorate and potassium cyanide. The gas evolved was condensed in a receiver cooled with ice water. The liquid collected had a slight yellowish green tint which might have been due to the presence of some free chlorine. The liquid was then allowed to evaporate into the absorption cell, which consisted of a Pyrex tube 183 cm. in length, closed at the ends with quartz plates attached by sealing wax. When the absorption spectrum of the gas was photographed immediately after preparation, the chlorine bands as well as bands in the rather far ultraviolet due to cyanogen came out rather strongly. After the gas had stood for some time, these dis-

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[1] D. S. Villars, THIS JOURNAL, 53, 405 (1931).

[2] R. M. Badger and J. L. Binder, *Phys. Rev.*, 37,800 **(1931).**

appeared completely. No polymerization occurred even when the gas was kept in the tube for several days.

Cyanogen Bromide.—The preparation of this substance was similar to that of the chloride. Potassium bromide and bromate were used instead of the corresponding chlorine compounds. The gas was driven from the solution of these substances and potassium cyanide by heating to 70–80°, and was condensed as a solid in the form of white crystals in a receiver cooled in ice water. These crystals were then sublimed into the absorption cell and the pure solid condensed there could be preserved for over a month without any polymerization being evident. The gas used in the absorption experiments was that in equilibrium with the solid at room temperature, and was confined in an absorption cell 91 cm. in length.

Cyanogen Iodide.—In the preparation of this substance pure iodine was resublimed and dissolved in ether to which an excess of mercuric cyanide was then added. After vigorous shaking the solution became colorless, indicating the completion of the reaction. The mercuric iodide which precipitated and the excess mercuric cyanide were removed by filtration. On evaporation of the filtrate cyanogen iodide was obtained, mixed with considerable mercuric iodide. A purification by recrystallization from ether solution, and by sublimation, yielded a product with only a very faint orange tint. The 91-cm. absorption cell was used in this case; but, as the absorption of the gas in equilibrium with solid ICN at room temperature was rather small, it was found necessary to heat the absorption cell, which contained some crystals of the solid, to about 60". In order to eliminate any absorption of free iodine which might be liberated by the dissociation of the compound, some cyanogen was introduced into the absorption cell. This gas gives rise to a set of discrete bands beyond λ2100, which are easily identified and were in no way troublesome.

Optical Apparatus.—As a source of continuous spectrum in the ultraviolet a conventional hydrogen discharge tube was used. The spectra were photographed with a small Hilger quartz spectrograph. Eastman D-C ortho plates were used, and in order to obtain a greater sensitivity in the ultraviolet they were oiled with a light transformer oil which was found to be especially suitable for the purpose.

Experimental Results and Discussion

In the case of each gas only continuous absorption was found, and a careful search failed to detect any discrete bands. The spectra of the three compounds are entirely similar except that in the order ICN, BrCN, ClCN the absorption regions are displaced toward the short wave side, and the absorption becomes weaker in the same order. In the iodine compound two absorption regions were found, in the other cases only one, undoubtedly for the reason that the analogous second regions were further in the ultraviolet than could be reached by the quartz spectrograph. Since the absorption regions shade off rather gradually on the long wave side (and on the other side as well, where it can be observed) and since the apparent long wave limit shifts toward the red when the depth of absorbing gas is increased, it is not possible to give any definite long wave absorption limit. However, it is certain that absorption extends on the long wave side at least as far as the wave lengths given in Table I.

It is reasonable to assume that as a result of light absorption in the continuum of any of the halogen cyanides, a dissociation of the molecule

TABLE I

LONG WAVE LENGTH LIMITS OF THE CONTINUOUS ABSORPTION OF THE HALOGEN CYANIDES

Gas	Region a λ	Region a ν	Region b λ	Region b ν	Upper limit for dissociation energy (volt-electrons) a	Upper limit for dissociation energy (volt-electrons) b
ICN	>2900	<34470	>2100	<47600	4.26	5.88
BrCN	>2450	<40800			5.05	
ClCN	>2270	<44040			5.43	

takes place. This being the case, we may calculate from the long wave limit of the absorption region an upper limit for a dissociation energy of the molecule. Values so obtained are given in the right of Table I. Before discussing the nature of the dissociation products, we must consider the probable structure of the halogen cyanide molecules. As mentioned above there has been considerable discussion in this regard, though particularly relating to the molecules in solution. As regards the gaseous molecules, the similarity of the spectra, and the fact that they fall into a reasonable series, strongly indicates a similarity of structure for the three. In a previous paper[2] it has been shown that the hydrogen cyanide molecule has a linear structure represented by the formula HCN, and that the HNC molecule, if it exists, must be energetically very unstable. Similar but much stronger arguments may be advanced in this case. From a study of the heats of formation of carbon tetrachloride and carbonyl chloride we may estimate the energy of the carbon–chlorine bond to be of the order of 3.5–4.5 volts, while the energy of the nitrogen–chlorine bond is much smaller, say about 2 volts, as may be seen from data on nitrosyl chloride and nitrogen trichloride. Consequently a ClNC molecule which would be formed from an excited CN radical, probably that in the $^2\Pi$ state with 1.78 volts excitation energy, should lie at least 3.3 volts (75,000 cal.) higher in the energy scale than ClCN formed from the normal CN radical. Though ClNC should consequently be very unstable, the argument of course does not exclude the possibility that isocyanide molecules may be produced under certain conditions, and may have a relatively long lifetime. However, in the case of gaseous iodine cyanide it is known that an equilibrium is readily reached between this gas and iodine and cyanogen. It seems unlikely then that this gas can exist for an appreciable length of time in the unstable form. We shall assume for the time being that all three gases exist in the stable cyanide form, and as will be seen later this assumption is justified by the energy relations.

Since the optical dissociation energies are far too small to account for the splitting of the carbon nitrogen bond, we may conclude that the dissociation products are a CN radical and a halogen atom, one or both of which may be in excited states. We may compare the spectroscopic values with the dissociation energies of the molecules calculated from the chemical heats of formation, the known energies of activation of the products, etc. The necessary data are expressed by the equations

E_0 $\mathrm{C(graphite)} + {}^1/_2\mathrm{N_2} = \mathrm{CN\ (normal)} - 3.4$ volts (78,200 cal.)[2]
H_{298} $\mathrm{C(graphite)} + {}^1/_2\mathrm{N_2} + {}^1/_2\mathrm{Cl_2} = \mathrm{ClCN\ (g)} - 1.58$ volts (36,400 cal.)[3]
H_{298} $\mathrm{C(graphite)} + {}^1/_2\mathrm{N_2} + {}^1/_2\mathrm{I_2\ (c)} = \mathrm{ICN\ (c)} - 1.83$ volts (42,000 cal.)[3]
E_0 ${}^1/_2\mathrm{Cl_2} = \mathrm{Cl} - 1.23$ volts (28,400 cal.)[4]
E_0 ${}^1/_2\mathrm{I_2\ (c)} = \mathrm{I\ (g)} - 1.10$ volts (25,000 cal.)[3,4]

Unfortunately heat data on BrCN are lacking. Specific heats are also lacking for correcting the chemical heats of formation at room temperature to the absolute zero, but in any case the correction will be small in comparison with the dissociation energies. The heat of sublimation of ICN is not known but we shall probably not be greatly in error if we estimate it at −0.4 volt.

The dissociation energies of ClCN and BrCN into normal halogen atom and normal cyanide radical, and into normal halogen atom and excited CN radical (${}^2\Pi$ with 1.78 volts excitation energy), as calculated from the above data are tabulated in Columns 2 and 3, respectively, of Table II. In Columns 4 and 5 are given the spectroscopic values for all three substances.

Table II

Dissociation Energies of the Gaseous Halogen Cyanides

	Dissociation energy			
	From chemical data		From spectroscopic data	
Gas	Products: halogen (normal) + CN (normal)	Products: halogen (normal) + CN* (${}^2\Pi$)	(a)	(b)
ClCN	3.04 volts (74,700 cal.)	4.82 volts (112,000 cal.)	$<$5.43 volts	..
BrCN	..	..	$<$5.05 volts	..
ICN	2.27 volts (52,000 cal.)	4.05 volts (93,000 cal.)	$<$4.26 volts	$<$5.88 volts

It is seen that the energy of dissociation into normal products, calculated from the chemical heat of formation, is about what one would expect for the breaking of a carbon–halogen bond, and is much larger than would correspond to breaking a nitrogen–halogen bond. We may conclude that the molecules in their normal state are built from the normal CN radical and normal halogen atom. Since the spectroscopic dissociation energies are much larger than the energy of dissociation into normal products, dissociation by light absorption must result in at least one excited product. Since the lowest excitation energy of the iodine atom is 0.94 volt, it is evident that only one of the dissociation products of ICN can be excited when dissociation takes place as a result of absorption in region **(a).** The rough agreement between the spectroscopic value and the second chemical value in the table indicates that it is the CN which is excited. This is confirmed by the data on ClCN, since the excitation energy of chlorine is only 0.11 volt. The relatively large discrepancy in this case between the spectroscopic value and the second chemical value is to be explained by the

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[3] "International Critical Tables."

[4] J. Franck, Z. *Electrochem.*, 36, 581 (1930).

weak absorption of this gas, which leads one to estimate the long wave absorption limit relatively farther in the ultraviolet than in the other cases. To make the results strictly comparable it would have been necessary to use a much longer tube of gas than circumstances permitted.

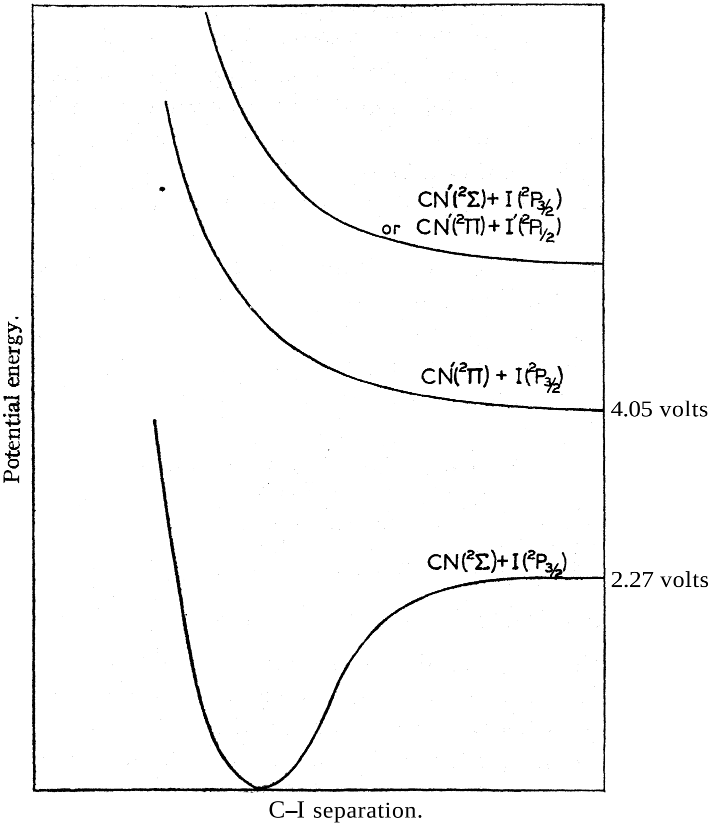

Fig. 1.—Approximate potential energy curves showing the potential energy of the ICN molecule as a function of the carbon–iodine separation, for three electronic states.

It is not possible to decide definitely whether absorption in the region (b) of ICN results in dissociation into an excited iodine atom with 0.94 volt energy and a CN radical ($^2\Pi$) with 1.78 volts energy, or into a normal iodine atom and a CN radical ($^2\Sigma$) with 3.19 volts energy.

Several attempts were made to demonstrate directly the nature of the dissociation products by fluorescence experiments, but unfortunately they were unsuccessful. One might expect that when the gases are illuminated with light of a wave length lying in the region of continuous absorption one should obtain the red cyanogen bands in fluorescence. The conditions are, however, very unfavorable for obtaining such a fluorescence. The absorption, even at the maximum of the continuum, is not very strong and if one uses sufficient gas pressure to obtain appreciable absorption one should expect the fluorescence to be almost completely quenched. Some experiments were made in which ICN gas was illuminated with a mercury arc, and some in which BrCN was illuminated with a cadmium arc. No fluorescence was visible to the eye even under very satisfactory conditions as to a black background, etc. In an investigation using a very fast glass spectrograph and dicyanin plates it was found that any fluorescence present was weaker than stray light which was excluded as far as possible.

As noted above the chemical dissociation energies show that the halogen cyanide molecules in the lowest energy state are formed from normal halogen atom and normal cyanide radical. The nature of the absorption spectra is strong indication that in the two next higher excited electronic states we have a case of repulsion at all distances, or possibly a very small minimum in the potential energy curve at a relatively large distance of separation of halogen atom and cyanide radical. The probable state of affairs is represented in Fig. 1.

This is indeed what one should expect. The normal cyanide radical, since it is formed from a normal nitrogen atom and a carbon atom in the ^5S state (tetravalent),[5] is capable of forming one shared electron pair bond between the carbon atom and some other atom and radical. The $^2\Pi$ cyanide radical, on the other hand, is formed from the ^3P carbon atom (divalent) and one should expect no tendency for molecule formation when an atom is brought up on the carbon side of this radical.

Summary

1. The absorption of the gaseous halogen cyanides has been investigated in the ultraviolet. Regions of continuous absorption only were found, with the following long wave length limits: ClCN, $\lambda > 2270$; BrCN, $\lambda > 2450$; ICN, $\lambda > 2900$ and $\lambda > 2100$.

2. The similarity of the spectra and their relation to each other suggest a similar structure for all three molecules.

3. Consideration of thermochemical and spectroscopic data together shows that in the normal state the halogen cyanide molecules are built from normal halogen atoms and normal cyanide radical, and in the first excited electronic state from normal halogen atom and an excited CN radical in the $^2\Pi$ state. The structures are probably those represented by the formulas: ClCN, BrCN, ICN.

4. The thermochemical heats of formation of the ClCN and ICN seem to be in substantial agreement with the spectroscopic values.

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[5] Heitler **and Herzberg,** *Z. Physik,* **53,** 52 (1929).

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

GENERALIZED THERMODYNAMICS INCLUDING THE THEORY OF FLUCTUATIONS

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In the present paper I shall assume without discussion the conservation of energy, at least in the sense in which this principle is used in thermodynamics. I shall not discuss the various discoveries of quantum theory which have exerted so great an influence upon present scientific thought. To these subjects I may later revert, but at present I wish to examine only those ideas which have been in the minds, almost since the beginning of thermodynamics, of those who have been troubled by the contradiction between the second law of thermodynamics and the existence of the so-called fluctuations which many systems exhibit, and which it is believed that more and more systems will exhibit as our means of measurement become more refined.

Willard Gibbs, in his early paper, first showed the incompatibility between molecular theory and the statement of classical thermodynamics that every system proceeds steadily toward a unique final state. We now have abundant experimental evidence also that a system left to itself for an indefinite time assumes no single equilibrium state, but passes back and forth through a great number of different states which, however, are not easily distinguishable.

Therefore classical thermodynamics, although aclmittedly invalid, is an extremely good first approximation to the truth. The second approximation, indicated abstractly in Gibbs' "Statistical Mechanics," was given concrete expression by Einstein,[1] who combined the first approximation given by classical thermodynamics with the famous theorem of Boltzmann relating entropy and probability. He thus obtained an equation which is of great value in determining the probability that any one observation will lie within a given range of fluctuation.

Our science is therefore in a position in which it is able to give an answer with almost any desired accuracy to any problem, not only of the older thermodynamics, but also of the theory of fluctuations. But since the science is not quite exact it fails to satisfy our logical desires and also our pedagogic needs, for no valid statement of the second law of thermodynamics has as yet been formulated.

I have long sought the proper way to place thermodynamics upon an exact basis, deriving the laws corresponding to those of classical thermodynamics, as well as the laws of fluctuations, from a single postulate, The task, however, has been a puzzling one and only in recent years have I perceived how

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[1] **Einstein,** *Ann. Physik*, **22,569** (1907).

simple the solution really is. The problems in which the second law of thermodynamics has been employed are all concerned with the partition of some quantity, such as energy, or some kind of matter, between several systems. We may begin our discussion with the study of such partitions.

Before proceeding with the analysis it may not be superfluous to point out that wen when a mathematical science is made mathematically and logically exact, it is not precisely applicable to any actual physico-chemical system. It corresponds rather to an ideal system which may be regarded as a limit toward which actual systems can be made to approach as near as we please. Such a limit is implied when we define an ***isolated*** system as one which is cut off from all other systems with respect to the passage of matter or energy. In this sense we speak of completely impermeable walls, perfect mirror surfaces and the like.

In a similar way we define ***independent*** systems as those which do not influence the thermodyiiamic properties of one another by their mere propinquity. Thus two bottles of water become more nearly independent as they arc separated spatially, and even the upper and lower halves in the same bottle may be regarded as nearly independent since, owing to the small range of molecular forces, only a very little of one part is much influenced by the other. On the other hand, in dealing with surface phenomena we are often obliged to discuss systems which are far from independent.

A similar idealization is necessary when we discuss equilibrium. If we are studying the relation between the pressure and volume of a mixture of oxygen and hydrogen at 0°, we ignore the fact that the two gases are very slowly combining to form water. If we are measuring the solubility of potassium chloride, we forget that at the end of a trillion years a considerable part of the potassium will have suffered radioactive decay. So in our idealized system we assume that certain specified processes occur at a rate which is infinitely greater than that of all other processes. The former may be spoken of as ***permitted*** and the latter as ***prohibited*** processes. In our present treatment of thermodynamics we may replace the idea of the time required for the attainment of equilibrium by the idea of the time sufficient to give a representative statistical sample of all the permitted states of a system. This length of time, however, does not enter directly into our considerations, and, indeed, time is not one of the variables with which pure thermodynamics is concerned.[2]

Partition Between Two or More Systems

Let us consider the partition of some quantity X between two independent systems. This quantity X may be the energy, of some chemical substance, or, if the two systems are separated by a movable partition, it may be the volume. If such a partition varies from time to time it will not be our present duty to seek the cause; whether the individual parts of the system follow the old mechanics, or the new mechanics, or no mechanics at all, need not concern us now.

If we wish to study some momentary partition we fix or "freeze" that partition by interrupting communication between the two systems.[3]

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[2] Lewis, "The Symmetry of Time," ***Science,*** 71, 569 ***(1930).***

[3] I have considered it sufficient in the present paper to state what seems **to** me true, without explicitly correcting some false ideas that have crept into thermodynamic literature. However, there is one thing that must be said to avoid serious confusion. If the thermodynamic properties of a system, such as temperature, entropy and pres-

In other words, we isolate them from one another and then we may proceed to determine experimentally what the content of the quantity X is in the system I and in the system II. If such a determination is made from time to time and the results are recorded, they may not permit a satisfactory prediction of what partitions will occur in the future, but if the intervals between the observations, and also their number, are increased without limit, our data may be said to become representative, in the sense that the fraction of all partitions lying within a given range may be equated to the probability that any new observation will lie within that range.

Instead of having our systems I and II isolated from all others, we may have a third system which we may call a reservoir, in communication with these two, and this reservoir may be considered capable of being increased indefinitely in size (without changing its intensive properties, such as density, composition and density of energy). Now when the quantity X is partitioned between these three systems, the probability that the content of X in system I will lie between C_1 and $C_1 + \lambda$ may be designated by $\alpha_1\lambda$, while $\alpha_2\lambda$ will express the probability that the content in system II lies between C_2 and $C_2 + \lambda$. If λ be chosen indefinitely small, there will be the same probability that the content in system II will lie in one or the other of the two equal and adjacent ranges, C_2 to $C_2 + \lambda$ and C_2 to $C_2 - \lambda$. Henceforth we shall choose the latter expression on account of its convenience in the discussion of the distribution between two systems alone.

If the two systems are independent and if the reservoir be made indefinitely large, the probability that the content of system I lies between C_1 and $C_1 + \lambda$, and at the same time that the content of system II lies between C_2 and $C_2 - \lambda$ is given by the expression[4]

$$P = \alpha_1\alpha_2\,\lambda^2 \qquad (1)$$

where α_1 is now independent of the system II, and α_2 of the system I. While the range λ may be made as small as we please, having once chosen this range for a given quantity X, we shall regard it as constant throughout our equations.

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sure, are to be unambiguously determined by certain independent variables such as the mass, the energy and the volume of a system, it follows that it is meaningless to say, for example, that the temperature of a system is the same or is not the same in all its parts. The temperature of an isolated system must have one and only one value. On the other hand, it is possible, with due caution, to assign a meaning to such a phrase. We may agree to say that the temperature of each part is the temperature it would have if it were suddenly isolated from the rest.

[4] If at the same time we wish to consider the partition of several quantities X, Y, Z, . . ., and choose λ_x as the range of the first quantity, and so on, the equation becomes

$$P = \alpha_1\alpha_2\,\lambda_X^2\,\lambda_Y^2\,\lambda_Z^2\ldots \qquad (1a)$$

where the α's have the same meaning as before, except for a constant factor depending upon the chosen values of λ_Y, λ_Z, etc. Since we gain in simplicity and lose nothing in generality, we shall continue to consider the partition of one quantity at a time.

If C_1' is another content of the first system and C_2' another content of the second system, but such that the total content is the same, namely, $C_1' + C_2' = C_1 + C_2$, the probability P' that the content of the first system will lie between C_1' and $C_1' + \lambda$, and *also* that the content of the second system will lie between C_2' and $C_2' - \lambda$ is given by the corresponding expression

$$P' = \alpha_1'\alpha_2'\lambda^2$$

The ratio of the probabilities of the two partitions is then

$$\frac{P}{P'} = \frac{\alpha_1\alpha_2}{\alpha_1'\alpha_2'} \qquad (2)$$

The product $\alpha_1\alpha_2$ which belongs to a certain pair of systems with contents C_1 and C_2 may be called the *specific probability*, while the a's may be called the probability factors.

We are now in a position to state the cardinal postulate which is designed to validate, and at the same time to generalize, the second law of thermodynamics, and from which the laws of thermodynamics and the laws of fluctuations may both be derived. However, before making this postulate, it may be well to make certain comments which may serve to display its character and contribute to its plausibility.

When we have spoken of two systems as connected we have said nothing concerning the mode of connection. If we were considering a gas distributed between two vessels, they might be joined by a very narrow tube, or a very large one. If we were considering the passage of heat, the systems might be connected by a rod of very low or very high thermal conductivity. In any case, if the connection is a poor one and, having determined some partition, we soon after determine the partition once more, these two partitions will be almost the same. We have tried to eliminate such effects by making infinitely long the interval between two partition measurements, but that we have succeeded in making the relative probability of the various partitions independent of the mode of connection of the systems is, after all, an assumption which must be embodied in our fundamental postulate.

When we consider two systems and a reservoir we might make the connection between the two systems so good, and the connection between each system and the reservoir so poor, that during a time which is long enough to be almost completely representative with respect to all possible partitions between the two systems, there would be almost no exchange with the reservoir. In such case we should expect that the probability of the several partitions of the quantity X in the two systems would depend only upon the total amount of X in the two systems, and not at all upon the nature of the reservoir. Thus if the two systems were in very poor thermal contact with a reservoir and at a certain time the two systems should contain E units of energy, then if the same two systems were in poor contact with another reservoir, for example one of much higher temperature, but if as a result of some rare fluctuation the total content of energy in the two systems were again E, then we should expect the laws of partition of this quantity E between the two systems to be the same in both cases.

The Cardinal Postulate.—Plausible as these ideas may be, they must be embodied in a formal postulate which will serve as a generalization of the second law of thermodynamics. This postulate is as follows: *when a given content is partitioned between two systems, the ratio of the specific probabilities of any two partitions of this content depends solely upon the nature of the two systems and upon the respective contents.* In other words, such a ratio as occurs in Equation 2 depends in no way upon the mode of connection between the systems nor upon the existence, or nature, or mode of connection of other systems.

It is evident from the way in which the probability factors were first introduced that each α depends upon the kind of reservoir chosen, and upon the amount that it contains of the quantity whose partition is being studied, but it now follows from our postulate that the *relative* values of α for a given system are independent of such choices. Aside then from an undetermined, and for the present purposes unimportant, constant multiplier, each α depends solely upon a system and its content. It is therefore a corollary of our postulate that the specific probability for a given partition is (except for the undetermined constant) the product of two factors, one of which depends solely upon the first system and its content, the other solely upon the second system and its content. This corollary might itself have been taken as the generalization of the second law of thermodynamics and then our fundamental postulate would have appeared as a corollary.

In order to apply the methods of the differential calculus it would be convenient if α for any system could be regarded as a continuous function of its content, but in some cases at least we know that the content cannot be varied continuously. Thus we cannot take from the system less than one atom of any element. Nevertheless, we usually approach very close to the limiting case in which the loss of one atom produces the same change in the thermodynamic properties of a system as the loss of a second atom, or a third, thus justifying the use of the differential calculus. In the present paper we shall restrict ourselves to the case in which the calculus is applicable, reserving the more general case for a later occasion.

By the aid of the calculus we may write down immediately the probability that a partition of a certain content will lie within a certain range, divided by the probability that a second partition of the same content will lie within another given range. Let the total content, C, be the same in both cases and let the specification of the first range be that C_1 lies between a and b (and therefore that C_2 lies between C-a and C-b), while the corresponding specification for the second range is that C_1 lies between a' and b'. The ratio of the two probabilities is then given by the formula

$$\frac{P}{P'} = \frac{\int_a^b \alpha_1\alpha_2 \mathrm{d}C_1}{\int_{a'}^{b'} \alpha_1\alpha_2 \mathrm{d}C_1} \tag{3}$$

where $\mathrm{d}C_1 = -\mathrm{d}C_2$. If we wish to make the second range cover all possible values, we obtain as the *absolute* probability that a partition lies within the range $C_1 = a$ to $C_1 = b$

$$P = \frac{\int_a^b \alpha_1\alpha_2 \mathrm{d}C_1}{\int_0^C \alpha_1\alpha_2 \mathrm{d}C_1} \tag{4}$$

These equations will enable us to solve any problem in the theory of fluctuations, as soon as α_1 is known as a function of C_1, and α_2 as a function of C_2, or $C - C_1$.

The Most Probable Partition

In classical thermodynamics some minor assumptions are made in order to eliminate certain cases which, if they ever existed, would have to be treated separately (corresponding to certain zero cases in mathematics). Thus it is assumed, at any finite temperature, that the solubility of one substance in another is always finite, and that the heat capacity of any substance is also finite. Our corresponding assumption is that the most probable partition of any quantity between two systems is not the one in which the whole content is in one system. If such a case did occur it would require a separate treatment.

If then we have a quantity X in total amount C, divided between two systems, there must be some one partition at which the specific probability $\alpha_1\alpha_2$ has at least as high a value as at any other, and since this most probable partition does not lie at $C_1 = 0$ or $C_1 = C$, it has the characteristics of a maximum. If $\alpha_1\alpha_2$ is at a maximum, its logarithm is also, and satisfies the condition

$$\mathrm{d} \ln \alpha_1\alpha_2 = \mathrm{d} \ln \alpha_1 + \mathrm{d} \ln \alpha_2 = 0 \tag{5}$$

If some one quantity whose content is $C = C_1 + C_2$, can vary alone, then

$$\frac{\partial \ln \alpha_1}{\partial C_1} \mathrm{d}C_1 + \frac{\partial \ln \alpha_2}{\partial C_2} \mathrm{d}C_2 = 0 \tag{6}$$

or since $\mathrm{d}C_1 = -\mathrm{d}C_2$

$$\frac{\partial \ln \alpha_1}{\partial C_1} = \frac{\partial \ln \alpha_2}{\partial C_2} \tag{7}$$

This is the simplest expression of the condition that C_1 and C_2 represent the most probable partition of the total content C. This is the partition which is represented by the grossly exaggerated curve shown in Fig. 1.[5]

[5] Aside from the case illustrated in Fig. 1, there is only one other way in which $\alpha_1\alpha_2$ can be at a maximum, that is, when α_1 diminishes with increasing C_1 and α_2 with diminishing C_2. It sometimes happens that this case also has thermodynamic interest, but we need not dwell on this question here, since what we have to say will be true of either case.

Our new thermodynamics makes distinctions which are not made in the older thermodynamics. In the latter there was just one equilibrium partition which was, of course, not only the most probable, but also the average partition. If we now recognize what was formerly called equilibrium, not as a single partition, but as a narrow region into which a vast number of individual partitions are crowded, the most probable partition will not always exactly coincide with the average partition. It is characteristic of our present method of treatment that it is the most probable partition and not the average partition which we must now employ to represent the equilibrium. Henceforth when we say that two systems are in equilibrium we shall mean that for every variable quantity that can be divided between the two systems, the two contents correspond to the most probable partition. We then obtain directly from Equation 7 the important law that *when two systems are in equilibrium with a third system, they are in equilibrium with each other.*

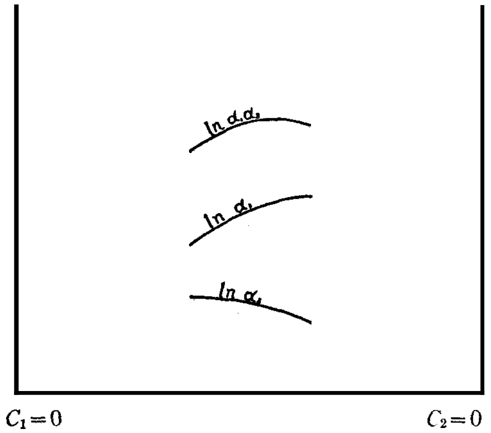

Fig. 1.

The Thermodynaniic Temperature.—If it is the energy whose partition between two systems is being studied, the equation for thermal equilibrium is

$$\frac{\partial \ln \alpha_1}{\partial El} = \frac{\partial \ln \alpha_2}{\partial E_2} \tag{8}$$

Let us define O by the equations

$$\frac{\partial \ln \alpha_1}{\partial E_1} = \frac{1}{\Theta_1}; \qquad \frac{\partial \ln \alpha_2}{\partial E_2} = \frac{1}{\Theta_2} \tag{9}$$

At equilibrium $\Theta_1 = \Theta_2$, but if we depart from equilibrium in such a direction that E_1 is less and E_2 is greater than the values at the most probable partition, then we might show, from a study of the second derivative of $\ln \alpha_1\alpha_2$, that Θ_2 cannot be less than Θ_1. Hence Θ obeys the qualitative laws of temperature, and might be defined as the thermodynamic temperature.

Combination of Abstract Thermodynamics with Experimental Knowledge.—We have now set forth all the essential abstract principles of generalized thermodynamics. In developing them I have endeavored to proceed with the utmost logical rigor. As we now approach the task of applying our abstract science to actual systems, we may afford to be a little more informal, since there are endless ways of making contact between our theoretical principles and experiemnt, and the choice of a particular method of making such contact will be largely a matter of taste.

There is nothing indeed in our preceding development which could possibly enable us to calculate for any physical system how its ln α changes with the several thermodynamic variables. To obtain such information we must either make some experimental study of a system, or some deduction concerning an idealized system based on generalizations of actual experiments. If one is interested in what is called statistical mechanics, it is at this point, and no earlier point, that the special laws of mechanics should be introduced.

At the corresponding stage in classical thermodynamics it is customary to introduce the properties of the actual substance, or rather that idealization of an actual substance, that we call the perfect gas. Thus, for example, the thermodynamic temperature is compared with the temperature recorded by a perfect gas thermometer. There are, however, many equally good ways of introducing the empirical properties of substances. Thus, in place of a gas thermometer we might use as a measure of temperature the potential of the galvanic cell, or the volume of a crystal, or the pressure of a Hohlraum.

We shall choose as our thermometer an idealized system composed of N similar molecules which for simplicity we may assume to be fixed in position, far apart, and subject to no change except that each molecule can exist in either of two states differing in energy by the amount ϵ. Thus the energy of the system over that of the same system with all molecules in the lower state is

$$E = M\epsilon \tag{10}$$

where M is the number of molecules in the higher state. Then $N - M$ are in the lower state, and we may define the temperature T by the equation

$$\frac{M}{N - M} = e^{-\epsilon/kT} \tag{11}$$

The classical work of van't Hoff and Boltzmann showed that this temperature scale may be identified with that of the perfect gas thermometer.

We shall now make the simple assumption that no molecule is more likely to be in the higher state than any other molecule. Let us arbitrarily divide the N molecules into two systems, the first having N_1 and the second N_2 molecules. Suppose that M_1 of the former and M_2 of the latter are in the higher energy state. If now by some method which need not be specified there is a flow of energy from the first system to the second, then M_1 diminishes and M_2 increases so that $M_1' + M_2' = M_1 + M_2$. According to our assumption the relative probabilities of these two partitions is equal to the relative number of ways in which the two partitions can be obtained.

The number of ways in which we may have the M units of energy distributed among N molecules is the number of ways in which M unnumbered objects can be placed in N numbered boxes, no more than one to a box. It is $N!/(M!(N-M)!)$, so that the relative probability of the two partitions is

$$\frac{P}{P'} = \frac{\dfrac{N_1!}{M_1!\,(N_1-M_1)!}\;\dfrac{N_2!}{M_2!\,(N_2-M_2)!}}{\dfrac{N_1!}{M_1'!\,(N_1-M_1')!}\;\dfrac{N_2!}{M_2'!\,(N_2-M_2')!}} \tag{12}$$

Each of the four quotients appearing in the last member depends only upon a single system and its content. These quotients satisfy all the rules that we have laid down for our probability factors and each therefore is to be identified with the corresponding α. Thus we find in general for this type of thermometric system

$$\alpha = \frac{N!}{M!(N-M)!} \tag{13}$$

and

$$\ln \alpha = \ln N! - \ln M! - \ln (N-M)! \tag{14}$$

If again we have the same N molecules, but $M + 1$ in the higher level, we may bear in mind that

$$\ln (M+1)! = \ln M! + \ln (M+1);\quad \ln (N-M-1)! = \ln (N-M)! - \ln (N-M)$$

and say that $\ln \alpha$ has been increased by

$$\Delta \ln \alpha = -\ln (M+1) + \ln (N-M) \tag{15}$$

Let us make the system large enough and M great enough so that M can be used in place of $M + 1$. Using the differential notation we have

$$\frac{\partial \ln \alpha}{\partial M} = \ln \frac{N-M}{M} \tag{16}$$

and now employing Equations 10 and 11 we find

$$\frac{\partial \ln \alpha}{\partial E} = \frac{1}{kT} \tag{17}$$

We see from Equation 17 that kT is equal to our thermodynamic temperature Θ. Having proved this for one system, we have proved it for all, for if we have any other system in thermal equilibrium with our thermometric system so that the Θ and T are the same for both, and if $\Theta = kT$ for one system, this is also true of the other.

If we are dealing with a pure substance under such conditions that the properties of a given mass are completely determined by its energy and volume, all that we need to know further about $\ln \alpha$ is the way it changes with the volume. Here also we must make use of some empirical information. We may take it as experimentally established that any physicochemical equilibrium which is obtained on the first floor of a laboratory will not be changed by taking the whole system to the second floor. This means that if the various α's change with the height, they all change in the same proportion. Since the α's already contain undetermined factors, we may say that the α for each system is independent of its position in a constant gravitational field.

Let us consider a cylinder divided into two parts by a movable piston of unit area and of weight P. The lower part, or system I, contains any substance whose properties are determined solely by the energy and the volume. The upper part, or system II, is exhausted and contains only the piston. As the height of the piston[6] fluctuates there will be one position that is most probable. At this equilibrium position we may say that the pressure in system I is equal to the pressure P exerted by the piston. When this position of equilibrium is reached d ln α, by Equation 5, will be numerically the same for the two systems, but according to our assumption d ln α is zero for the upper system, and therefore is also for the lower system. Hence for the latter

$$\mathrm{d}\ln\alpha = 0 = \frac{\partial \ln\alpha}{\partial V}\,\mathrm{d}\,V + \frac{\partial \ln\alpha}{\partial E}\,\mathrm{d}\,E \qquad (18)$$

By applying the first law of energy to this system

$$\mathrm{d}\,E = -P\,\mathrm{d}\,V$$

Combining the last two equations with Equation 17, we find for any system whose properties are determined by energy and volume

$$\frac{\partial \ln\alpha}{\partial V} = \frac{P}{kT} \qquad (19)$$

Entropy, and its **Use** in Calculating Fluctuations.—If we compare Equations 17 and 19 with those which in classical thermodynamics completely define the entropy, namely

$$\frac{\partial S}{\partial E} = \frac{1}{T} \qquad \frac{\partial S}{\partial V} = \frac{P}{T}$$

we may immediately identify the entropy with k ln α, except for an undetermined additive constant, which need not concern us, since by our definition ln α is determined only to an additive constant, and this is also true for the classical entropy. Hence, in general, we write

$$S = k\ln\alpha \qquad \alpha = e^{S/k} \qquad (20)$$

We have now completely bridged the gap between the new and the old thermodynamics. It is true that we have made use only of a pure substance under such conditions that it is subject only to the variables, volume and energy. However, we may also consider the partition of any quantity between such a substance on the one hand, and on the other hand a substance which is in solution, or which depends upon other variables, such as electric and surface forces. The resulting equations will be the familiar

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[6] In order to avoid the need of considering the kinetic energy of the piston we may make it as heavy as we please. Indeed, according to the principle of Heisenberg, it is only when the mass of the piston is infinite that we may assign to it zero velocity and also a fixed position.

equations of thermodynamics. To obtain them is a matter of mere routine. From the simple principles with which we started we have therefore obtained the whole of classical thermodynamics.

Moreover, we may now give an equally exact and more useful form of Equation 4. Substituting the values of α from Equation 20, and writing $S = S_1 + S_2$, we have

$$P = \frac{\int_a^b e^S \, \mathrm{d}C_1}{\int_0^C e^S \, \mathrm{d}C_1} \tag{21}$$

This equation enables us to solve any problem regarding fluctuations when the entropies are known as functions of the several contents.

For practical purposes it usually suffices to know the value of S, not over the whole range from zero to C, but over a very small range in the neighborhood of the equilibrium point $C_1 = C_1^\circ$. Indeed by a familiar method we may obtain a very good approximation if we know only the second derivative of S with respect to C_1 at this point. Dividing both numerator and denominator in Equation 21 by e^{S°, where S° is the combined entropy of the two systems at the equilibrium point, the integrals with which we have to deal have the form

$$\int e^{S - S^\circ} \, \mathrm{d}C_1$$

Now if $S - S^\circ$ is developed by Taylor's formula in terms of $C_1 - C_1^\circ$, then, because of the existence of the maximum, the first term in the expansion will be the one containing the second derivative. Neglecting higher terms we have

$$S - S^\circ = \frac{1}{2}\frac{\partial^2 S}{\partial C_1^2}(C_1 - C_1^\circ)^2 \tag{22}$$

The integral with which we are dealing is now in the form of the well-known probability integral, for which there are satisfactory tables.

If we now compare these equations with those given by Einstein, we see a resemblance which becomes an identity if we subject his equations to the interpretation given in the present paper, of which the most important is the interpretation of the classical equilibrium as the partition of highest specific probability.

Summary

By a method which differs radically from the methods used either in classical thermodynamics or in statistical mechanics, it is shown that the laws of thermodynamics and the laws of fluctuations constitute together a generalized thermodynamics which is derivable from a single cardinal postulate. It is claimed, moreover, that this postulate is the first really valid statement of the second law of thermodynamics.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE CLASSICAL DISSOCIATION CONSTANT OF BENZOIC ACID AND THE ACTIVITY COEFFICIENT OF MOLECULAR BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS[1,2]

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In a previous paper[3] the authors reported the hydrogen-ion concentration of a series of benzoic acid–benzoate buffers in aqueous potassium chloride solutions. From these values and the composition of the buffer the product of the concentration of hydrogen and benzoate ions was calculated. In all cases the solutions were saturated with benzoic acid so that a determination of the solubility of the acid in these solutions enables one to calculate the classical dissociation constant and the activity coefficient of the molecular benzoic acid. The solubility of the molecular acid is obtained by subtracting the hydrogen-ion concentration from the total concentration of benzoic acid as determined by titration. Column 3 of Table I gives the solubility of benzoic acid in the various solutions and Column 5 gives the amount present as molecular acid.

TABLE I

THE SOLUBILITY OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS AT 25.15°

Moles per liter					
Electrolyte KCl + NaB	Benzoate × 10^5	Total benzoic acid	$C_{H^+} \times 10^5$	Molecular benzoic acid	Average
0.0013	131.0	0.02781	131.0	0.02650	0.02650
.1000	529.4	.0261	48.5	.0256	
	767.3	.0256	32.8	.0253	
	1025	.0259	25.1	.0256	.0255
.2000	761.6	.0251	34.3	.0248	
	1660	.0250	15.9	.0248	
	3301	.0254	7.79	.0253	.0250
.3000	1663	.0242	15.6	.0240	
	1744	.0241	15.0	.0239	
	2481	.0244	10.5	.0243	
	3301	.0244	7.94	.0243	.0241
.4000	1663	.0235	15.6	.0233	
	1744	.0228	15.0	.0226	
	2480	.0229	10.2	.0228	
	3302	.0236	7.82	.0235	.0231

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[1] Abstracted from the thesis of Elwyn F. Chase presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Paper presented before the Indianapolis meeting of the American Chemical Society, March 30–April 3, 1931.

[3] Kilpatrick and Chase, THIS JOURNAL, 53, 1732 (1931).

TABLE I (Concluded)

Moles per liter					
Electrolyte $KCl + NaB$	Benzoate $\times 10^5$	Total benzoic acid	$C_{H^+} \times 10^5$	Molecular benzoic acid	Average
0.5000	320.5	0 0232	80.1	0.0224	
	1989	.0223	12.9	.0222	
	4329	.0231	5.78	.0230	0.0225
.6000	1662	.0220	15.0	.0218	
	1743	.0219	14.3	.0218	
	2480	.0221	10.0	.0220	.0219
.7000	1661	.0213	14.3	.0212	
	2480	.0213	9 64	.0212	
	3300	.0216	7.09	.0215	.0213
.9000	1661	.0199	13.5	.0198	
	2479	.0200	8.88	.0199	
	3300	.0202	6.60	.0201	.0199
1.012	874.3	.0184	24 3	.0182	
	1334	.0192	15 8	.0190	
	1660	.0193	12 8	.0192	
	1987	.0191	10 5	.0190	
	3299	.0191	5 97	.0190	
	3336	.0193	6 36	.0192	
	4328	.0190	4.66	.0190	
	5004	.0194	4.14	.0194	.0190
1.500	296.2	.0169	55.8	.0163	
	1861	.0168	8 98	.0167	
	1984	.0164	8 17	,0163	
	4329	.0170	3.67	.0170	.0166
2.000	635.8	.0135	18.3	.0133	
	1245	.0138	10.1	.0137	
	1859	.0141	6.53	.0140	
	4301	.0139	2.81	.0139	.0137
2.500	632.3	.0120	14.8	.0119	
	1242	.0121	7.42	.0120	
	1980	.0123	4.54	.0123	.0121
3.000	597.1	.0102	11.1	.0101	
	994.7	.0103	6.69	,0102	.0102

These results and those in the previous paper can be calculated to mole fractions or molalities with an accuracy within that of the measurements by using the densities for potassium chloride solutions as given in the "International Critical Tables."

Figure 1 shows graphically the change of the solubility of molecular benzoic acid with the nature and concentration of the solvent electrolyte. With our values at 25.15° are shown those of Hoffmann and Langbeck,[4] and Freundlich and Seal[5] at 25° in potassium chloride solutions. Their solutions were not buffered and their determinations give only the total solubility of the benzoic acid. We have calculated the ionized part from

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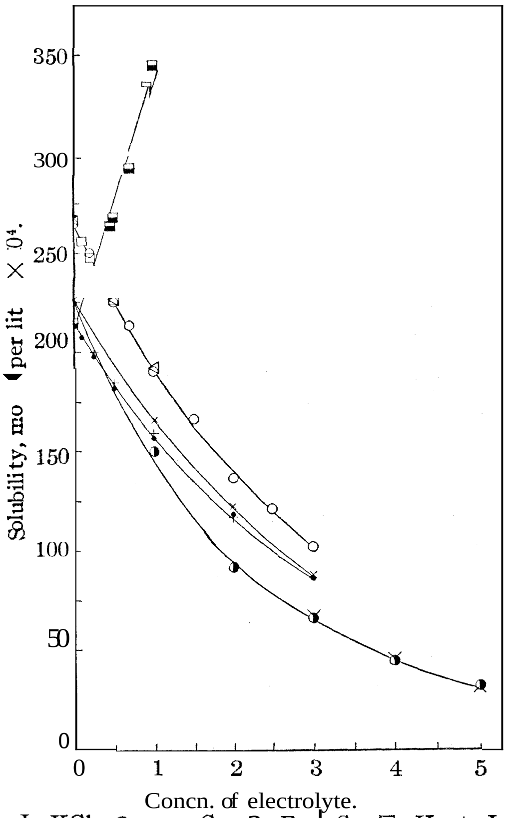
[4] Hoffmann and Langbeck, *Z. physik. Chem.*, 51,385 (1905).

[5] Freundlich and Seal, *Kolloid-Z.*, 11,257 (1912).

our values of the classical dissociation constant and have subtracted that part from their values. As the plot shows, the agreement is good. The values of Berry[6] in potassium chloride and sodium chloride solutions at 20° are shown with those of Güntelberg and Schiodt[7] at the same temperature. Finally the values obtained by Larsson at 18° are shown for potassium chloride and sodium benzoate solutions. Larsson finds a decidedly opposite effect for sodium benzoate, that is to say, the solubility of molecular benzoic acid is increased by the solvent salt, sodium benzoate.[9] The effect of sodium benzoate is noticeable in our buffers but is probably less than 1% for the benzoate ion concentrations used. It does, however, emphasize the dependence of the electrolyte effect upon the individual nature of the solvent salt. For the solvent salts potassium chloride and sodium chloride the solubility of molecular benzoic acid decreases rapidly with increasing salt concentration. The effect is greater for sodium chloride than for potassium chloride.



In KCl: ⊙, K.+ C.; a, F. + S.; ⊡, H. + L. at 25°; X, B. at 20°; +, ●, L. at 18°. In Na Benzoate: ▭, L. at 18°. In NaCl: ◑, B. at 20°; V,Λ, G. + S. at 20°; ● unbuffered + buffered.

Fig. 1.—Solubility of molecular benzoic acid.

In Table II the classical dissociation constant, $K_c = C_{H^+} C_{B^-}/C_{HB}$ has been calculated from our determination of $C_{H^+} C_{B^-}$ by the electrometric and catalytic methods, and

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[6] These determinations were carried out by Mr. W. H. Berry with one of us (M. K., Jr.).

[7] Güntelberg and Schiodt, *Z. physik. Chem.*, **135**, 393 (1928).

[8] Larsson, *ibid.*, **148A**, 304 (1930).

[9] Since this thesis was submitted Larsson has reported a number of salts which increase the solubility of benzoic acid. He has also investigated the effect of temperature on the activity coefficient of molecular benzoic acid. Larsson, *ibid.*, **153A**, 309, 466 (1931).

from the solubility of molecular benzoic acid in the solutions at each electrolyte concentration.

TABLE II

THE DISSOCIATION CONSTANT OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS AT 25.15°

KCl + NaB, moles per liter	$C_{H^+}C_{B^-}$ × 10^7, e. m. f.	$C_{H^+}C_{B^-}$ × 10^7, cat.	C_{HB}, moles per liter	K_c × 10^5, cat.	K_c × 10^5, e. m. f.
0.1	25.7	25.8	0.0255	10.12	10.08
.2	26.1	27.4	.0250	10.96	10.43
.3	26.1	26.8	.0241	11.12	10.83
.4	25.8	26.9	.0231	11.64	11.18
.5	25.5	24.9	.0225	11.07	11.32
.6	24.9	25.5	.0219	11.64	11.38
.7	23.7		.0213		11.12
.8		22.5	.0206	10.92	
.9	22.1		.0199		11.10
1.01	20.5	19.3	.0190	10.16	10.79
1.5	16.5	15.3	.0166	9.22	9.94
2.0	12.1	11.8	.0137	8.61	8.84
2.5	9.19		.0121		7.58
3.0	6.65		.0102		6.52

Figure 2 shows the change of the dissociation constant of the acid with increasing electrolyte concentration.

Table III gives the values of the dissociation constant obtained by Berry and by Guntelberg and Schiodt for potassium chloride and sodium chloride solutions.

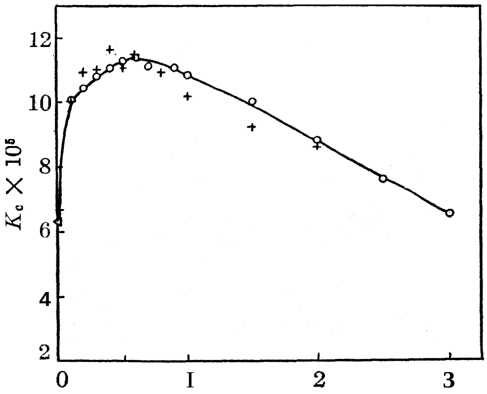

Fig. 2.—Electrolyte effect on the dissociation constant of benzoic acid.

In order to emphasize the fact that the change of dissociation constant with changing electrolyte concentration is different for different acids of the same type in the same solvent salt, we have plotted in Fig. 3 the ratio K_c/K_a for benzoic acid, acetic acid, formic acid and carbonic acid. The values for acetic acid and formic acid are calculated from the papers of Harned and Murphy[10] and Harned and Owen,[11] respectively. The values for the first dissociation constant of carbonic acid are from Guntelberg and Schiödt.[7]

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[10] Harned and Murphy, THIS JOURNAL, 53, 8 (1931).

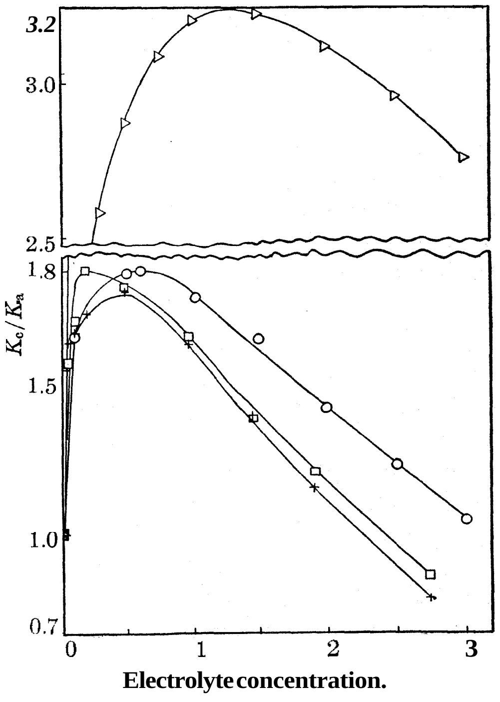
[11] Harned and Owen, *ibid.*, 52, 5079 (1930).

TABLE III

COMPARISON OF K_c FOR BENZOIC ACID IN SODIUM AND POTASSIUM CHLORIDE SOLUTIONS

KCl + NaB, moles per liter	$C_{H^+} C_{B^-}$ × 10^7, Berry, 20°	C_{HB} moles per liter. Berry, 20°	K_c × 10^5, Berry, 20°	K_c × 10^5, G. and S., 20°
1.0	16.9	0.0166	10.18	
2.0	9.81	.0123	7.98	
3.0	5.33	.0880	6.06	5.84
NaCl + NaB				
1.0	16.2	.01500	10.80	
2.0	8.61	.00918	9.38	
3.0	4.20	.00656	6.40	6.25
3.0	1.76	.00442	3.98	4.03
5.0	0.717	.00313	2.29	2.46

The curves for formic and acetic acids are similar, while that for carbonic acid is strikingly different, the maximum value of K_c for carbonic acid being over three times K_a. In general the K_c/K_a curve is different for different monobasic acids. These differences are attributed to two causes, the salting out effect on the ions and molecules and the interaction effect which depends on the deformability. Güntelberg and Schiodt[7] have given an interesting discussion of the effect of these factors upon the dissociation constant of a given acid in different solvent salt solutions.



All in KCl: ▷, carbonic acid, G. + S.; ○, benzoic acid; +, acetic acid, H. + M.; □, formic acid, H. + O.

Fig. 3.—K_c/K_a vs. electrolyte concentration.

The change of the mean activity coefficient of the ions' of benzoic acid with potassium chloride concentration as determined in a previous paper[3] is given by the extended Debye–Hückel equation

$$-\log \sqrt{f_{H^+} f_{B^-}} = \frac{0.5\sqrt{c}}{1 + \kappa b} + \beta c$$

where $\kappa = 0.33 \times 10^8 \sqrt{c}$, b is the apparent average ionic diameter, taken here as 5.15×10^{-8} cm., β is an empirical constant taken equal to -0.139, and c is the electrolyte concentration in moles per liter. Below we show that

$$\log f_{\mathrm{HB}} = 0.138\ c$$

Since

$$K_c = K_a \frac{f_{\mathrm{HB}}}{f_{\mathrm{H^+}} f_{\mathrm{B^-}}}$$

we have

$$\log K_c = \log K_a + \log f_{\mathrm{HB}} - \log f_{\mathrm{H^+}} f_{\mathrm{B^-}}$$

and substituting

$$\log K_c = \log K_a + 0.138\ c + 2\left[\frac{0.5\sqrt{c}}{1 + 1.70\sqrt{c}} + \beta c\right]$$

Taking $K_a = 6.31 \times 10^{-5}$, we have

$$\log K_c = -4.200 + \frac{\sqrt{c}}{1 + 1.70\sqrt{c}} - 0.140\ c$$

an equation which gives our values for K_c for solutions containing from 0.1 mole per liter to 3 moles per liter of potassium chloride within 2%.

Since all the solutions were saturated with benzoic acid, the activity of the molecular benzoic acid remained constant and equal to its solubility in pure water

$$a_{\mathrm{HB}} = f_{\mathrm{HB}}\ c_{\mathrm{HB}}$$

the activity coefficient, f_{HB}, being set equal to one at zero electrolyte concentration. Upon subtracting the ionized part as calculated from conductivity measurements from the solubility of benzoic acid in water, and upon making a small correction for the ion concentration ($\mu = 0.0013$), a value of 0.02650 mole per liter is obtained.[3] Thus

$$f_{\mathrm{HB}} = \frac{0.02650}{c_{\mathrm{HB}}}$$

The values of the activity coefficient calculated in this way are given in Table IV and for comparison we have included a summary of the results of Berry, Hoffmann and Langbeck, Giintelberg and Schiodt and Larsson.

An inspection of the table shows that for low electrolyte concentration the activity coefficient is practically independent of temperature over the range given.

Some of these values are shown graphically in Fig. 4, where the logarithm of the activity coefficient is plotted against the electrolyte concentration.

An equation of the form $\log f = kc$ expresses the results very well. For our results at 25.15° in potassium chloride solution

$$\frac{\log f}{\ } = 0.138$$

For the results of Berry at 20° and of Giintelberg and Schiodt at 25° in sodium chloride solution

$$\frac{\log f}{\ } = 0.176$$

TABLE IV

COMPARISON OF VALUES OF f_{HB}

Electrolyte, KCl, moles per liter	Buffers, 25°	Hoffmann and Langbeck, 25°	Freundlich and Seal, 25°	Larsson, buffers, 18°	Larsson unbuff., 18°	G. and S. buff., 20°	Berry, buff., $\frac{0.02265}{C_{HB}}$ 20°
0	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
0.05		1.02					
.1	1.04	1.04			1.04		
.2	1.06	1.07					
.26				1.08	1.09		
.3	1.10						
.33		1.11					
.4	1.15						
.5	1.18	1.18	1.18	1.18	1.18		
.6	1.21						
.7	1.25						
.9	1.33						
1.01	1.40		1.39	1.37	1.37		1.37
1.5	1.60						
2.0	1.94			1.86	1.81		1.84
2.5	2.19						
3.0	2.61			2.57		2.55	2.58
NaCl							
0				(1.00)	(1.00)	(1.00)	(1.00)
0.25				1.11			
.5				1.23	1.24		
1.0				1.51	1.49		1.51
2.0				2.26	2.25		2.47
3.0				3.38	3.35	3.40	3.46
4.0						5.05	5.14
5.0						7.50	7.25

At 18° Larsson gives the values

$$k = 0.137 \text{ for KCl}$$
$$k = 0.177 \text{ for NaCl}$$

When the concentrations are expressed in moles per 1000 g. of water, and log γ is plotted against m, the points do not lie on a straight line as in Fig. 3. The best line which can be drawn, however, is represented by the equation

$$\log \gamma = 0.12\, m$$

Using the data on the solubility of benzoic acid available at that time, Randall and Failey[12] gave $k = 0.13$ for potassium chloride and 0.18 for sodium chloride solution.

The activity coefficient of benzoic acid is larger in sodium chloride solution than in potassium chloride solution, that is to say, the solubility is less in sodium chloride than in potassium chloride solution of the same concentration. Since the salting out effect depends on the change in the

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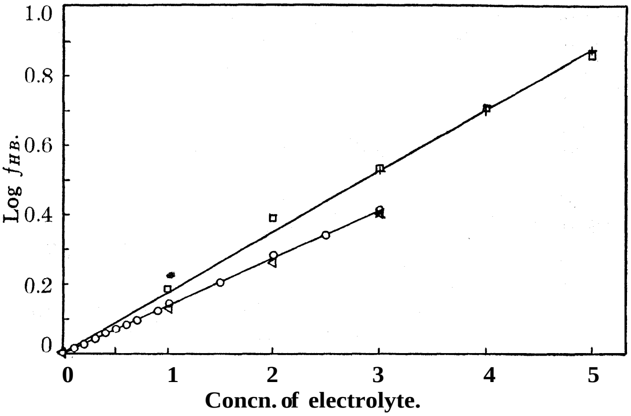
[12] Randall and Failey, *Chem. Reviews*, 4, 291 (1927).

orientation of the water molecules toward the neutral molecule, one would expect the smaller sodium ion to have a greater effect than the larger potassium ion. This is in agreement with the facts and theory as discussed by Debye and McAulay[13] and Scatchard and others.[14] As pointed out by Scatchard, various Hofmeister series have been put forward for the cations and anions. Glasstone and Pound,[15] who studied the electrolyte effect on the solubility of ethyl acetate, give the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$ for decreasing solubility of ethyl acetate. Linderström-Lang[16] shows the same order for hydroquinone, quinone and succinic acid (uncorrected for the dissociated part).



○, E. m. f., 25°; ◁, Berry, 20°; ×, G. + S., 20°, in KCl; □, Berry, 20°; +, G. + S., 20°, in NaCl.

Fig. 4.—Activity coefficients of molecular benzoic acid in potassium chloride and sodium chloride solutions.

Haesseler[17] finds the same general order for benzoic acid. Haesseler reports the solubility of total benzoic acid and has not corrected in any way for the part present as ions. Larsson demonstrated that the salting out of benzoic acid is, roughly speaking, an additive property of the ions of the solvent salt, *i. e.*

$$\log f = kc = [k_{C^+} + k_{A^-}]c$$

he arbitrarily set k_{K^+} equal to k_{Cl^-}, and calculated salting out constants for all the ions of the solvent salts studied.

In Table V we give some of Larsson's[18] ionic salting out constants and in

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[13] Debye and McAulay, *Physik. Z.*, 24,185 (1923).

[14] Scatchard, *Chem. Reviews*, 3,383 (1927).

[15] Glasstone and Pound, J. *Chem. Soc.*, 127,2660 (1925).

[16] Linderstrom-Lang, *Compt.-rend. trav. lab. Carlsberg, 15, 4* (1924).

[17] Haesseler, Dissertation, Columbia University, 1929.

[18] Larsson, Z. *physik. Chem.*, 153,289 (1931).

addition the radii of the ions as calculated by Pauling[19] for crystals. While these radii will not necessarily be the same in solution they will probably have the same relative magnitudes.

TABLE V

COMPARISON OF IONIC SIZE WITH SALTING OUT CONSTANT, k

Ion	Radius, Å.	k	Ion	Radius, Å.	k
Li^+	0.60	0.12	Mg^{++}	0.65	0.10
Na^+	0.95	.11	Ca^{++}	0.99	.10
K^+	1.33	.07	Sr^{++}	1.13	.09
Rb^+	1.48	.02	Ba^{++}	1.35	.08
Cs^+	1.69	−.08	Cl^-	1.81	0.07
			Br^-	1.95	0.00
			I^-	2.16	−0.02

From Table V it appears that *k* decreases with increasing ion size. In order to go further with any theoretical discussion, one would have to have information as to the change in dielectric constant and freezing points of these solutions, as pointed out by Debye and McAulay and Scatchard, as well as some knowledge of the deformability of the ions and molecules. Larsson points out that his results are qualitatively in agreement with the available dielectric data. The further study of the solubility of molecular benzoic acid in salt solutions offers a number of interesting possibilities, especially in view of the increase of solubility of benzoic acid in solutions of sodium benzoate (k = −0.21) and a number of other salts such as sodium β-naphthalene sulfonate (k = −0.75).

Summary

1. The solubility at 25.15° of benzoic acid in potassium chloride solutions has been determined and from determinations of the hydrogen-ion concentrations of these solutions the solubility of molecular benzoic acid has been calculated.

2. From these solubility values and the values of the ion product $C_{H^+}\ C_{B^-}$, the classical dissociation constant of benzoic acid has been calculated at the various electrolyte concentrations from 0.1 to 3.0 moles per liter.

3. A comparison of the change of the dissociation constant with electrolyte concentration has been given for different acids in the same solvent salt.

4. The activity coefficient of molecular benzoic acid in potassium chloride solutions has been evaluated. The results are expressed by the equation $\log f = 0.138c$.

5. A discussion of the relation of ion size to salting out has been given.

PHILADELPHIA, PENNSYLVANIA

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[19] Pauling, THIS JOURNAL, 49,765 (1927).

[CONTRIBUTION FROM LABORATORIES OF CHEMISTRY, NEW YORK UNIVERSITY]

REACTION OF AMINES WITH SULFUR DIOXIDE. I. ANILINE AND SULFUR DIOXIDE

BY ARTHUR E. HILL

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In the year 1909 experiments were conducted in this Laboratory in an effort to study the reactions of acid anhydrides upon basic anhydrides, by Mr. William A. H. Zink and myself. It was found that sulfur dioxide combines readily with aniline, either pure or in solution in anhydrous solvents, giving crystalline yellow compounds with moderately high dissbciation pressures; the same type of reaction occurs with the toluidines, with benzidine, with dimethylaniline and with any amine of a fairly pronounced basic character; the reaction appears to be quite general. Because of the partial decomposition and loss of sulfur dioxide which these compounds underwent during handling, it was not found possible to analyze them by the usual methods, and the work was therefore stopped. During the past year the work was taken up again and the composition of the compounds determined by the phase rule methods made familiar in the early study of the hydrates of copper sulfate and more recently by Bancroft[1] in his studies of salt formation among the proteins; vapor pressure measurements have been made and a study made of the behavior of the compounds upon melting.

Search of the literature has disclosed that previous to our investigation only a single case had been found in which this general reaction figures, namely, that of sulfur dioxide with aniline, and in this instance the facts are given correctly in part and quite incorrectly in other parts. Schiff[2] states, incidentally to his work upon organic amines, that "aniline absorbs sulfur dioxide, as previously noted by Hofmann," that the solid is yellow, appears to contain equivalent amounts of both substances, *i. e.*, has the formula $C_6H_5NH_2 \cdot SO_2$ and can exist only in presence of excess sulfur dioxide; the reference to Hofmann's work has not been located. On exposure to the air, the solid became quickly decolorized with loss of sulfur dioxide, changing to what he believed to be $2C_6H_5NH_2 \cdot SO_2$; his analysis gave 26–28% SO_2, the theory requiring 25.6%; the original yellow solid he did not analyze. Boessneck[3] mentions the original compound and found it to contain 32% SO_2, where the theory requires 40.8% for a 1:1 compound. Michaelis[4] by treating thionyl aniline (C_6H_5NSO) with aniline and water or with moist ether obtained the second of Schiff's compounds, the white solid said to be $2C_6H_5NH_2 \cdot SO_2$, melting at about 60°, and only slowly decom-

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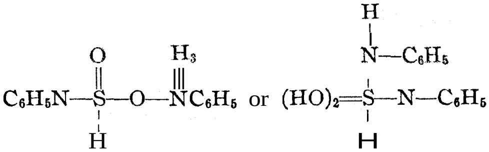
[1] Bancroft and co-workers, J. *Phys. Chem.*, *34*, 449, *753*, 1217, 1930,2433 (1930).

[2] Schiff, Ann., 140, 125 (1866).

[3] Boessneck, *Ber.*, 21, 1910 (1888).

[4] Michaelis, *ibid.*, 24, 749 (1891).

posing into its components; he proposes the structural formula of a phenylamidosulfinic acid for the yellow compound, and



$$C_6H_5N-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{S}}-O-\overset{\overset{H_3}{|||}}{N}C_6H_5 \text{ or } (HO)_2=\underset{\underset{H}{|}}{\overset{\overset{\overset{H}{|}}{N}-C_6H_5}{\overset{|}{S}}}-N-C_6H_5$$

for the second. Schiff also records that if sulfur dioxide is passed into a mixture of aniline and water, a heavy precipitate of a ***yellow*** crystalline body is obtained, which will lose sulfur dioxide rapidly until it has reached the composition $4C_6H_5NH_2{\cdot}SO_2 + n$ aq., which compound he regards as belonging to the class of the sulfites of aniline, no analysis being given.

Subsequent to our earlier work, Korezyǹski and Glebocka[5] investigated the action of sulfur dioxide upon a large number of amines and substantiated the formulas of the resulting compounds by the volume of sulfur dioxide absorbed under one atmosphere pressure. In the majority of the cases, although not in all, the ratio of one mole of sulfur dioxide to one amino group was observed. The dissociation pressures of these compounds were not measured.

The results which follow in this paper have established that sulfur dioxide acts upon anhydrous aniline to form only the yellow addition product $C_6H_5NH_2{\cdot}SO_2$, for which neither Schiff nor Boessneck could obtain a satisfactory analysis; that its exposure to the air results not only in the loss eventually of some of the sulfur dioxide, but also in the absorption of water with the formation of a white crystalline mass which is a mixture of the acid sulfite and the normal sulfite, the two true salts formed by aniline and sulfurous acid; the other formulas proposed by Schiff, Boessneck and Michaelis are not substantiated, and the yellow color of Schiff's compound obtained in the presence of water may be taken as evidence that this material held considerable quantities of discolored aniline. It should be remarked that in looking for descriptions of the salts of aniline and other amines with sulfurous acid, it was found that Beilstein's earlier edition, while giving in general the salts with hydrochloric acid, sulfuric acid, nitric acid, etc., gives no evidence that the salts of sulfurous acid have been prepared; the edition now being completed has not yet reached the volume on the aromatic amines. The generalization may be made, on the basis of this work, that amines form yellow addition products usually in the 1:1 ratio with dry sulfur dioxide, and that in the presence of water, as should be expected, normal or acid sulfites are produced, which are, of course, colorless.

For the preparation and study of the addition compound, Kahlbaum's aniline was used, redistilled and stored in a desiccator over sulfuric acid; the sulfur dioxide was

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[5] Korezyǹski and Glebocka, *Gazz. chim. ital.*, ***50,*** **I,** 378 (1920).

taken from a small commercial cylinder, which was allowed to run for a considerable time to free the gas from possible impurities. For the vapor pressure measurements by which the composition of the compound was determined, the apparatus consisted of a glass-stoppered 50-cc. distilling flask immersed in a water thermostat, connected by its side tube to a 50-cc. gas buret from which it could be shut off by a glass stopcock, and also connected to a mercury manometer and to a Hyvac pump shut off by a mercury-sealed stopcock. The aniline and sulfur dioxide, therefore, were in contact only with glass throughout the entire apparatus. Samples of about one gram of aniline were weighed into the reaction vessel for each run, with the addition of glass beads to increase the surface. After introduction of the aniline the system was connected with the pump, which in less than sixty seconds reduced the pressure to an amount too low to be noted by direct reading on the manometer. For the introduction of known amounts of sulfur dioxide, the gas buret was fitted with a side tube and a three-way stopcock; in filling the buret, the cylinder of sulfur dioxide was connected by rubber tubing to the three-way stopcock and the gas, previously dried by sulfuric acid in a small U-tube, passed through the by-pass to sweep out air for about twenty minutes. It was then turned into the gas-buret and allowed to displace the mercury with which the buret had been filled, care being taken that the gas entered always under a slight excess pressure so that possible leakage of air inward through the rubber tubing was eliminated. By calculation from the volume, pressure and temperature of the gas the weight admitted to the system was known. The initial absorption of the gas by the aniline is very rapid, and equilibrium appears to be reached within a few hours up to the point where the liquid has been largely changed to the solid, at which time entrance of the gas through the crust of solid is slowed up considerably; twenty-four hours were allowed to elapse before final readings of the manometer were made. By making correction for the amount of sulfur dioxide remaining in the apparatus, of known volume, pressure and temperature, the amount absorbed by the aniline could be calculated; these corrections are of relatively small amount only, since the total volume of the apparatus was only 92 cc. and the pressures are low. The probable errors in the reading of the manometer with the correction for variations in barometric pressure are of the order of ±0.5 mm. of mercury. The results of such a run are given in Table I.

TABLE I

VAPOR PRESSURE OF ANILINE + SO_2 AT 25°

Weight of aniline used, 1.311 g.

Pressure, mm.	SO_2 absorbed, mg.	Moles of SO2 absorbed per mole of aniline
17.5	49.4	0 055
37.0	99.2	.110
44 2	130.9	.145
44 2	247.1	.274
44 0	379.7	.421
45.7	596.9	.668
45 5	824.1	.914
56.0	885.5	.981
127.5	887.6	.984
475.5	888.2	.985
43.0	(Partial evacuation)	

From the plot of these results in Fig. 1 the interpretation can easily be made. Sulfur dioxide dissolves in liquid aniline at 25° up to a pressure of about 44 mm. and a concentration of about 0.14 mol of the gas per mole of aniline. At this concentration the solid addition product appears and the system, with three phases and a fixed temperature, remains invariant upon further additions of sulfur dioxide until the aniline has been completely converted into the compound, at which point further additions of gas cause an abrupt rise in pressure without further absorption in significant amount. The abrupt rise at an absorption of 0.98 mole is sufficient proof that the components combine in *a* 1:1 ratio to form the compound $C_2H_5NH_2{\cdot}SO_2$, and the absence of any break in the flat portion of the curve rules out the existence of any of the compounds lower in sulfur dioxide content assumed by Schiff and Boessneck. The slight rise which is noted in the nearly flat portion of the curve is due, it is believed, not to impurities in the gas but to incomplete attainment of equilibrium from the higher pressures, impeded by the crust of solid upon the liquid; partial evacuation, as shown in the last line of the table, gave **a** pressure as low as **43** mm., while the same sample, after the higher temperature and higher pressure of Table II, showed a pressure slightly over 44 mm.

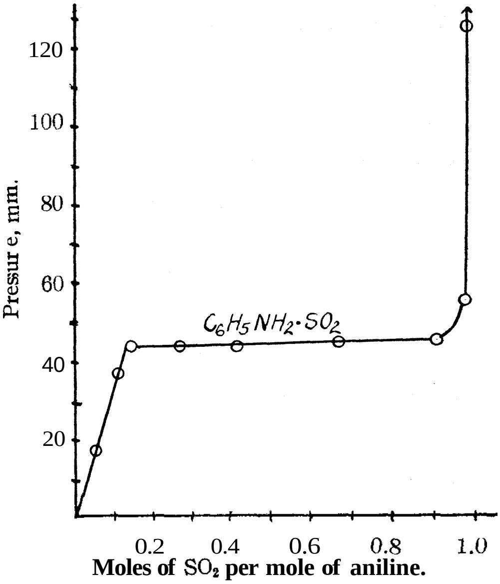

Fig. 1.—Pressure-composition diagram, aniline + SO_2 at 25°.

The color changes in this system are marked, and appear to be alike for all the amines upon treatment with sulfur dioxide. The liquid solution obtained from colorless aniline has *a* deep orange-red color, which appears also upon melting the solid in a sealed vessel; while the solid compound, if freed from all solution, and especially if sublimed, is of a lemon-yellow color.

Vapor pressure measurements were made at several temperatures by first exhausting the system below **43** mm. to insure absence of excess sulfur dioxide and then changing the temperature of the thermostat. **At** the higher temperatures equilibrium appeared to be reached in fifteen to thirty minutes. The results are given in Table II.

The vapor pressure curve, shown in Fig. 2, rises very steeply with the temperature. A plot of the logarithm of the pressure with the inverse of the absolute temperature, shown in Fig. 3, gives a good straight line, in which only the point at 3.5° appears misplaced. From this curve it ap-

TABLE II

VAPOR PRESSURE OF $C_6H_5NH_2 \cdot SO_2$ AT VARYING TEMPERATURES

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
3.5	3.7	45	360
25	43	50	630
30	72.5	52	(760) (by extrapolation)
35	125		

pears by extrapolation that the pressure reaches 760 mm. at a temperature of 52°, as given in the last line of Table II. The true melting point of the compound is distinctly higher, so that it would sublime without melting under atmospheric pressure. From the slope of the curve of Fig. **3** the heat of vaporization of the compound, calculated from the formula d In p/d T = X/RT^2, is 19,630 cal.

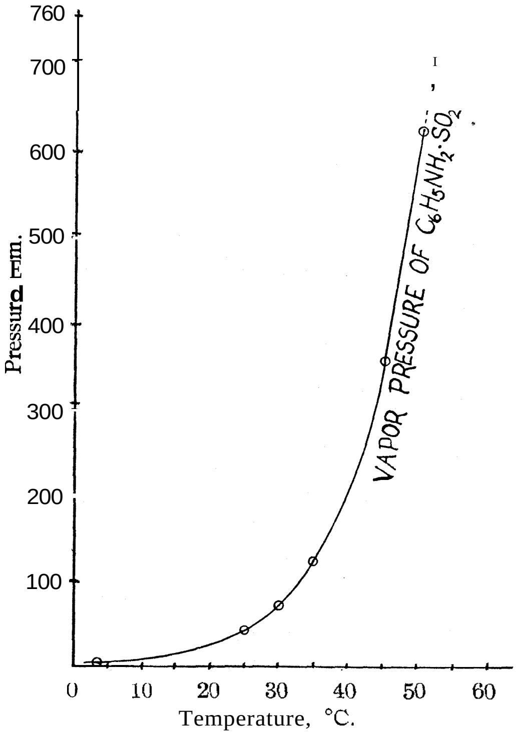

Fig. 2.—Vapor pressure of $C_6H_5NH_2 \cdot SO_2$ at varying temperatures.

Efforts to find the melting point of the compound gave only approximate results. The work, of course, must be conducted in a closed system, to prevent loss of sulfur dioxide. Because of the high pressures developed, only small amounts could be safely handled, and it was not found possible to keep the composition entirely under control. Amounts of 200 to 500 mg. of aniline were weighed into small tubes of total capacity of 2 to **3** cc. and dry sulfur dioxide introduced through a capillary; the tubes were sealed and reweighed to ascertain the amount of sulfur dioxide present, but in no case could the amount be brought up to the requisite one molecule. Samples holding over 90% of this amount came to complete liquefaction at temperatures slightly over 60°; the best sample, containing 0.969 mole of sulfur dioxide per mole of aniline, melted completely at 63.1°. If we assume that the melting point curve of this system forms a blunt angle with the composition axis, as should be true for a compound which dissociates largely into its components, the melting point cannot be greatly higher than the temperature found, and may be set at about 65° and a pressure of about 3.5 atmospheres, from the curve of Fig. 3.

Inspection of Fig. 1, which is a pressure–composition isotherm for 25°, will show that for higher temperatures, since the solubility of the solid in liquid aniline increases, the horizontal section of the curve will become shorter, until it reaches the dimensions of a point and a position at 1:1 composition on the ordinate at the congruent melting point, where the composition of liquid phase and solid phase is the same. A search was made to find some treatment in the literature which should include the effect of the three variables, temperature, pressure and composition, upon a compound having a congruent melting point. Such a treatment is not in Roozeboom's "Die Heterogenen Gleichgewichte," and I have not found it elsewhere. For that reason it seemed worth while to construct a model showing these relationships so that they can be easily visualized; Fig. 4 is a perspective view of such a model, including the three variables and showing the regions of stability for the solid, liquid and gaseous phases. Though drawn to illustrate the system aniline–sulfur dioxide, it may be applied without change to any binary system forming a compound which melts congruently, at temperatures above the melting points of the two components. The curve *bge* will be recognized at once as the solubility curve for the compound, which in the representation of condensed systems is familiarly drawn as a projection upon the composition–temperature surface. What is left out of the familiar projection, however, is that not only is the solubility curve *bg* moving in the direction of higher pressures with increase in temperature, but that *ge* also is moving in the direction of higher pressures with decrease in temperature. To the well-known fact that the solid phase may be in equilibrium at a constant temperature with either of two liquid phases of differing composition (*i. e.*, has two solubilities) is to be added the fact that, of course, the two liquids have different vapor pres-

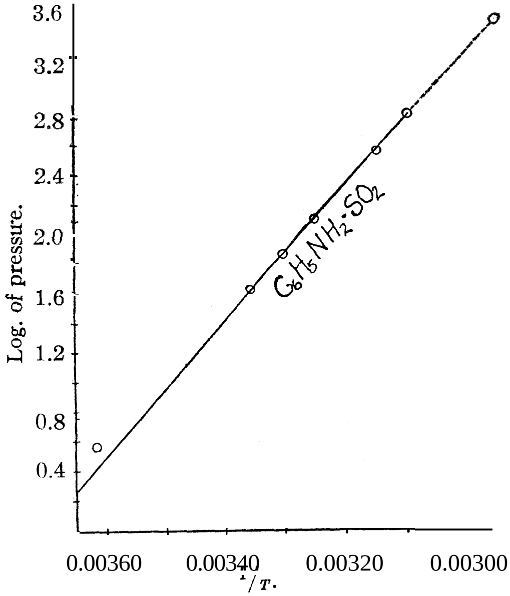

Fig. 3.—Log of pressure *vs.* $1/T$ for $C_6H_5NH_2{\cdot}SO_2$.

sures. The front view of the figure, here given, shows in perspective the regions of stability for the solid, for liquid solution and for vapor alone.

The projection of an isotherm such as t_0 upon the composition–pressure surface is shown in Fig. 5. This is a complete representation of what has been shown in part in Fig. 1 and in the usual representation of vapor pressures in two-component systems. The line ab, shown in both Fig. 5 and Fig. 1, represents the change in solubility of sulfur dioxide in liquid aniline with increase in pressure; at pressures lower than b the system can consist only of a liquid phase conjugate with vapor of the same pressure and a different composition, expressed by a point on the vapor curve *axyf*. At the pressure b solid appears, and addition of sulfur dioxide results only in variation in the amounts of the three invariant phases, b (liquid), *c* (solid compound) and *x* (vapor). Upon addition of sulfur dioxide up to the composition *c* the liquid has all been changed to solid compound; further additions of sulfur dioxide result only in a change in pressure without any change in composition of the compound, *i. e.*, the system is isothermally univariant and consists of solid conjugate with vapor of the compositions shown along the section *xy* of the vapor curve. At *d*, a high pressure not measured in this instance, there is condensation of a new liquid phase *e*, rich in liquid sulfur dioxide, and the system is again isothermally invariant, consisting of compound, liquid phase *e* and gaseous phase y. Additions of sulfur dioxide result now in diminishing the amount of the solid and increasing the amount of the liquid until the solid disappears entirely at e; further addi-

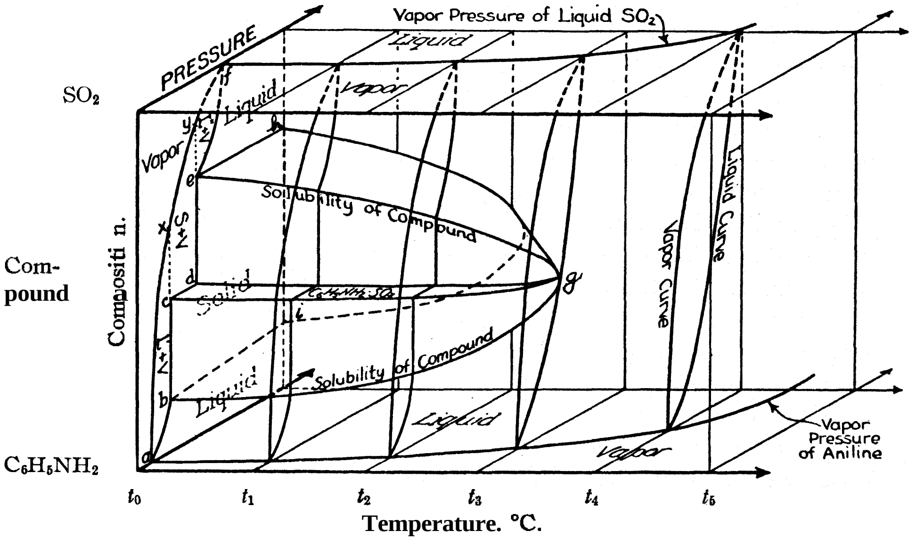

Fig. 4.—Pressure–temperature–composition diagram for a compound with congruent melting point.

tions give the isothermally univariant system consisting of liquid represented on the curve *ef* and vapor represented on the curve *yf*. The pressure at d may be looked upon not only as the second vapor pressure of the system compound–liquid–vapor, but also as the deliquescence pressure of the compound. The curves *bi* and *eh* are boundary curves between the area for the solid and the areas for the two liquid phases; they will tend to meet at high pressures or to separate further according as the volume of the system tends to decrease or increase upon dissolving of solid phases. If isotherms are drawn at successively higher temperatures, the distance cd and the distances bc and de will become shorter; at the congruent melting point the four points will have met at a single point, represented by g in Fig. 4. Above this temperature only liquid and vapor can exist, up to the point where the vapor curve and the liquid curves meet, at the critical temperatures for varying solutions of the two liquids.

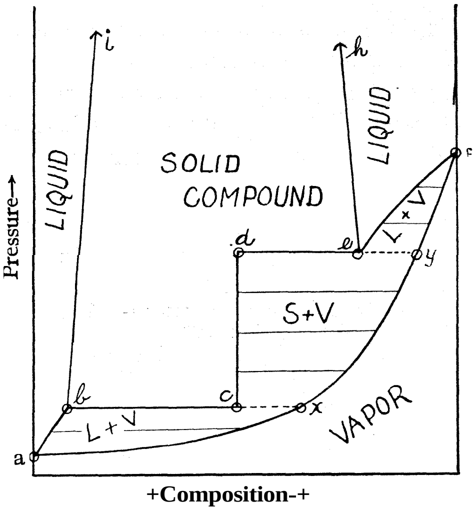

Fig. 5.—Pressure-composition diagram for a compound with congruent melting point.

Experimental work has also been carried out upon the ternary system consisting of aniline, sulfur dioxide and water, in order to determine whether or not normal sulfites and acid sulfites exist, and to explain the observation that the yellow addition product previously discussed turns white on exposure to the air. It is possible to determine the composition of ternary systems such as this by the measurement of vapor pressures as used above, but not with the same simplicity either as to theory or as to practice. Considering that aniline and water have but small mutual solubility, it becomes clear that the addition of sulfur dioxide will, upon the appearance of solid sulfite, give rise to an isothermally invariant system consisting of two liquids, solid and vapor; but in the absence of previous knowledge as to the solubility of the solid in the liquids, it is impossible to predict just what quantities of the two liquids should be taken to insure the appearance of the solid. Again, the absorption of the gas without increase of pressure will not cease abruptly at the point where the composition of the solid is reached, because of the solubility of gas in the liquid phase, but by keeping this liquid at a minimum the amount of this correction can be minimized. Another isothermally invariant system will consist of solution, vapor, solid normal sulfite and solid acid sulfite, if the solubility relations can be properly controlled, with the same error in determining the composition due to absorption of excess gas by the liquid phase. The experiments were therefore begun with aniline and a quantity of water only slightly in excess of the one mole required for the reaction. It was found in this case, and in others in which the water was increased by successive amounts up to eight moles, that the initial absorption of sulfur dioxide was rapid and that an approximately constant pressure was obtained, but that when the absorption had reached from 0.6 to 0.8 mole it ceased quite abruptly and that high pressures allowed to remain in contact with the system for periods up to two weeks caused no further absorption in significant amount. It is believed that this behavior is due solely to mechanical obstruction; that the salt, forming a hard and impenetrable crust in an apparatus in which agitation is almost impossible, acts as a barrier between the water and the gas, and that the reaction with water present only as a vapor is too slow to be followed. This hypothesis was justified by the results of experiments in which larger amounts of water were used, of which the results are given in Table III.

TABLE III

ANILINE, SULFUR DIOXIDE AND WATER AT 20°

Curve 1
Molar ratio, aniline/water = 34
Wt. of aniline 0.605 g.

Pressure, mm.	Moles SO_2 absorbed per moles aniline
17.5	0
17.2	0.154
17.7	.473
19.0	.794
38.0	.960
80.5	1.055

Curve 2
Ratio = 18.5
Wt. of **aniline** 0.594 g.

Pressure, mm.	Moles SO2 absorbed per moles aniline
17.5	0
18.0	0.171
18.5	.486
18.6	.538
20.5	.848
23.5	.956
43.4	.997
84.0	1.03

In calculating the moles of sulfur dioxide absorbed, the assumption was made that its partial pressure in the system was the total pressure minus that of pure water, since the aqueous pressure of the solutions was not known. The error introduced by this assumption can affect the position of the points as shown in Fig. 6 only by a fraction of one per cent. The temperature of 20° was used to avoid the distillation of water into the outer parts of the vessel, which occurred at 25°. The two curves, shown in Fig. 6, show that the gas is absorbed with small continuous rise in pressure up to an amount approximating one mole of sulfur dioxide to one of aniline, the approximation being closer where the amount of excess water is smaller (Curve 2) and the error introduced by its presence smaller; above this ratio of sulfur dioxide to aniline, the absorption increases very slowly with large increase in pressure and the upright branches of the curve represent an approximation to Henry's law. In case 1 solid phase appeared at about 0.6 mole of gas present, in case 2 at about 0.3 mole. The curves may be taken as establishing the existence of the 1:1 compound containing water, which would be the acid sulfite, $C_6H_5NH_3HSO_3$, but give no evidence as to the existence of the normal sulfite or other salts.

The effort to prepare the various sulfites in condition for analysis by precipitation from aqueous solution meets with obstacles because of the difficulty in finding such a drying agent for ternary compounds as would absorb the water from the mother liquor upon the crystals without leading to loss of water of composition. The nearest approach to such a desiccant is the anhydrous compound, $C_6H_5NH_2\cdot SO_2$, which has been shown capable of combining with water, but it is not the hydrate immediately below the acid salt, $C_6H_5NH_2\cdot H_2O\cdot SO_2$, and therefore is not the correct drying agent for that compound. It was used, however, with a sample of salt prepared by passing sulfur dioxide to saturation into a 2:3 mixture of aniline and water, from which the white salt crystallized copiously. After rapid centrifuging it was placed in a desiccator over a large amount of the yellow addition product. Loss of weight occurred continuously for thirty-four days, after which the loss dropped to an amount of less than 0.01% per day, which loss doubtless occurred during the transfer of the sample to the balance. At this point an analysis was made for the SO_2 content, by evolving the gas from a sample by addition of acid and passing it into a known solution of iodine in potassium iodide; the sulfur dioxide content found was 23.46%, which is close to that calculated for the normal sulfite, $(C_6H_5NH_3)_2SO_3$ (23.88%). It appears then that aniline forms a crystalline normal sulfite and a crystalline acid sulfite which may be precipitated from aqueous solutions, but

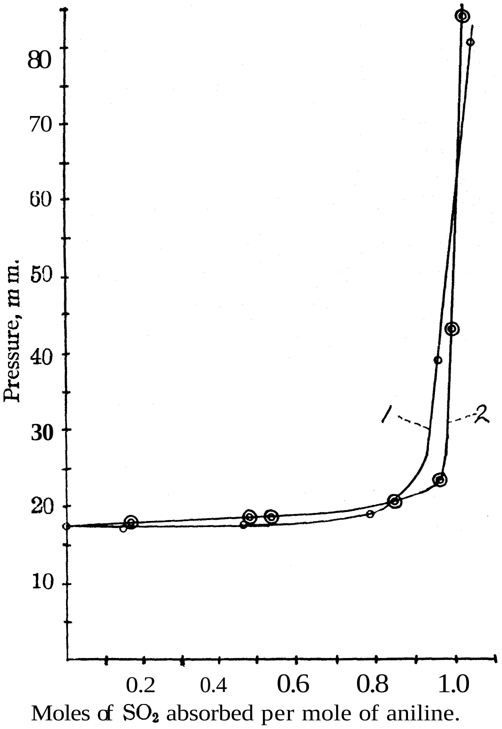

Fig. 6.—Absorption of sulfur dioxide by aniline in the presence of water at 20°.

which have (as shown in Table III and what follows) sufficiently high decomposition pressures to prevent their easy preparation in pure form.

The decomposition pressure of the anhydrous addition compound has been shown, in Table I, to be 44 mm. at 25°. That of the acid salt could not be measured, but is some rather small fraction of the 18–20 mm. of Table III at 20°. That of the normal salt was determined at 20° by direct addition of the dry compound to the apparatus and repeated evacuation with the pump: it is found to be 3.5 mm. ±0.5, of which but half is sulfur dioxide. We may therefore explain the action of the yellow compound on exposure to air as an addition of water and a loss of sulfur dioxide passing through the composition of the acid salt to that of the normal salt.

A sample of the normal sulfite, taken in a closed tube with excess sulfur dioxide, melted incompletely to a red liquid, beginning at 62°, in sufficient proximity to the melting point given by Michaelis[4] to make it probable that his white solid was the normal sulfite.

From the high dissociation pressure which the yellow addition product displays, it seems preferable to consider that the sulfur dioxide is held by secondary valence and that the structural formulas proposed are likely to be misleading. However, it was found that when samples are heated in a closed tube at 100° for about sixteen hours, they change to a nearly colorless solid, not liquefying at 100°, and with no appreciable sulfur dioxide pressure. The nature of these compounds will be the subject of further investigation, as will also vapor pressure measurements of the addition products of sulfur dioxide with other aryl amines and the measurement of the solubility of the two sulfites of aniline in water.

Summary

1. Aniline combines with sulfur dioxide in the 1:1 ratio to form a yellow crystalline solid.

2. The vapor tension of the addition compound was measured between 3.5 and 50°, and the heat of dissociation calculated.

3. A diagram has been constructed and discussed for a binary compound above the melting points of its two components, showing temperature, composition and pressure as variables.

4. In the presence of water aniline combines with sulfur dioxide to form a normal sulfite and an acid sulfite, both of which have dissociation pressures markedly less than that of the anhydrous addition compound.

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GRADUAL TRANSITION IN SODIUM NITRATE. I. PHYSICO-CHEMICAL CRITERIA OF THE TRANSITION

BY F. C. KRACEK

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Until a few years ago the only transitions recognized in pure crystalline solids were of the polymorphic kind, that is, inversions from one crystalline modification of a substance to another. Inversions of this type are characterized by a more or less great change in the crystal lattice, and each modification has well-defined physical properties which alter by discontinuous steps, theoretically at a point at which two neighboring modifications can be considered to be in equilibrium. From the standpoint of thermodynamics these inversions are analogous to melting in the sense that we can express all the quantities involved by means of a Clapeyron equation and, particularly, there is an equilibrium value of the (latent) heat of transition and of the (latent) volume change at the inversion point which is a function of the temperature and pressure. The salient characteristic of the polymorphic inversions is the phenomenon of hysteresis; the transformations are prompt in some cases, but often they are so sluggish that geologic times have failed to effect the conversion from the unstable to the stable modification in certain minerals. A consequence of this retardation in the inversion is that there is a (hysteresis) band of temperature and pressure values within which two modifications can *co*-exist with little or no tendency to transform.

Some substances exhibit apparent transitions which are abnormal when contrasted with the true polymorphic changes. The specific heat curves, for example, increase gradually over a long interval below the transition point; instead of a discontinuous change at this point, the specific heat merely reaches gradually a high value, and then gradually but more rapidly sinks to a normal value. Other criteria have not yet been sufficiently investigated in most cases, but it is fairly certain from the measurements that have been made that there is very little change in the crystal lattice, and that the volume alters gradually rather than discontinuously on changing the temperature.

The examples hitherto described all occur at temperatures below 0°. The first was ammonium chloride, studied by Simon,[1] who later investigated other ammonium salts. These investigations showed that the heat capacity curves pass through well-defined maxima in the neighborhood of -30 to $-50°$, the different anions in combination with the NH_4^+ altering

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[1] F. Simon, Ann. *Physik,* 68, 241 (1922); Simon and Simson. *Naturwiss.,* 38, 880 (1926); Simon, Simson and Ruhemann, *Z. physik.* Chem., *129,* 339 (1927); Simon and Bergmann, *ibid.,* 8B, 255 (1930).

the temperature of the peak of the curve only a few degrees. Structurally there is apparently no change, and the expansion curves are gradual, but with abnormal contours in the neighborhood of the transition temperatures (when defined as the temperatures of the peak of the specific heat curves). On the basis of these results it has been suggested that the phenomenon is due to intramolecular rearrangement of the ammonium ions. Other examples are found in the specific heat curves for a number of condensed gases,[2] for which unfortunately other criteria are lacking. Hendricks[3] on the other hand has noted that crystal structure studies on the primary alkyl ammonium halides at room temperature lead to the postulate of a collinear carbon chain, whereas at liquid air temperatures the staggered chain is the more probable. This is in accord with a suggested explanation based on the quantum mechanics, offered by Pauling,[4] who postulates a transition from oscillatory to rotatory motion within the lattice of a crystal. Smits[5] has studied the thermodynamic aspects of the problem, and arrives at a series of pseudo-binary diagrams, without definite suggestions as to the nature of the pseudo-components.

It should be emphasized that the experimental evidence presented in the literature is lacking in one important aspect, namely, that of the reproducibility of the physical properties measured. The specific heat curves give us the best example of this; different investigators agree in general on the form of the curve, but often disagree seriously as to the exact values of the specific heat. The question of reproducibility is of particular importance when any given property is employed to differentiate between a gradual transition and a sluggish polymorphic inversion, for obvious reasons. It must be admitted, however, that this objection is largely of academic interest only, since the very nature of the methods of specific heat measurements at low temperatures is such as to assure the general correctness of the results.

In addition to the two types of transitions mentioned above, it is likely that there exists a third type in which a true polymorphic inversion is preceded by an abnormal change in specific heat and other properties. Quartz appears to belong to this mixed class; it is well known that its properties (specific heat, thermal expansion, optical properties) undergo large changes over a considerable temperature interval below the inversion point at 573° where the crystals suddenly change from trigonal to hexagonal symmetry. No other cases of this type appear to be known.

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[2] Eucken and Karwat, *Z. physik. Chem.*, 112, 467 (1924), HBr and HI; Giauque and Wiebe, THIS JOURNAL, 50, 2193 (1928); 51, 1441 (1929), HBr and HI; K. Clusius, *Z. physik. Chem.*, **3B**, 41 (1929), N_2, O_2, CO, CH_4.

[3] S. B. Hendricks, *Z. Krist.*, 67, 465 (1928); 68, 189 (1928); ***Nature***, 126, 167 (1930).

[4] L. Pauling, ***Phys. Rev.***, ***36***, 430 (1930).

[5] *A.* Smits, ***Physik.*** Z., **31**, 172, 376, 435, 768 (1930).

The investigation reported in this and a following paper is concerned with a gradual transition in sodium nitrate. This substance occupies an apparently anomalous position among the nitrates of univalent metals. With the exception of lithium nitrate, which forms a trihydrate at ordinary temperature, all the other univalent nitrates exhibit one or more normal polymorphic inversions. Bridgman,[6] who studied these inversions under pressure, remarks upon the similarity of the phase diagrams and discusses the crystallographic analogies between the various forms encountered. Sodium nitrate is rhombohedral of the calcite type at ordinary temperature. This crystal type is found in anhydrous lithium nitrate, and as the high temperature modification of potassium nitrate and rubidium nitrate. None of these, however, appears to be completely isomorphic with sodium nitrate.

An unsuccessful search for an inversion in sodium nitrate has been made by Bridgman[6] and by Hissink.[7] Both investigators stopped at temperatures below that at which the gradual transition is completed.

In many respects the thermal behavior of sodium nitrate parallels that of ammonium chloride as already described. The specific heat begins to increase abnormally and reaches a peak value at 275°. Optical examination with a heating microscope fails to show any decided change between room temperature and the melting point, but the thermal expansion curve exhibits an abnormal course between 150 and 275°. The behavior is reproducible, and hysteresis phenomena are completely lacking. Studies have also been made of the solubility in water up to the melting point of the salt, and of the crystal structure at various temperatures.

The results are in good agreement with the postulate of intramolecular rotation[4] of the NO_3 ion at temperatures between 275° and the melting point, the deciding factor being the information gained from the analysis of the structure. This portion of the work, in collaboration with E. Posnjak and S. B. Hendricks, is published separately in a following paper. The results collected in the present article deal with the purely physicochemical determination of the gradual transition, and are independent of any postulate as to the nature of this phenomenon.

Part I. Thermal Capacity

In 1909 a paper was published by Goodwin and Kalmus[8] on the determination of specific heats and latent heats of melting for a number of salts, among which was included sodium nitrate. There is an anomaly in the course of the specific heat curve for the crystals of this substance, which was passed over unnoticed, but which certainly exceeds a reasonable

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[6] *P. W. Bridgman, Proc. Am. Acad. Sci., 51, 581* (1916).

[7] D. J. Hissink, *Z. physik. Chem.*, 32, 537 (1900).

[8] Goodwin *and Kalmus, Phys. **Rev.**, 28,* 1 (1909).

experimental error,[9] amounting to 5–10 cal./g. in the value of the total heat of the crystals. During the course of another investigation[10] I had occasion to take thermal analysis curves of sodium nitrate, and found an abnormal heat effect in appropimately the same region as that exhibited by the results of Goodwin and Kalmus. The characteristics of this heat effect were different from those usually associated with normal polymorphic inversions, and hence a closer study was made of the phenomenon.

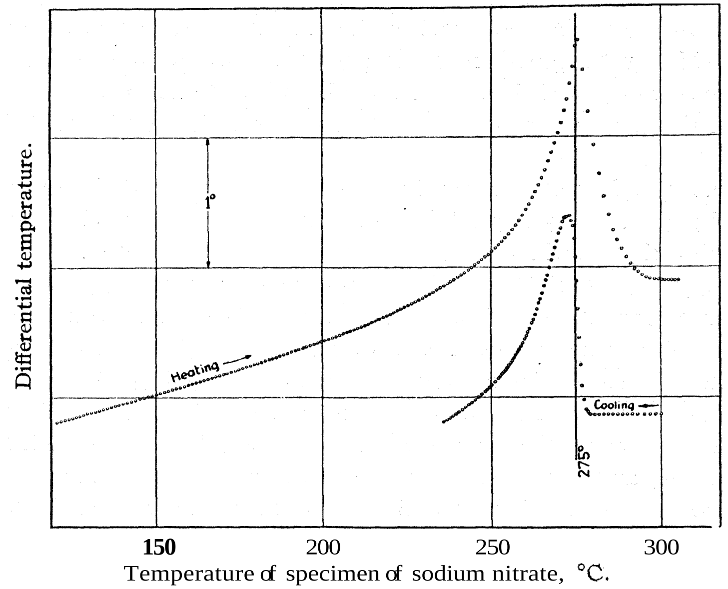

Fig. 1.—Differential heating and cooling curves for sodium nitrate. Note the absence of location of the beginning of the heat effect and its sharp termination on the heating curve.

The accessory apparatus used for thermal analysis was the same as in my earlier work. In order to secure maximum sensitivity and freedom from minor fluctuations of the differential temperature, the furnace was provided with a hollow copper block within which the sample of sodium nitrate contained in a platinum thimble crucible was suspended upon the thermocouple, which was immersed in the salt, but protected from corrosive attack by a capsule made from platinum tubing 1.5 mm. in diameter. The reference thermocouple was located in a well in the copper block. This arrangement has proved to be entirely satisfactory in that the differential temperature readings were perfectly steady. Readings were made to within 0 2 microvolt, using copper–constantan couples, which corresponds to a sensitivity of 0.005°, far in excess of what was actually needed. The thermocouples were calibrated with accepted standards.

The sodium nitrate used for the experiments was recrystallized, starting with the best C. P. material available. About 2.5 g. of the salt was used in each experiment.

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[9] The melting points quoted in their Table II, p. 12, for sodium nitrate and potassium nitrate are transposed.

[10] F. C. Kracek, *J. Phys. Chem.*, **34,** 225 **(1930).**

Single crystals were produced by melting the samples in place in the furnace and slowly coaling. It may be mentioned, however, that single crystals and crystal aggregates showed no difference in behavior.

Typical results of the thermal analysis experiments are shown in Figs. 1 and 2. The important feature of these curves is that, on heating, the rise in the differential temperature ceases sharply at 275.5°, but on cooling, heat begins to be evolved by the sample at a temperature which is higher, namely, about 279°. This is contrary to all experience with normal polymorphic inversions,[11] in which the heat effect on cooling, in consequence of hysteresis, however slight in amount, always begins at a temperature which is *lower* than that at which the heat effect begins on heating. The second unusual feature of these curves is that *no point of beginning* of the heat effect can be located on the heating curve. The heat capacity increases gradually as temperature rises to 275.5°, and then suddenly decreases sharply to a normal value, within 2 or 3 degrees, as shown by the contour of the recovery curve, and the beginning of the heat effect on cooling. Just below 275.5° the increase in heat capacity is rapid, but it does not have the character of a latent heat, for in the latter case we should expect in a single crystal a fall in the temperature of the sample with a rising

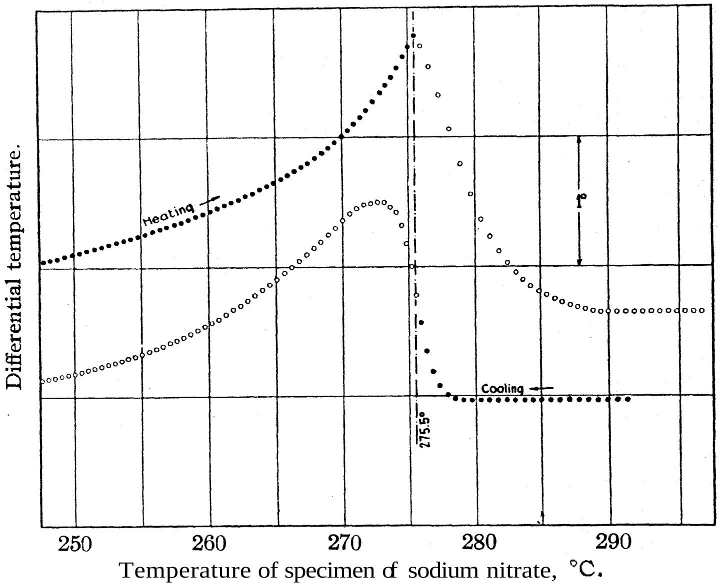

Fig. 2.—Differential heating and cooling curves for sodium nitrate near the peak of the curve. Compare the black circle curves with the curve of the expansion coefficient in Fig. 6.

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[11] Consult J. *Phys. Chem.*, **34**, 225 (1930), for typical heating and cooling curves obtained with potassium nitrate.

differential temperature, with a heat effect which is so prompt. While these experiments do not yield an absolute value for the heat capacity, they nevertheless furnish relative values, and they describe the character of the behavior as exactly as could be done with a strictly calorimetric procedure.

The results of these experiments on the abnormal increase in the heat capacity, which extends for at least 100° below the temperature at which the peak of the curve is reached, favor the conclusion that the change which takes place in the crystals of sodium nitrate is not that of a typical inversion from one modification to another, but rather a gradual alteration instead of an abrupt one in the properties of the same physical phase.

Part II. Thermal **Expansion** of Sodium Nitrate

The measurements of the volume change which a polymorphic substance undergoes during the transition from one crystal phase into another is important from the standpoint of thermodynamics since the ratio of the heat of inversion to the volume change per unit mass enters into the calculation of the slope of the transition curve in consequence of the Clapeyron equation. In addition to the quantitative consequences of such measurements, there is obtained usually a considerable amount of pertinent information regarding the characteristics of the transition, particularly with respect to the promptness and the rate with which it proceeds. In typical rapid polymorphic transitions the crystals expand uniformly and reproducibly up to the inversion point. At the inversion point the rate of transition is zero, so that it is necessary to raise the temperature some distance beyond that point by an amount dependent upon the characteristics of the substance, for the inversion to proceed. It is well recognized that the growth of nuclei of the new crystal phase is an important factor in determining the rate. Once initiated, the rapid inversions proceed readily to completion, usually within a few degrees above the equilibrium temperature. On cooling, the phenomena are reversed, so that ordinarily there is a hysteresis band extending on both sides of the transition point; within this band the volume measurements are not reproducible. After the volume change of transition is completed, the substance once more exhibits a normal expansion, which is not necessarily the same above and below the transition point.

The expansion of sodium nitrate does not proceed in the manner outlined above through the transition region, and in this respect the salt again differs from typical polymorphic behavior. The measurements were made with a mercury-in-glass dilatometer, and they gave, with suitable auxiliary measurements, values of the specific volume of the salt at various temperatures.

The **apparatus** is shown diagrammatically in Fig. 3. The dilatometer was made of Pyrex glass, in the simple form indicated.[12] The bulb of the dilatometer was in an

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[12] Compare Kracek and Gibson, *J. Phys. Chem.*, ***34***, 188 **(1930).**

air-bath thermostat heated by electric current, and controlled by a bare five-junction copper–constantan thermocouple which operated a special potentiometer controller. The temperature control was sensitive to ±0.05° at any given setting. The air was kept in motion by a propeller fan rotated at about 800 r. p. m.; this fan maintained the whole enclosure at a uniformly distributed temperature. The reading thermocouple of copper-constantan (calibrated) was fastened to the dilatometer bulb by two clips, and was enclosed in a small porcelain tube, partly for protection, and partly to give it a thermal lag somewhat comparable with that of the contents of the dilatometer.

The exposed portion of the dilatometer was of heavy capillary Pyrex tubing. The reading portion of the capillary was in vertical position, and was placed against a mirror which had a scale engraved upon it. The readings were made with the aid of a cathetometer to avoid parallax, and were recorded to 0.1 mm. Corrections were made for the exposed stem to reduce all the readings to 25°, which was the approximate temperature of the room.

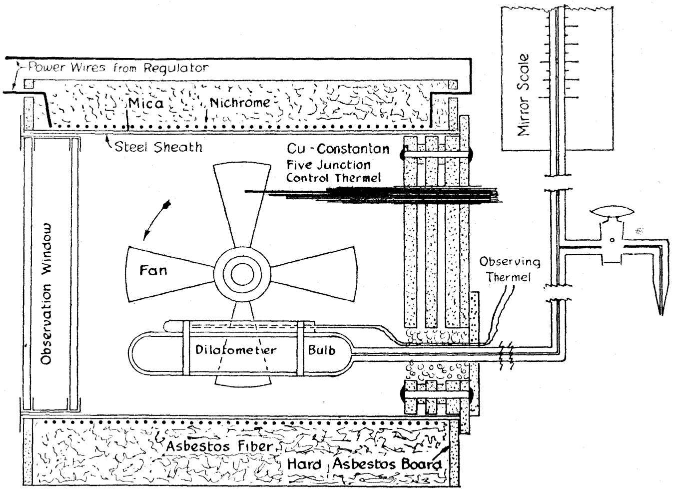

Fig. 3.—The thermostat as used with the dilatometer.

The capillary was calibrated with a weighed thread of mercury in the usual manner, against the same portion of the scale employed in making the observations. The results of the calibration were integrated to give the cubical contents of the capillary from a reference mark to any given reading of the meniscus. The capillary was fairly uniform in cross section.

Filling the Dilatometer.—The bulb of the dilatometer was provided with a side tube through which a known amount of the salt was introduced. This side tube was later sealed off at the entrance to the bulb. Some trouble was experienced at first owing to liberation of occluded moisture by the crystals; this persisted even when the salt was fused before introduction into the bulb. It was found necessary to melt the salt in the bulb under vacuum. The salt used had been recrystallized, and was quite free from all impurities. It was first fused in a platinum dish, then crushed, and screened to remove all dust smaller than 30-mesh. A known amount of this preparation was introduced into the bulb, which was then evacuated and heated to melt the salt. After evolution of bubbles had ceased, the bulb was cooled while still evacuated and mercury was introduced, care being taken to avoid any trapped bubbles of air.

After the conclusion of the measurements the salt was dissolved out, an aliquot portion of the solution evaporated to dryness, carefully fused and weighed. This determination gave 18.824 g. of sodium nitrate, compared with 18.836 g. by direct weighing of the salt introduced into the bulb. The glass showed no evidence of attack by the salt during the fusion, and the salt showed no evidence of decomposition.

The Experimental Procedure.—The thermostat was brought up to the desired temperature and readings were taken of the position of the mercury meniscus in the capillary at five-minute intervals until three successive readings showed no change. The thermostat was then readjusted to another temperature and readings were taken as before. In this fashion a series of determinations was obtained at successively higher temperatures, followed by a series with descending temperatures. At the end of the first cycle another set of observations was begun, allowing thirty to sixty minutes at each constant temperature, to ascertain whether any secular changes were taking place. The readings in all cases remained unchanged during the whole time the temperature was held constant at each point, proving definitely that each final reading represented equilibrium conditions. At a few points in the neighborhood of 275° the temperature was held constant for several hours.

During the first cycle of readings a slight readjustment took place, probably owing to more intimate penetration of the mercury into the cracks in the block of salt in the bulb. In all the succeeding cycles the readings fell reproducibly **3.1** mm. below those for the first cycle. The readings of the first cycle were disregarded. The position of the mercury meniscus at 25° was 8.9 mm. below the zero of the scale at: the end of the first cycle, and remained unchanged thereafter.

The data obtained in these experiments were converted by calculation to give the specific expansion of sodium nitrate from 25°. For this calculation it was necessary to know (a) the total volume of the bulb, the weight of sodium nitrate and the weight of mercury in the bulb at 25°, (b) the specific volume of sodium nitrate at 25°, equal to 0.4426 cc./g. [calculated from Andreae, *Z. physik. Chem.*, **82,** 109 (1913)], (c) the specific volume of mercury at the temperature of the experiment (taken from "International Critical Tables," Vol. II, p. 457), (d) the cubic expansion coefficient of the Pyrex bulb, equal to 9.6×10^{-6}, taken from measurements by the Corning Glass Works, in addition to (e) the effective diameter of the capillary.

The greatest source of uncertainty in ΔV_t lies in the correction for the expansion of the glass bulb, which accounts roughly for 10% of ΔV_t. Some error is also introduced by the assumption that the temperature of the mercury in the capillary at the point of emergence from the thermostat dropped sharply from t to the temperature of the room. These factors introduce systematic errors which may affect the absolute accuracy of the value of ΔV_t by as much as 2%, but which do not affect the relative precision of the calculated values, so that a graph of ΔV_t vs. t°C. has the same relative precision as the original readings of the mercury meniscus.

The results of the dilatometric experiments are collected in Table I, arranged in the order in which the readings were taken. Figures 4 and 5

TABLE I

THERMAL EXPANSION OF SODIUM NITRATE MEASURED WITH A DILATOMETER

t, °C.	Position of meniscus corrected to 25°, mm.	Specific expansion of $NaNO_3$ from 25°, cc./g.
Series II		
Temperature was held constant about thirty minutes at each point		
25.0	−8.9	0.0
102.5	66.6	0.00573
114.8	78.4	.00663
135.5	97.7	.00814
173.2	134.1	.01109
188.2	149.8	.01241
199.2	161.8	.01347
215.2	180.1	.01511
233.8	204.2	.01741
251.1	230.4	.02011
264.8	252.8	.02272
269.1	261.5	.02380
272.0	269.0	.02475
276.2	281.1	.02630
280.6	286.8	.02690
286.2	292.5	.02748
293.1	299.3	.02812
298.1	304.8	.02860
275.5	280.3	.02620
270.2	264.3	,02417
265.3	253.7	.02283
25.0	−8.8	....
Series III		
Temperature was held constant thirty to sixty minutes at each point, with the exception of a period of twelve hours at 208.0". At the end of the second day's run, held overnight at about 265"		
25.0	−8.8	0.0
104.8	68.7	.00589
125.5	87.4	.00742
155.1	115.9	.00960
165.2	126.0	.01041
176.8	137.9	.01140
177.1	138.3	.01143
182.3	143.6	.01186
189.3	151.0	.01248
197.7	160.3	.01330
206.1	170.4	.01422
208.0	172.4	,01440
222.4	189.4	.01595
241.0	214.3	.01847
257.6	240.2	.02127
262.8	249.3	.02231
267.9	259.4	.02353
270.8	266.0	.02436
272.9	271.8	.02511
275.0	278.1	.02597
276.4	280.8	.02628
282.9	289.1	.02716
294.0	300.8	.02825
299.3	305.7	.02867
288.0	294.4	.02765
278.4	284.3	.02663
274.2	276.4	.02570
269.3	262.0	.02386
268.4	260.4	.02366
269.0	261.5	.02380
269.1	261.8	.02383
Series IV		
After preceding series temperature was held at about 265° overnight, then adjusted to 269.1° and successive readings were taken holding thirty to sixty minutes at constant temperature at each point		
269.1	261.7	0.02382
271.2	267.1	.02451
273.0	272.1	.02515
274.8	277.7	.02587
275.9	280.6	.02625
278.5	284.4	.02665
281.9	288.0	.02703
284.9	291.1	.02733
287.6	293.8	.02760
285.7	291.7	.02740
281.2	287.4	.02696
277.7	283.2	.02653
276.2	280.4	.02624
274.7	278.6	.02585
273.6	275.1	.02560
270.1	264.1	.02412
266.6	256.4	.02316
25.0	−8.9	....

give a graphical representation of the total expansion per gram of sodium nitrate from 25 to t°C. plotted against the temperature. These figures show the relative precision and the reproducibility of the results. Figure 4 contains data for the third series only; Fig. 5, on the other hand, contains data for series II, III and IV without distinction except for that between ascending or descending order with respect to temperature, the ascending points being marked with open circles, the descending ones with black circles.

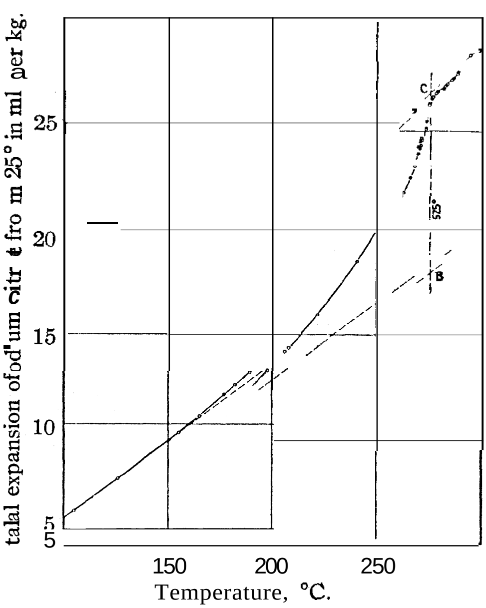

Fig. 4.—The expansion curve of sodium nitrate from 100° upward. The open and the black circles differentiate between ascending and descending sequence of constant temperatures. The distance BC is a measure of the anomalous expansion. Note the gradual character of the curve.

The value of the expansion coefficient $\alpha = 1/v_a \times \Delta v_a/\Delta t$ was obtained at a number of even temperatures from large scale graphs of Figs. 4 and 5. This is represented in Fig. 6. It should be noted that the curve of total expansion does not break sharply, but is rounded in the neighborhood of 275°; the peak of the α-curve of Fig. 6 falls close to 275.5' in agreement with the location of the peak on the differential heating curve of Fig. 2.

The amount of the anomalous expansion was determined from Fig. 4, as the distance BC on the graph, corresponding to 0.00811 cc./g. or 1.73% of the specific volume at 275°. It must be remembered that this does not represent a transition volume change in the usual sense, since the curve represents equilibrium values of expansibility at each temperature.

Extrapolation of the total expansion curve to 309.5°, the melting point of sodium nitrate, yields 0.02963 cc./g. from 25°. The specific volume at 25°, from Andreae's measurements of the density, is 0.44262 cc./g. Jaeger's[13] and Goodwin and Mailey's[14] measurements on the density of fused sodium nitrate yield p = 1.915 ± 0.015, or 0.5223 ± 0.0050 for the specific volume of liquid sodium nitrate at the melting point. We obtain from these, in round numbers, 0.0500 ± 0.005 cc./g. for the change of volume

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[13] F. M. Jaeger, *Z. anorg. allgem. Chem.*, *101*, *16 (1917)*.

[14] Goodwin and Mailey, *Phys. Rev.*, 25, *469 (1907)*.

during melting, corresponding approximately to 9% of the volume of the liquid.

The most important features of the expansion curve are its complete reproducibility with rising and falling sequence of constant temperatures, the absence of a noticeable break in the curve where the anomalous expansion begins, and the slight round of the curve at 275°. The expansion coefficient rises gradually to a peak value near 275.5°, as has already been pointed out, and then quite rapidly diminishes to a nearly steady value beyond 280°. The character of the expansion curve precludes definitely the possibility of speaking of a finite transition volume change; it adds weight to the results on thermal analysis which indicate that there is no finite latent heat of transition.

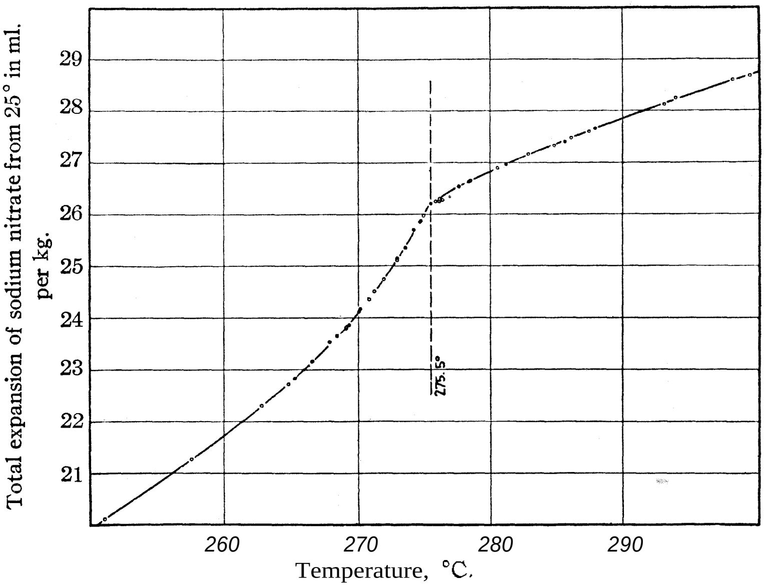

Fig. 5.—The expansion curve of sodium nitrate near 275°. Note the reproducibility of the curve as indicated by the open and black circles which differentiate between rising and falling sequence of constant temperatures, and the absence of a sharp break at 275°.

Part III. Optical Examination

Sodium nitrate at ordinary temperature is optically uniaxial and negative, $\omega = 1.5874$, $\epsilon = 1.3361$. Observation with a microscope equipped with a heating stage[15] shows that the optical character remains unchanged up to the melting point of the salt. The anomalous volume change described in the preceding chapter is clearly observable under the microscope,

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[15] A very compact heating stage built by Mr. C. J. Ksanda of this Laboratory was used.

particularly during cooling, but it is not accompanied by an alteration in the optical character. No attempt was made to measure the change in the magnitude of the refractive indices with temperature, but it can be stated with confidence that the birefringence does not change suddenly at 275°, the only point at which a sharp change could be expected.

The results of these observations lead to the conclusion that crystalline sodium nitrate does not pass through a change of phase during the gradual transition, the same crystal phase persisting up to the melting point.

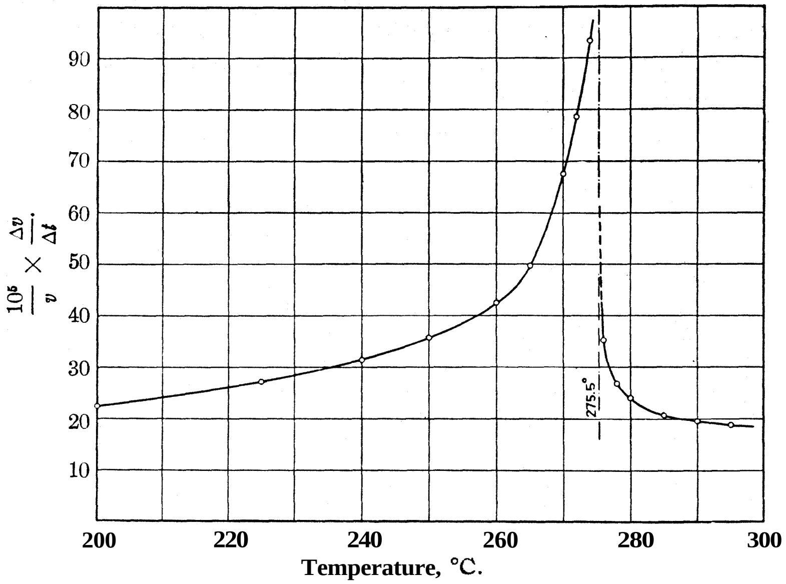

Fig. 6.—Curve of the expansion coefficient of sodium nitrate. Compare with Fig. 2.

Part IV. Solubility in Water up to the Melting Point of Sodium Nitrate

The solubility was determined by the synthetic method in sealed tubes of Pyrex glass, the reliability of the method having already been tested with other systems.[16] The thermostat and accessory apparatus used with the dilatometer (see Fig. 3) were also used in the solubility work, with appropriate modifications. The fan shaft of Fig. 3 is hollow, to allow for the introduction of a smaller shaft which is provided with an arm to carry and rotate the solubility tube. Transparent windows are provided at both ends of the thermostat, for visual observation. The thermocouples are introduced through an opening in one of the windows, the thermocouple for reading the temperature of the thermostat being arranged to hang free in the immediate neighborhood of the rotating solubility tube. The junction

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[16] F. C. Kracek, J. Phys. Chem., 35, 417, 947 (1931).

of this couple is enclosed in a small mass of alundum to provide an appropriate thermal lag. The fan is rotated at about 800 r. p. m., the solubility tube at about 30 r. p. m., just fast enough to keep the contents of the tube well stirred. Under these conditions the temperature control is sensitive to about ±0.05°.

The results of the individual solubility experiments are given in Table II. The supersolubility limits[17] were also determined in several of the experiments; the temperature of spontaneous crystallization is in general 4° below the solubility curve for this system. Figure 7 represents the data obtained, together with the more significant results from the literature. Below the normal boiling point the solubility curve passes smoothly through the points established by Berkeley,[18] in continuation of the results obtained in this study, and hence no determinations were made below 90°. At higher temperatures we have determinations by Étard,[19] who apparently failed to attain complete saturation in most of his experiments.

TABLE II

DETERMINATIONS OF SOLUBILITY OF SODIUM NITRATE IN WATER

	Grams of				NaNO$_3$, %		
Expt.	Water	NaNO$_3$	r_w[a]	r_m[b]	Weight	Mole	t, °C.
16	2.5192	4.1794	1.6590	0 35160	02.39	26.01	94 05
17	3.2924	6.1186	1.8584	,39385	65 02	28.26	106 80
18	3 5975	7.1976	2.0007	,42401	66.78	29.78	114 90
15	2.0543	5.0425	2.4546	52021	71.05	34.22	136 90
1	2.2501	6.4247	2 8553	,60512	74.06	37.70	151 60
2	1.7556	5.9874	3.4105	.72278	77.33	4195	168.90
3	1.4843	5.6214	3.7872	,80263	79.11	44.53	17800
4	1.4471	5.8784	4.0622	,86090	80.25	46.26	18'380
5	1.2897	6.5597	5.0862	1.0779	83.57	51.88	201 60
6	0.8925	5.8163	6.5169	1.3811	86.70	58.00	218 90
7	.9096	6.5353	7.1848	1.5227	87.78	60.36	224.70
8	.7477	7.3838	98754	2.0929	90.81	67.67	242.25
14	.5867	7.3266	12.4880	2.6465	92.59	72.58	253.55
13	.5409	8.0582	14.898	3 1573	93.71	75.95	260.90
9	.4499	6.9026	15.343	3.2515	93.88	76.48	261.75
10	.3883	7.4794	19.262	4.0822	95.07	80.32	270.00
11	.2134	8.6472	40.521	8 5876	97.59	89.57	289.20
12	.1466	8.5451	58.289	12.353	98.31	92.51	295.35
..	....	....	....	....	100.0	100.0	309.5

[a] r_w = g. of NaNO$_3$ per g. of H_2O. [b] r_m = moles of NaNO$_3$ per mole of H_2O.

The solubility curve at the higher temperatures is shown in Fig. 8, in a $1/T$ *vs.* log N_2 plot, to bring out the trend of the solubility results as fully as possible. It will be seen that a smooth curve, with a very slight reverse S curvature, fits the results better than one with a sharp break at 275.5°.

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[17] **Miers and Isaacs,** *J. Chem. Soc.*, 89,413 (1906).

[18] **Berkeley,** *Phil. Trans. Roy. Soc.*, **203A,** 189 (1904).

[19] **Étard,** *Ann. chim. phys.*, 2, 503 (1894).

No exact conclusions can be drawn from the solubility curve regarding the nature of the gradual transition, other than that the solubility results do not vitiate the conclusions obtained from the other types of evidence, to the effect that the same physical crystalline phase of sodium nitrate persists up to the melting point. These solubility results are hence published more for their intrinsic value rather than as a deciding criterion for the gradual transition. To attempt drawing more definite conclusions from these solubility data would necessitate ascribing much higher accuracy to these results than they warrant.

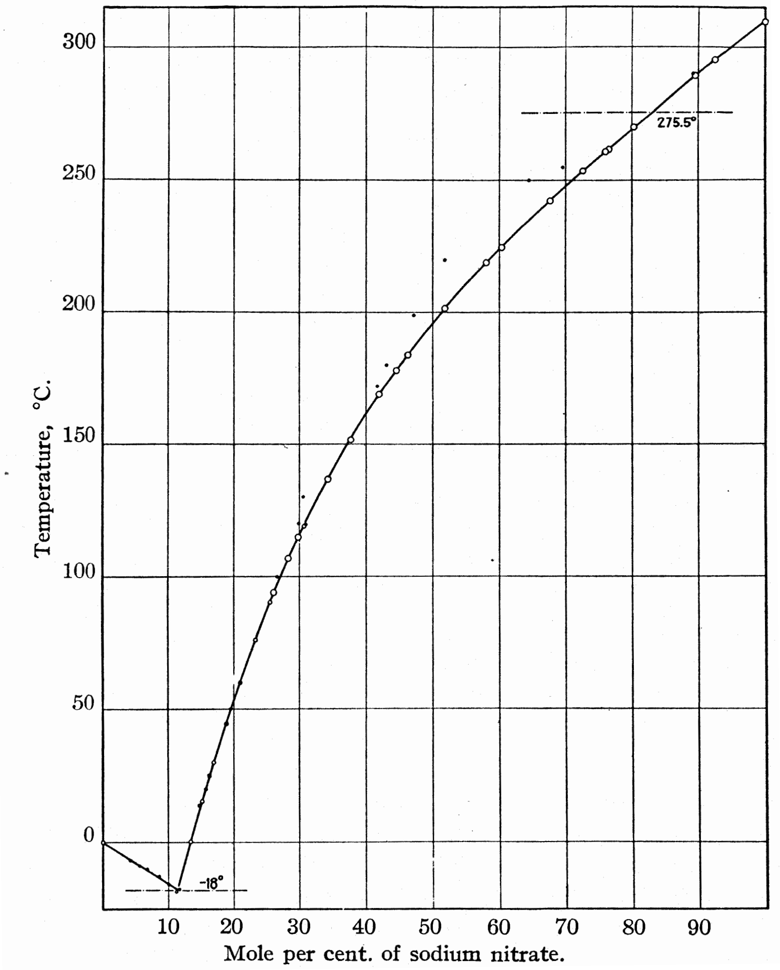

Fig. 7.—The solubility of sodium nitrate in water. The larger, open circles by Kracek. The small black circles above 100° are by Etard. Results below 100° by Berkeley and others.

Part V. Discussion

In transitions of this type the phase change, if we can speak of it as such, must take place gradually, rather than discontinuously, as is the case in normal polymorphic transformations. We cannot write down an expression for the entropy difference between the "phases" when the heat of transition is zero, that is, the Gibbs zeta potential is the same for the two "phases"; even though there may be a considerable difference in properties of the substance at two different temperatures, there can be no finite change at any one given temperature. Strictly speaking, there would be only one phase undergoing abnormal alteration in properties gradually, but the major portion of the transformation may be accomplished over a comparatively narrow range of temperature, as in the case of sodium nitrate near 275°. Similarly, the expression $\Delta H/(T\Delta v)$, which determines the pressure variation of the transition temperature in the Clapeyron equation, is indeterminate, since it has a value of 0/0. The effect of pressure then cannot be calculated, but it should be possible to determine it experimentally; since the anomalous expansion is positive in

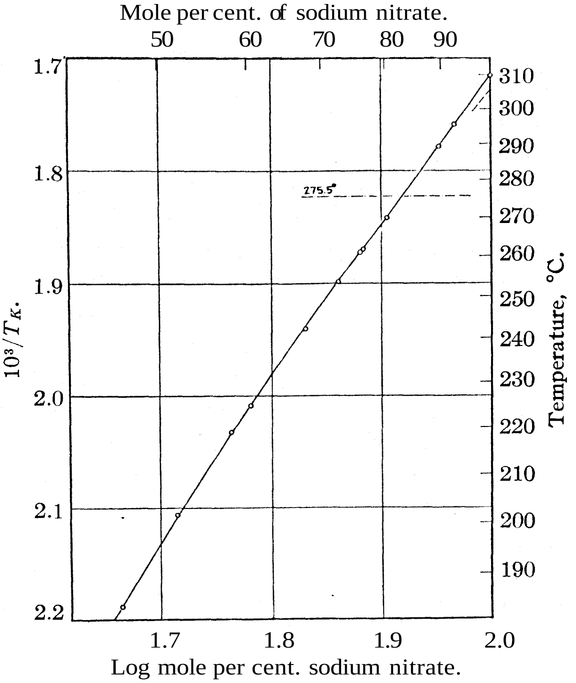

Fig. 8.—$10^3/T$ *vs.* log N_2 graph of solubility of sodium nitrate in water between 180° and the melting point. Note the slight reverse S curvature in the neighborhood of 275°.

sodium nitrate, it is to be expected that the temperature of the completion of the gradual transition should rise with increasing pressure.[20] All the experimental results quoted are in good accord with the view advanced here, to wit, that the gradual transition represents an anomalous change in the properties of a single phase. The rounding of the expansion curve in the neighborhood of 275° (see Fig. 5) appears to be of special significance in this respect. From the standpoint of thermodynamics, it is the Le Chatelier rule, and not the Clapeyron equation, which must be applied.

The most completely investigated other case of the gradual transition is that of the ammonium salts, in which, as already mentioned, the transitions end at temperatures between −50 and −30°. Simon and Bergmann[1] have recently published data on the thermal expansion of the chloride, bromide and phosphate. Their curve for ammonium chloride is very similar to the curve for sodium nitrate, and, although they make no statement with regard to the reproducibility of the curve for a given specimen, it is very probable that it represents equilibrium conditions. The curves for the bromide and phosphate exhibit gradual contractions over a range of temperatures. Simon ascribes the transitions in the ammonium salt to the ammonium ion, but offers no adequate suggestion as to the mechanism. On Pauling's theory the gradual transition in the ammonium salts is due to the initiation of rotation of the ammonium ion in the crystal. There is a possible objection to this in the case of ammonium bromide and the phosphate in view of the contraction encountered with these salts.

The physical conditions in the case of sodium nitrate are such that the above objection to intramolecular rotation of the nitrate ion does not hold. This question will be considered in more detail in the paper which will deal with the structure of sodium nitrate at various temperatures.

The principal conclusion that can be drawn from the physico-chemical study reported in this paper is that sodium nitrate undergoes a gradual transformation accompanied by a change in the specific heat and volume in a manner such that there is at no point a finite discontinuity in the properties of the substance.

Summary

Crystalline sodium nitrate undergoes a gradual transition which ends at 275.5°. The characteristics of the transition differ from those of a normal polymorphic inversion in that there is no finite discontinuity in the properties of the substance during the transition. The results on thermal capacity and expansion, optical properties and solubility in water are presented and discussed in comparison with the behavior of normal inversions.

WASHINGTON, D. C.

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[20] Since this was written Professor Bridgman has announced the determination of the effect of pressure on the gradual transitions in ammonium chloride and ammonium bromide.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 284]

THE THERMODYNAMIC CONSTANTS OF IODINE MONOBROMIDE

BY JOHN MCMORRIS AND DON M. YOST

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Introduction

The properties of the diatomic interhalogen compounds are, in general, intermediate between those of the elements from which they are formed, and it is therefore of interest to determine whether or not their thermodynamic constants are also intermediate between those of the elementary substances. Moreover, these compounds lend themselves readily to spectroscopic investigations, and it is desirable to have thermodynamic data to confirm the interpretations of such investigations. For these reasons the present research upon one of these conipounds, iodine monobromide, was undertaken.

A determination of the extent to which combination takes place when two diatomic halogen molecules react to form two other diatomic molecules cannot, of course, be made by direct-pressure measurements; but if a substance can be found which is in equilibrium with one of the halogens and does not react with the other, then the extent of combination can be determined either by pressure measurements or by analysis of the vapor phase. In the present case cupric bromide was chosen for this purpose, since the careful work of Jackson[1] has shown that over the temperature range 100–200° convenient partial pressures of bromine vapor were to be expected without any complications arising from indeterminate solid phases. His measurements were made between 281 and 166°; and the log P–$(1/T)$ graph is a straight line. Jackson also found that the solid phases consist of cuprous bromide and cupric bromide. Furthermo , iodine will not replace the more electronegative bromine in either of these bromides.

Experimental Method

A number of experiments were carried out in which a weighed amount of pure iodine and a large excess of cupric bromide were placed in a 200-cc. Pyrex bulb equipped with a click gage. After carefully evacuating and baking out at about 150°, the bulb was sealed off and completely submerged in an oil thermostat. By means of a barometer the pressures were determined at various temperatures. Although this method gave results reproducible in order of magnitude when approaching equilibrium from either direction, the variation of the click constant with temperature

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[1] **Jackson,** *J. Chem. Soc.,* 99, 1066 (1911).

and the possible presence of adsorbed gases or water rendered the method unreliable. Indeed, the presence of only one milligram of water at 127° gives rise to a pressure of 7 mm., which is unallowably large where the total pressure is less than 100 mm. These experiments did show, however, that the reaction

$$CuBr_2(s) + {}^1/_2I_2(g) = CuBr(s) + IBr(g) \qquad (1)$$

takes place reversibly and at a reasonable rate.

In the experiments whose results are here presented, the composition of the gaseous equilibrium mixture was determined by chemical analysis instead of by pressure measurements. The experiments were carried out in Pyrex bulbs of known volume, each being equipped with a narrow side-arm into which the vapors could be condensed by means of liquid air. Another side-arm was used for the introduction of the cupric bromide and iodine, the latter being contained in an easily breakable evacuated glass capsule. After charging, the bulbs were carefully evacuated and baked out until about one-third of the cupric bromide had been converted to cuprous bromide. The bulbs were sealed off, the tips of the iodine capsules were broken by moderate shaking, and the bulbs then immersed in an electrically heated oil thermostat whose temperature was maintained constant to within 0.1°.

After equilibrium had been reached a bulb was quickly removed from the bath, and the side-arm was plunged into liquid air and then sealed off from the bulb. This whole process required only twenty seconds, of which only a few seconds were necessary for the condensation of the vapor. Blank experiments carried out with cupric bromide alone yielded quantities of bromine which were in very good agreement with those corresponding to the pressures calculated by equation (4) given below. It follows therefore that the evolution of bromine from the cupric bromide is not rapid enough to introduce any serious errors.

That all of the vapors had condensed into the side-arm was shown by the fact that the bulb after again heating contained no iodine.

The side-arm containing the condensed vapor was broken under an acidified solution of potassium iodide, and the liberated iodine was titrated with standard thiosulfate, thus affording a measure of the total number of moles of iodine, bromine and iodine bromide, since they are all diatomic molecules.

The thermometer used was compared with one from the Bureau of Standards.

Preparation of the Materials

Iodine.—A high quality product, purchased on the market, was used. The quality was confirmed by analysis.

Cupric Bromide.—The best quality of material obtainable was dissolved in distilled water, filtered and then recrystallized and dried in a vacuum over phosphorus pentoxide at room temperature.[2] Only cupric bromide which contained initially no acetic acid or acetates was used.

Standard Solutions.—The chemicals used were of the best quality obtainable. The thiosulfate was standardized by the method of Bray and Miller.[3]

Results of the Experiments

The reaction whose equilibrium constant is to be found is

$$\mathrm{IBr(g)} = {}^1/_2\mathrm{I_2(g)} + {}^1/_2\mathrm{Br_2(g)} \tag{2}$$

The corresponding mass action expression is

$$\frac{(\mathrm{I_2})^{1/2}\,(\mathrm{Br_2})^{1/2}}{(\mathrm{IBr})} = K \tag{3}$$

The partial pressure of the bromine at a given temperature is fixed, since it is in equilibrium with the cupric–cuprous bromide mixture. The value of this pressure was calculated from the following formula, which was constructed from Jackson's data

$$\log_{10} p_{\text{mm.}} = -\frac{4921.2}{T} + 11.6682 \tag{4}$$

In an equilibrium mixture the total iodine is known since a weighed amount is introduced initially. The titration of the material condensed out by the liquid air gives the total number of moles of halogen present. If, then, x is the total number of moles of halogen determined by titration, y the moles of iodine weighed out, and z the moles of free bromine calculated from its pressure and the volume of the bulb, then

$$2(x - y - z) = \text{moles of IBr} \tag{5}$$

$$2y - x + z = \text{moles of } \mathrm{I_2} \tag{6}$$

The equilibrium constants were calculated by substituting these derived quantities directly into mass-action equation (3) since the constant K is, in this case, independent of the units in which the quantities on the left-hand side of equation (3) are expressed. In Table I are presented the results of experiments made at three different temperatures.

That equilibrium was attained is shown by the fact that the equilibrium constants are independent of the time, as may be seen from the table and further, that first heating the bulbs to a higher temperature before making the measurements at a lower temperature did not affect their values. Also, in the click-gage experiments, the reaction showed itself to be readily reversible. It is to be noted that the partial pressure of bromine varied fifty-fold over the range of temperatures investigated.

The values for the constants at any given temperature are seen to agree very satisfactorily among themselves. They show a maximum deviation from the mean of 5%, and an average deviation of less than 2%.

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[2] Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Longmans, Green and Co., London, Vol. III, p. 192.

[3] Bray and Miller, THIS JOURNAL, *46*, 2204 (1924).

TABLE I

RESULTS OF THE EQUILIBRIUM MEASUREMENTS

Expt. no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temperature, °C	115	115	115	115	115	150.5	151.2	151.2	151.2	151.2	176	176	176	176
Volume of bulb, cc.	221.5	115.5	115.5	423	430	116	119	116	114.5	117.5	116	118	118	111
Time in hours	16.5	6	16.5	24	24	6	6	7.5	5.5	6	2	6	5	12
Initial moles of $I_2 \times 10^4$	7.57	3.85	3.62	12.64	12.74	10.69	10.80	10.75	10.80	7.86	10.57	11.15	11.30	11.20
Total moles of halogen $\times 10^4$	9.10	4.60	4.33	15.25	15.37	13.98	14.34	14.19	14.24	10.71	15.99	16.90	17.07	16.90
Moles of free $Br_2 \times 10^6$	0.891	0.465	0.465	1.70	1.73	4.94	5.29	5.16	5.09	5.23	21.27	21.64	21.64	20.35
Moles of free $I_2 \times 10^4$	6.05	3.10	2.91	10.05	10.13	7.45	7.31	7.36	7.41	5.06	5.36	5.62	5.75	5.70
Moles of IBr $\times 10^4$	3.04	1.49	1.41	5.14	5.22	6.48	6.98	6.78	6.78	5.60	10.42	11.06	11.10	11.00
$K \times 10^2$	7.63	8.06	8.25	8.05	8.02	9.36	8.91	9.09	9.09	9.18	10.24	9.97	10.05	9.80
$K \times 10^2$, average	8.00 (115.0°)					9.20 (151.2°)					10.01 (176.0°)			
$K \times 10^2$ calcd. by eq. (8)	8.00					9.14					10.00			

Thermodynamical Calculations

The free energy equation which represents the results to within the experimental error was found for the reaction

$$^1/_2I_2(g) + {}^1/_2Br_2(g) = IBr(g) \qquad (7)$$

to be

$$\text{AF}'' = -1270-1.7449\ T \qquad (8)$$

The assumption is made that ΔC_p is negligible, which for a reaction of this type is no doubt justifiable. The error in the heat content term has been estimated to be fifty calories, that is, AH = −1270 ± 50 cal. This value is in good agreement with the recently determined spectroscopic one, −1220 cal.[11]

It is of interest to compare the values of the equilibrium constants found by Müller[4] at 304.8' and by Bodenstein and Schmidt[6] at 1222° with those calculated by Equation 8. Müller's value depends on his interpretation of the rate of the reaction between hydrogen and bromine in the presence of iodine whereas the value at the higher temperature was determined from vapor density measurements, as it is a region in which considerable dissociation of iodine into the monatomic gas occurs. At 304.8°, Equation 8 gives for K the value 0.137, for the reverse of reaction (7), while the average of Müller's results is 0.114, with a variation of ±15% from this value. The agreement is satisfactory and increases our confidence in his interpretation.

For 1222°, Equation 8 gives for K the value 0.271, as compared with Bodenstein and Schmidt's value of 0.305, which was the average from two experiments whose values differ by 8%. Taking into account the long extrapolation and the fact that deviations from the perfect gas laws at the higher temperatures may be considerable, the results are in very good accord.

The thermodynamic constants for iodine monobromide may be calculated from the present results by combining them with the following data. We use for the free energies and entropies of iodine and bromine vapors the values given by Giauque[6a] and by Lewis and Randall.[6b] For the heats of sublimation and of vaporization of one-half mole of solid iodine[6"] and liquid bromine[6b] we take 7438 cal. and 3795 cal., respectively; and we use Berthelot's[7] value of 2470 cal. for the heat of formation of solid iodine monobromide from the elements in their standard states. The heats of dissociation of iodine and bromine[8] into the monatomic gases were taken as

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[4] Muller, *Z. physik. Chem.*, 123, 1 (1926).

[5] Bodenstein and Schmidt, *ibid.*, **123**, 28 (1926).

[6] (a) Giauque, THIS JOURNAL, 53, 507 (1931); (b) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 464, 512, 522.

[7] *Cf.* Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Longmans, Green and Co., London, **1922**, Vol. II, p. 123.

[8] R. Mecke, "Bandenspektra und ihre Bedeutung für die Chemie," Gebrüder Borntraeger, Berlin, **1929**, p. 61; J. Franck, *Z. Electrochem.*, 36, 581 (1930).

35,400 cal. and 45,200 cal., respectively. The entropy values used for monatomic iodine and bromine were 40.15 and 38.77 entropy units,[6b] respectively.

Table II gives the so-calculated thermodynamic constants (expressed in calories) for one mole of the substance given in the first column. The standard states for the elements are indicated in each case.

TABLE II

THERMODYNAMIC CONSTANTS OF IODINE MONOBROMIDE AT 25°

Substance	Reference substances	Free energy	Heat content	Entropy	Heat of sublimation
IBr(g)	I_2(g), Br_2(g)	−1790	−1270	60.8	
IBr(g)	I_2(s), Br_2(1)	903	9,963		
IBr(s)	I_2(s), Br_2(1)	(−1830)	−2470	(31.8)	12433
I_2(g)	I(g)	−30,030	−35,400	62.29	
IBr(g)	I(g), Br(g)	−36,105	−41,570	60.6	
Br_2(g)	Br(g)	−38,600	−45,200	55.4	

The values in brackets for IBr(s) were calculated on the assumption that the vapor pressure of solid iodine monobromide is 7.6 mm. Its vapor pressure is certainly greater than that of iodine[9] (0.305 mm.), and less than that of iodine monochloride[10] (30 mm.), and doubtless lies closer to the former than to the latter value. If the estimate is in error by two-fold, an error of about 410 cal. will have been made in the free energy, and the value of the entropy will differ by 1.37 entropy units from the one given. The bracketed values are probably not in error by more than these amounts.

Discussion

The entropy of gaseous iodine monobromide (60.6) lies between the value 62.29 for iodine and the value 55.4 for bromine. However, it does not lie midway between them.

The free energy and heat content changes of the monobromide with respect to the monatomic elements in the gaseous form likewise lie between the corresponding values for iodine and bromine. These intermediate characteristics extend to the energy differences between the lowest vibrational levels of the molecules.[11] The entropy of another interhalogen compound, bromine monochloride gas, also lies between those of the gaseous diatomic elements of which it is composed as may be seen from an easy computation of the recent results of Jost.[12] In order to make a similar statement for the case of iodine monochloride it would be necessary to have further experimental data, although the results of Gibson and Ramsperger[13] indicate that such is indeed the case. Whether or not one

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[9] Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907).

[10] Recently determined by one of us [D. M. Y.].

[11] Badger and Yost, *Phys. Rev.*, 37, 1548 (1931); also *cf.* Ref. 9, p. 24.

[12] Jost, *Z. physik. Chem.*, [A] 153, 143 (1931).

[13] Gibson and Ramsperger, *Phys. Rev.*, 30, 598 (1927).

would be justified in generalizing the statement to cover all diatomic interhalogen compounds is not certain, but if one may judge by physical properties alone it would seem that even chlorine monofluoride[14] might not prove an exception. The present results show, however, that the entropies of the compounds are not in general the average of those of the elements from which they are formed.[15]

Summary

The equilibrium between solid cupric and cuprous bromides and gaseous iodine and iodine monobromide has been measured. From the results, the free energy equation for the reaction $^1/_2I_2(g) + ^1/_2Br_2(g) = IBr(g)$ has been found to be $\Delta F^\circ = -1270 - 1.7449\ T$. The increases in free energy, heat content and the entropy for this reaction at 25° were found to be (ΔF°_{298}) -1790 cal., (ΔH_{298}) -1270 cal., and (ΔS_{298}) 1.75 cal./degree, respectively. The degree of dissociation of the gaseous monobromide, at this temperature, into gaseous iodine and bromine has the value 8.9%.

With iodine and bromine in their standard states of solid and liquid, respectively, the free energy of formation of IBr(g) is $\Delta F^\circ_{298} = 903$ cal. The heat of sublimation of the solid monobromide has been calculated to be 12,545 cal.

The entropy of iodine monobromide gas is 60.6 and lies between that of gaseous iodine, 62.29, and bromine, 55.4, but is not the average of these. The increase in free energy and heat content at 25° attending the formation of the gaseous monobromide from monatomic iodine and bromine have values which lie between those for the formation of diatomic iodine and bromine from the monatomic elements. From the data for iodine and bromine monochlorides the same was found to be true; and it was suggested that this might be generally the case for diatomic interhalogen compounds in the vapor state.

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[14] Ruff and Laass, *Z. anorg. allgem. Chem.*, 183, 214 (1929).

[15] Using recently published spectroscopic data [Curtis and Patkowski, *Nature*, 127, 707 (1931); Gale and Monk, *Astrophys. J.*, 69, 77 (1929)], the entropies of gaseous iodine monochloride and fluorine were calculated. These values, together with those already known or cited above, for the gases at 25° and one atmosphere, are: I_2, 62.29; IBr, 60.6; ICl, 59.2; Br_2, 55.4; BrCl, 54.1; Cl_2, 53.3; ClF, ?; F_2, 48.0. The order is that suggested above. Some of these values, but probably not the order, are subject to revision.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 244]

HEATS OF NEUTRALIZATION AT CONSTANT CONCENTRATION AND THE HEAT OF IONIZATION OF WATER[1]

BY RAYMOND H. LAMBERT AND LOUIS J. GILLESPIE

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In an extensive series of investigations Richards and his collaborators have studied the heats of neutralization[2] of a number of pairs of acids and bases, and the heats of dilution[2b,3] of these and of their salts. Unfortunately, from the point of view of those who prefer things simple, the effect of further dilution was in most cases perceptible in the case of each neutralization, the heats of reactions leading to the formation of various salts differed perceptibly even in the most dilute solutions, and the conclusion of a previous generation—that the heats of neutralization of all strong bases and acids are the same, and are equal to the heat of the formation of water from its ions—was shown to be but a rough approximation.

Richards and Rowe[2a] discussed at length the difficulties involved in the extrapolation of the heats of neutralization to infinite dilution in order to find the heat of ionization. As pointed out by Richards and Hall,[2b] their new values for sodium salts improve the extrapolation considerably. Richards and &lair[2'] plot the heats of neutralization for the cases of sodium chloride, sodium nitrate and sodium acetate and estimate the heat of ionization at 20° as 13,650 20"-calories. They also[3'] find the heats of neutralization in the case of the sodium citrates to be much smaller than for the strong inorganic acids, and note that they do not approach the value to which these stronger acids tend at infinite dilution. They note also that citric acid and the acid citrates "are only slightly ionized even in the most dilute solutions investigated, so that it is probable that heat effects due to their ionization continue into solutions infinitely dilute."

Experiments with the continuous-flow calorimeter have confirmed[4] the heats for sodium and potassium chloride in the dilute region at 20°, though measurements at higher temperatures do not appear consistent with the existing temperature coefficients.

Lange and Messner[6] have observed with a 1000-junction thermocouple

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[1] Original manuscript received June 7, 1930.

[2] (a) Richards and Rowe, THIS JOURNAL, 44, 684 (1922); (b) Richards and Hall *ibid.*, 51, 731 (1929); (c) Richards and Mair, *ibid.*, 51, 737 (1929).

[3] (a) Richards and Rowe, *ibid.*, 42, 1623 (1920); (b) *ibid.*, 43, 770 (1921); (c) Richards and Gucker, *ibid.*, 51, 712 (1929); (d) Richards, Mair and Hall, *ibid.*, 51, 726 (1929); (c) Richards and Mair, *ibid.*, 51, 7-10 (1929).

[4] (a) Keyes, Gillespie and Mitsukuri, *ibid.*, 44, 707 (1922); (h) Gillespie, Lambert and Gibson, *ibid.*, 52, 3806 (1930).

[5] Lange and Messner, *Naturwissenschaften*, 15, 521 (1927).

significant heats on the further dilution of solutions of univalent salts as weak as 0.01 normal.

Object and Scope of the Work.—At the time of the appearance of the paper of Richards and Rowe we were working with the continuous-flow calorimeter on heats of neutralization. We were much impressed with the difficulties emphasized by them in the extrapolation of the data for various salts to the same point at infinite dilution in order to find the heat of ionization. The suggestion occurred that there is a dilution involved in any experiment on neutralization, a dilution attended by a heat effect which varies from salt to salt. If a systetnatic "correction" were made for this dilution, the results for various products of neutralization reactions ought to be more consistent. Application of the idea to the results of Richards and Rowc bore out the expectation: the picture was very clear, provided we assumed an error of about 25 calories in their result for sodium chloride in the dilute region. This assumption has since been shown true by the data of Richards and Hall[2b] and Gillespie, Lambert and Gibson.[4b] Since our first calculations, the available data have been greatly extended in the publications to which reference has been made above, and we have taken the new data into consideration.

We hoped that the application of our method (1) might give a clearer picture of the relations for various acids and bases, and that better extrapolated results might be obtained for (2) the heat of ionization and **(3)** its temperature coefficient. To anticipate, we think that our hopes have been justified with reference to points (1) and **(3).** As to the heat of ionization, we have not found it expedient to seek to improve by curve-plotting the recent estimation by Richards and Hall[2b] of the limiting value for the heat of neutralization for sodium chloride, based on especially accurate data, but are content to point out that their value gives directly the limiting value of the heat of neutralization at constant concentration and hence the heat of ionization, and to show by a new plot that the data for six inorganic salts appear consistent with their limiting value.

The objects of this paper are (1) to define the heat of neutralization at constant concentration; (2) to give an improved definition of the heat of ionization, in terms of the heat of neutralization at constant concentration; **(3)** to examine by curve plotting the extrapolation to infinite dilution of heats of neutralization at constant concentration for various acids and bases; and (4) to derive a value for the temperature coefficient of the heat of ionization.

The Heat of Neutralization at Constant Concentration and the Neat of Ionization.—When a mole of a (monobasic) acid, dissolved in x moles of water, is neutralized with a mole of a (monoacid) base, dissolved in x moles of water, the change of state may be written

$$[\mathrm{MOH}\cdot x\mathrm{H_2O}] + [\mathrm{HB}\cdot x\mathrm{H_2O}] = [\mathrm{MB}\cdot(2x + 1)\mathrm{H_2O}] \qquad (1)$$

Supposing complete ionization it may also be written in the ionic form

$$[M^+(c_1) + OH^-(c_1)] + [H^+(c_1) + B^-(c_1)] = [M^+(c_2) + B^-(c_2)] \qquad (2)$$

where c_1 in the first solution is the concentration of M^+ and of OH^- in gram ions per liter in the solution of MOH, and there is a similar meaning of c_1 and c_2 for the other two solutions. In all cases the substances whose formulas are represented within brackets are supposed to be mixed, and substances whose formulas, not within the same bracket, are separated by plus or equality signs are supposed to be physically separated.

Since the salt solution contains all the water present in the original solutions (plus one mole), and there is little volume change on mixing the solutions, the concentration c_2 of the ions of the salt is about one-half of c_1. It is therefore clear from equation (2) that in the neutralization experiment there occurs not only a disappearance of OH^- and H^+, but also a dilution of the ions M^+ and B^-. It is generally supposed at present that strong acids, bases and salts are completely ionized at any reasonable dilution. The fact observed and emphasized by Richards and Rowe that the heat attending reaction (I) varies with the nature of the salt formed and with the dilution points therefore to the possible importance of the heat effects attending the dilution of these ions.

Muller[6] obtained nearly the same heats of neutralization at infinite dilution for potassium chloride and sulfate, by subtracting the heat effect for the acid in question on dilution from a molal solution to infinite dilution, from the extrapolated value of the heat of neutralization—a method of finding the heat of ionization not wholly clear, as remarked by Richards and Rowe.

We wish to obtain the heat effect of the reaction

$$H^+\,aq + OH^-\,aq = HOH\,aq \qquad (3)$$

Now it is not clear that equation (3) defines sufficiently a change of state, even if definite values are assigned to the symbol aq (and, of course, the temperature and pressure are fixed) For the equation does not represent the effect of the other ions necessarily present, and we dare not assume that an extrapolation to infinite dilution, when it is conducted without reference to these other ions, will necessarily give a correct or even a definite result.

If we subtract, from the heat effect H_1 of reaction (1), the heat effect H_4 of the reaction

$$MB{\cdot}xH_2O + (x + 1)H_2O = MB{\cdot}(2x + 1)H_2O \qquad (4)$$

we obtain the heat effect H_5 of the reaction

$$MOH{\cdot}xH_2O + HB{\cdot}xH_2O = MB{\cdot}xH_2O + (x + 1)H_2O \qquad (5)$$

Such a reaction will be termed a neutralization at constant concentration. If this is written in the ionic form we have

$$[M^+(c_1) + OH^-(c_1)] + [H^+(c_1) + B^-(c_1)] = [M^+(c_1) + B^-(c_1)] + [H_2O + aq] \quad (6)$$

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[6] Muller, *Bull. soc. chim.*, [4] **23,** 8 (1918).

This change of state (5) is worth attention. When the ionization is supposed complete, equation (6) shows a disappearance of OH^- and H^+ to form a mole of water, and a bringing together in the same solution of the other ions M^+ and B^-. So far as these ions are concerned, they experience no change of concentration, and are, in fact, associated with the same number of moles of water and the same number of ions of opposite sign after the change of state, as before. At infinite dilution there should be no heat effect involved in replacing an ion A with an ion B of the same sign and charge at the same distance from an ion C of opposite sign. Consequently the limiting value of the heat effect of reaction (5), provided all the electrolytes are strong, may be taken as the heat of formation of water from its ions.

$$\lim_{1/x \to 0} H_5 \text{ (strong electrolytes)} = \text{heat of formation of } H_2O \text{ from its ions} \quad (7)$$

Equations *(5)* and (7) define completely the heat of ionization of water.

The limiting value of H_1 also will be the heat of ionization according to the above definition, provided that the value of H_4 approaches zero at infinite dilution, or provided that the heat effect of the following reaction becomes zero as x becomes infinite

$$MB \cdot xH_2O + xH_2O = MB \cdot 2xH_2O \quad (8)$$

We cannot immediately state that the limiting value of H_8 for this reaction is zero simply because the limiting value is zero for the reaction

$$MB \cdot xH_2O + H_2O = MB \cdot (x + 1)H_2O \quad (9)$$

Nor do the recent data on heats of dilution establish zero as the limit of H_8, though the only cases in which values other than zero are rather definitely suggested by the plots are for lithium nitrate,[3b] citric acid[3'] and sodium acetate.[3c] Yet a *priori* notions suggest the value zero, and in our hands plots of H_1 and of H_5 do not lead to different values for the heat of ionization.

The advantage of the heat of neutralization at constant concentration for finding the heat of ionization by curve-plotting does not depend on a difference in the limits, but lies in the manner in which the limit is approached. The disturbing effect of the dilution, which finally disappears at infinite dilution, is present at the dilutions at which measurements are made.

The method outlined above for finding the heat of ionization of water implies that the electrolytes are strong. In the case of the weak acids, the ionization is but slight at the greatest dilutions in question, and we can hardly expect that the course of the curve in the infinitely dilute region will be definitely established by the available data. Consequently, one may expect to be limited, in any method of extrapolation, to the case of strong electrolytes.

Plots of the Heat of Neutralization

Richards and Hall[2b] combined one value for the heat of neutralization (for sodium chloride) at a finite dilution with three heats of dilution, each extrapolated to infinite dilution, though from rather high dilutions. If the addition of the thermochemical equations is carried out, it is found that their value for the heat of neutralization in the case of sodium chloride at infinite dilution, 13,653 20"-calories at 20°, is for the reaction

$$\mathrm{NaOH}\cdot w\,\mathrm{H_2O} + \mathrm{HCl}\cdot\infty\,\mathrm{H_2O} = \mathrm{NaCl}\cdot\infty\,\mathrm{H_2O} + (\infty + 1)\mathrm{H_2O} \qquad (10)$$

which is strictly of the type of a neutralization at constant concentration. When the measured heats of neutralization, which extend to value of 400 for x of equation (1), are plotted against $1/x$, the course of the curves obtained (reference 2c, Fig. 1) for sodium chloride and nitrate does not suggest so low a value, and Richards and Mair[2c] introduce a bending downward of the curves for these salts, and a bending upward for the curve for sodium acetate, which brings the extrapolated values to 13,650. When the heats at constant concentration are plotted over the same range of values of x, the bending for sodium chloride and nitrate is already in evidence, and the use of a different variable as abscissa is indicated.

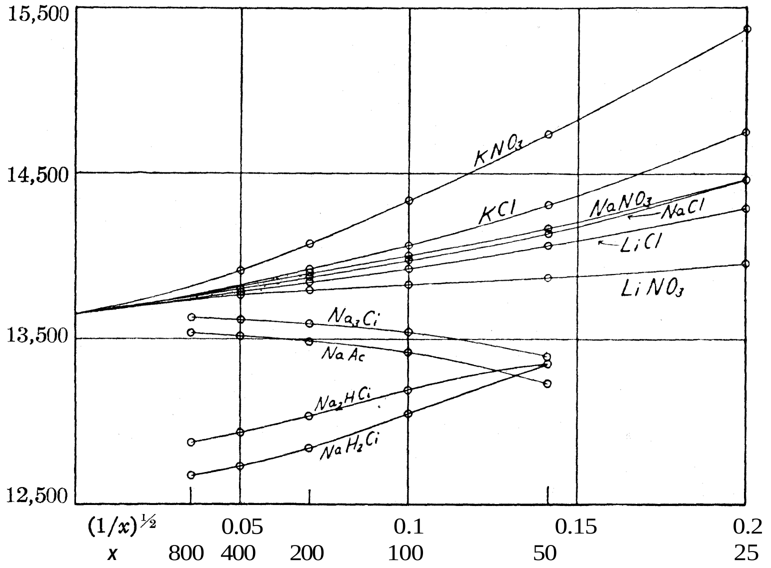

Fig. 1.—Heats of neutralization at constant concentration at 20° in 20°-calories.

The square root of $1/x$ has been used as abscissa for the plots of heat of neutralization at constant concentration shown in Fig. 1, where x and the heat effect are defined by equation (5). Lange[7] has recently published

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[7] Principally in *Z. Elektrochem.* and *Z. physik. Chem.*

many heats of dilutions of salt solutions, but heats at 20° would have to be determined by interpolation at other temperatures, which interpolation is in some cases uncertain. The results for strong electrolytes at x = 400 were obtained by combining the heat at x = 200 with the heats of dilution of acid and base from 200 to 400 and the estimated heat of dilution of the salt from 400 to 401.

The value 13,650 was found to be an excellent compromise point for the strong electrolytes. No curves intersect below about the concentration $1/x = 0.02$, which is not true of the plots of the ordinary heats of neutralization. At x = 400 four of the six points for inorganic salts lie exactly on the curves; the points for potassium chloride and sodium nitrate are a little lower (10--20 cal.) than indicated by the smooth curves. The plot shows that the value 13,650, given by Richards and Hall for the heat of neutralization at 20° of hydrochloric acid and sodium hydroxide at infinite dilution, is supported by the curves for the six inorganic salts and may be taken therefore as the heat of ionization of water. The curves for the organic salts, with the exception of trisodium citrate, do not point to this value, but this appears to be of little consequence.

The Temperature Coefficient of the Heat of Ionization

The temperature coefficient of the heat of neutralization at constant concentration, $\mathrm{d}H_5/\mathrm{d}t$, is evidently equal to the difference, $\mathrm{d}H_1/\mathrm{d}t - \mathrm{d}H_4/\mathrm{d}t$. The limiting value at zero concentration should be equal to the temperature coefficient of the heat of the formation of water from its ions, and one may expect an easier extrapolation than in the case of the ordinary temperature coefficient, $\mathrm{d}H_1/\mathrm{d}t$.

From the data of Richards and his collaborators both temperature coefficients were computed, using besides the necessary heats of dilution the molal heat capacities given by Richards and Rowe, except when new specific heat values were available, as in the cases of hydrochloric acid[3*] and sodium hydroxide.[3c] In the computations the same atomic weights were used as by Richards, and the new specific heats at 18° in 20"-calories were converted into values at 18° in 18"-calories by multiplication with the factor 0.999737, which was obtained by interpolation from the paper of Osborne, Stimson and Fiock.[8] All the intermediate calculations were referred to 18"-calories at 18°, as consistency is necessary when dealing with the large numbers involved. The results, being small numbers obtained by taking differences, may equally well refer to 20"-calories, and in view of their uncertainty may be taken to refer to the temperature of 20°.

Table I gives the temperature coefficients corresponding to the value of x. A denotes the ordinary coefficient and B the coefficient at constant con-

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[8] Osborne, Stimson and Fiock, *Mech. Eng.*, 51, 125 (1929), Table III.

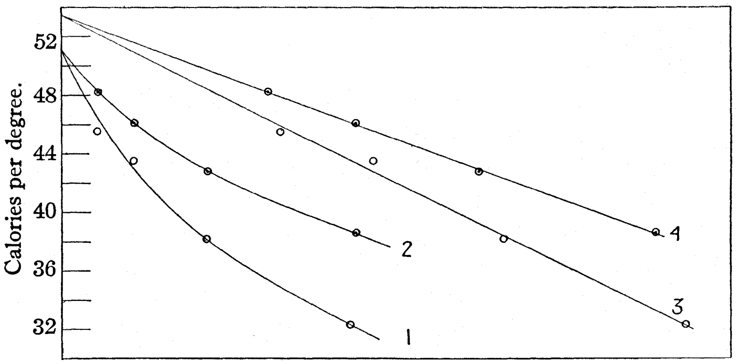
centration. The average values for the six salts are also given for each value of x.

TABLE I

TEMPERATURE COEFFICIENTS OF HEATS OF NEUTRALIZATION

	KCl		NaCl		LiCl		KNO_3		$NaNO_3$		$LiNO_3$		Average	
x	A	B	A	B	A	B	A	B	A	B	A	B	A	B
25	36.2	41.5	33.6	40.6	29.0	31.2	36.0	46.8	33.6	42.0	25.5	29.6	32.3	38.6
50	40.8	44.5	39.3	43.6	34.9	37.7	39.8	47.0	39.9	46.7	34.7	37.4	38.2	42.8
100	45.1	47.0	45.0	47.0	38.7	41.4	45.3	48.0	46.5	49.7	40.4	43.5	43.5	46.1
200	46.1	49.5	46.3	51.4	41.1	42.3	47.2	49.8	60.6	52.8	41.8	43.4	45.5	48.2

When the values for each salt were plotted against the concentration, a confused picture resulted. The extrapolation in any particular case usually appeared uncertain, and it seemed out of the question to find a compromise intercept on the axis of zero concentration, to which a family of curves might be drawn. This was true for the ordinary temperature coefficient, as well as for the one at constant concentration. Such plots are a very severe test of the precision of data on heat capacity.



Concentration (1, 2), square root concentration (3, 4).

Fig. 2.—Temperature coefficients of heats of neutralization.

The data should furnish, however, a means of obtaining a better value for the temperature coefficient of the heat of ionization than has previously been obtained. The average coefficients were therefore plotted, in spite of the large departures from the average shown by the various salts. Figure 2 shows the plot obtained. Curve 1 shows the ordinary temperature coefficient, and curve 2 that at constant concentration, plotted against the final concentration, $1/(2x + 1)$ and $1/x$, respectively. The curves bend sharply upward, curve 2 being the better defined. The straight lines 3 and 4 show the ordinary coefficient and that at constant concentration, respectively, when plotted against the square root of the final concentration. The square root plots help to estimate the degree of bending necessary near the axis of zero concentration in the case of the first two curves. The scales of abscissas are not the same, but are uniform for each curve.

The introduction of a slight curvature in lines **3** and 4 would permit an excellent compromise point for all four lines at 52 calories per degree, which is therefore accepted as the result for $d\Delta H/dt$ for the heat absorption AH for the formation of water from its ions. The indirect computations of Noyes, Kato and Sosman[9] give about 49.4.

Summary

The heat of neutralization at constant concentration is defined to be the heat effect (– AH) of the reaction: $MOH{\cdot}xH_2O + HB{\cdot}xH_2O = MB{\cdot}xH_2O + (x + 1)H_2O$. It was found possible, using the recent precise heats of neutralization and of dilution of Richards and Rowe, Hall, Gucker and Mair, to extrapolate satisfactorily such heats of neutralization to the same point at infinite dilution for six inorganic salts (K, Na, Li; chlorides and nitrates). The square root of $1/x$ was taken as abscissa. The value 13,650 20"-gram calories (or 57.07 kilojoules) found by Richards and Hall for the heat of neutralization at 20° at infinite dilution in the case of *sodium* chloride was found to be an excellent extrapolated value for the family of six curves, and it may be taken as the heat ($-\Delta H$) of the formation of water from its ions at 20°. This is in agreement with the conclusion of Richards and Mair, who introduced, however, bending in the plots in the region of extrapolation and gave considerable weight to the heats for sodium acetate, neither of which has been done in the present case.

For the temperature coefficient of the heats, individual extrapolations for the various salts could not be made. On plotting the average values for the six inorganic salts, the temperature coefficients at constant concentration were distinctly a smoother function of the concentration or of its square root. The temperature coefficient of the heat of formation of water from its ions ($-d\Delta H/dt$) was estimated to be -52 calories, or —217 joules, per degree in the neighborhood of 20°.

CAMBRIDGE, MASSACHUSETTS

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[9] Noyes, Kato and Sosman, THIS JOURNAL, 32,159 (1910).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE IDENTIFICATION OF SOLIDS BY MEANS OF THE BOILING POINT ELEVATION IN SATURATED SOLUTIONS

BY J. O. HALFORD[1]

RECEIVED MAY 27, 1931 PUBLISHED JULY 8, 1931

Compounds which decompose before melting, or immediately after melting, are frequently encountered. These compounds cannot be tested and identified, with certainty, by the familiar measurements of melting points and mixed melting points. In such cases a procedure based on solubilities may be substituted. Suppose, for example, that we wish to compare samples of two materials which are suspected of being identical. If we measure first the individual solubilities, then that of a sample made by mixing the two, we have the required information. If the two materials are identical, all three solubilities must be equal, but, if they are different, that of the mixture will be greater than that of either individual. This is a procedure which has not been employed as frequently as its usefulness would warrant. Recent examples are found in the work of Montgomery and Hudson,[2] and that of Austin,[3] who have identified sugar derivatives in this way.

The tests which will be described here may be looked upon as applications of the solubility procedure in which the concentrations of the solutes are evaluated by boiling point measurements, and are based on the fact that the addition of a pure non-volatile solid to a solution can cause an increase of the boiling point only when the solution is not yet saturated with that solid. The substitution of boiling point determinations for analytical measurements, wherever feasible, should effect a saving of time and apparatus. In fact, in some cases, our procedure is as expeditious as the melting point method. Its principal disadvantage is that the best combination of solvent and apparatus for a given measurement is not always evident.

We are not in a position to state exactly which form of ebullioscope will be most useful for our purpose. Probably a small boiling tube of the Beckmann type, fitted with a side-arm condenser, internal heater and a small Beckmann thermometer, will cover the widest range of situations. Our tests have been carried out mainly with the ebullioscope described by Menzies and Wright.[4] This gives satisfactory results, but is perhaps too limited in temperature range to be suitable for general use. However, the high sensitivity of this apparatus is an advantage, for our present purpose, for we have considered it worth while to try out the procedure under

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[1] **Alfred** H. Lloyd Fellow in the Graduate School, University of Michigan.

[2] Montgomery and Hudson, THIS JOURNAL, 52,2105 (1930).

[3] Austin, *ibid.*, 52, 2111 (1930).

[4] Menzies and Wright, *ibid.*, 43, 2314 (1921).

conditions near the limit of its applicability, and have found it desirable to be able to measure small temperature differences.

The principal application of our method is in the comparison of materials which may be identical, However, it may also be used to test the purity of individual samples of material.

Comparison Tests

The procedure employed in the test for identity, analogous to the mixed melting point, follows that of the determination of molecular weight, with the simplification that the sample need not be weighed and is preferably added in the form of powder, rather than pellets. After the first addition of solid, the temperature increases slowly and reaches a constant value, indicating saturation, in fifteen to twenty minutes. If the addition of a second portion produces no further temperature increase, the substance may be considered pure and the material to be compared is added. If the two samples are identical, the temperature will not rise, but if they are different, the second substance being soluble, a decided increase of boiling point follows in a few minutes. A second measurement should be made with fresh solvent, reversing the order of addition of the substances. Identical materials, when tested individually, will produce saturated solutions of the same boiling point, and the addition of one to the boiling saturated solution will cause no additional boiling point elevation.

We have tested this procedure with several amino acids, using methyl and ethyl alcohols as solvents. Although the boiling points of individual saturated solutions were somewhat variable, there was no doubt in any case of the identity of two samples of the same material, or the non-identity of samples of different materials.

The first comparison attempted, that of dl-alanine and dl-valine, is typical of the results. The addition of dl-valine to boiling ethyl alcohol produced a temperature elevation of 0.0217°, which was increased to 0.0449° by the addition of dl-alanine. Starting with dl-alanine the initial rise was 0.0211°, increased to 0.0493° by the introduction of dl-valine.

In Table I, the results of similar tests with several amino acids in ethyl alcohol are summarized. Table II is similar for the methyl alcohol solutions. The names above and to the left of any figure show the substances

TABLE I

ELEVATION OF THE BOILING POINT OF ETHYL ALCOHOL IN SATURATED SOLUTIONS OF SEVERAL AMINO ACIDS AND THEIR MIXTURES

	Glycine	dl-Alanine	dl-Valine	*l*-Tryptophane	d-Glutamic Acid
d-Glutamic acid					0.0023
l-Tryptophane	0.0318	0.0392	0.0472	0.0180	
dl-Valine	.0424	.0493	.0292		
dl-Alanine	.0265	.0191			
Glycine	.0143				

TABLE II

ELEVATION OF THE BOILING POINT OF METHYL ALCOHOL IN SATURATED SOLUTIONS OF SEVERAL AMINO ACIDS AND THEIR MIXTURES

	Glycine	*dl*-Alanine	dl-Valine	*l*-Tryptophane	*d*-Glutamic acid
d-Glutamic acid					0.0052
l-Tryptophane	0.0500	0.0626	0.0757	0.0356	
dl-Valine	.0644	.0635	.0392		
dl-Alanine	.0479	.0278			
Glycine	.0244				

compared in the individual test. Where these names are different, the reading recorded was obtained in a single test. The values given for the individual substances are averages of two or three determinations made in starting different comparisons. The values with d-glutamic acid have been included, not because of faith in their accuracy, but to illustrate a case in which comparison by mixing is unnecessary, where the solubilities of the individual substances suffice to distinguish between them.

The results of similar tests with three isomeric leucines are given in Table III.

TABLE III

BOILING POINT ELEVATIONS OF METHYL AND ETHYL ALCOHOLS IN SATURATED SOLUTIONS OF ISOMERIC AMINO ACIDS AND THEIR MIXTURES

Alcohol	I-Leucine	dl-Leucine	*dl*-Isoleucine	1-Leucine + dl-Leucine	dl-Leucine + *dl*-Isoleucine	*dl*-Isoleucine + 1-Leucine
Methyl	0.033	0.031	0.040	0.043	0.050	0.063
Ethyl	.019	.013	.025	.025	.037	.037

The combination of dl-leucine with dl-isoleucine showed a value in methyl alcohol much lower than the sum of the individual elevations. However, the result in ethyl alcohol brings out the difference. The mixture of dl-leucine with I-leucine is interesting, showing a sufficient elevation after the addition of the second substance to indicate that the two are not identical. The fact that 1-leucine alone produces a greater elevation than dl-leucine is sufficient to establish the latter as a racemic compound, for a racemic mixture should produce approximately twice the effect of one of the isomers.

We have also run comparison tests on sulfanilic acid and two isomeric disodium naphthol-di-sulfonates in aqueous solutions. The apparatus consisted of a test-tube with side arm condenser and a mercury thermometer graduated in tenth degrees. The thermometer was first tested in the vapor phase over boiling water, and thereafter the boiling point of water was determined for any one experiment from the barometer, since it is almost impossible to obtain a constant reading with a thermometer immersed in pure water. However, in the presence of excess of the solid materials, readings consistent to 0.1° were obtained. The results are summarized below

Sulfanilic acid	0.25°	
		Mixture 1.9°
Disodium 2-naphthol 6,8-disulfonate	1.7°	
		Mixture > 4°
Disodium 1-naphthol 3,8-disulfonate	..	

As a further example, we have compared triphenylmethyl peroxide and 9-phenylfluorenyl peroxide in benzene, using the Menzies apparatus. The two samples melted with decomposition, respectively, at 179–181° and 193–194". The mixed melting point with the lower melting substance in excess was 178–180°. The results with the ebullioscope were more satisfactory, although not as definite for the individual substances as those with the amino acids. With triphenylmethyl peroxide, the temperature elevation lay between 0.10 and 0.13°, and was a function of the amount of solid added, giving 0.13° as the maximum value for the true elevation. With 9-phenylfluorenyl peroxide a constant value of 0.166° was recorded, and when the former was added to the boiling saturated solution of the latter, the reading increased rapidly to 0.246°, which represents a minimum for the mixture and definitely brings out the difference.

Tests for Purity

The measurement of boiling points of saturated solutions is not sufficiently sensitive to permit the accurate determination of small amounts of impurities. However, when the percentage of impurity is high enough, useful information may be obtained.

In testing for purity, three procedures are available. The first of these we have not tried out, considering it sufficiently evident. It is analogous to the comparison of melting points after successive recrystallizations, and consists of a similar comparison of boiling points. The samples of material added to the apparatus in successive tests should have approximately the same weight, and should be introduced in considerable excess if the procedure is to be sensitive, since a sufficiently high concentration of the impurity must be obtained.

The second test for purity is a variation of the first. A relatively large sample of the substance is boiled with successive portions of the solvent, and the boiling point (or, more frequently, the boiling point elevation relative to the pure solvent) recorded after each change of solvent. In this way the extraction of the impurity by the solvent may be observed. Removal of the hot liquid is effected by a combination of decantation and filtration, and the residue from filtration is returned to the apparatus. A decrease of the boiling point between any two successive measurements indicates the presence of impurity. Erroneous results may be obtained when testing a mixture of two or more similar materials in approximately equal amounts, where it is impossible to extract any one of the substances without dissolving the entire sample.

As an example of this procedure, 0.5 g. of a mixture containing 10% of glycine and 90% of dl-alanine was boiled with three successive 32-cc. portions of ethyl alcohol. The temperature elevations, relative to the boiling point of alcohol, were 0.027, 0.021 and 0.021°, showing that the amount of impurity was sufficient to produce a measurable concentration in 32 cc. of solvent, and that it was extracted almost entirely by the first portion. An estimate from the data indicates 5% of glycine. This could be made more reliable by using a larger sample.

The third test for purity depends upon the difference in concentration of the impurities produced by varying the amount of solid added to a single portion of the solvent. The substance is added to the boiling liquid in small weighed portions, and the boiling point is recorded as a function of the amount of material. This procedure is roughly quantitative, since the change of boiling point between successive additions is determined by the amount of material extracted from a weighed quantity of solid.

Two mixtures of dl-alanine and dl-valine, containing, respectively, 10 and 20% of the latter, were tested by this procedure. Each of the weighed portions contained more dl-alanine than was required to saturate the solution. The volume of boiling alcohol was 32 cc. The results are summarized in Table IV, in which the first row shows the total weight added, and the second and third rows give the temperatures with the 10 and 20% mixtures.

Table IV

Test for Purity Applied to Mixtures of *dl*-Alanine and dl-VALINE

Weight added, g.	0.10	0.15	0.20	0.25	0 30	0.35	0.40	0.50	0.60	0.70
Elevation (10% **valine)**	.019		.027		.032		.035	.038	,042	.045
Elevation (20% **valine)**	.024	.029	.035	.038	.041	.045				

The presence of impurity, greater in quantity in the second sample than in the first, is demonstrated by the fact that a given weight of the 20% mixture produces a larger elevation of the boiling point than the corresponding amount of the 10% mixture. The quantitative interpretation depends principally on an accurate knowledge of the boiling point of a solution saturated with dl-alanine. If the temperature is plotted as a function of the total weight added, and a straight line is drawn through the points to intersect the temperature axis at the value 0.0265, taken from Table I, for dl-alanine, the slope of the line gives a measure of the concentration of impurity built up from unit weight of the solid. If the volume is known, this may be converted to moles per unit weight. Since, in the above tests, the molecular weight of the impurity is known, it may be expressed as weight per cent. The results for the above mixtures were

9.8 and **19.0%.** In the general case, of course, results are expressed as moles per unit weight.

The writer is indebted to Professor James B. Conant, who suggested carrying out the above tests.

Summary

The measurement of the boiling points of saturated solutions is suggested as an aid in identifying and testing the purity of compounds to which the familiar melting point procedure is not applicable because of decomposition. Examples of the method are given.

Negative results in the tests for impurities are not necessarily conclusive. Any of the procedures is subject to essentially the same limitations as the analogous test by the melting point method.

CAMBRIDGE, MASSACHUSETTS

NOTES

A Diaphragm Valve.—In connection with some experiments in which a greaseless device for regulating gas flows was needed, the diaphragm valve described in this note was developed. It consists of an aluminum diaphragm A, about **0.3** mm. in thickness, resting on the flange of a glass cup B, which has an outlet tube C, and a capillary inlet tube D, as shown in Fig. **1.** The upper end of tube D and the flange are ground flat with fine carborundum powder. Around the edge of the diaphragm and the flange of the cup is a rubber gasket, E. These parts are held 'together by a brass frame F. The position of the diaphragm is adjusted by a differential screw G. The lower surface of the diaphragm is roughened with very fine emery paper, so as to have better contact with the ground end of the capillary tube for the regulation of the low flows.

In cases where the gas used is likely to react with or corrode aluminum, a thin piece of mica is cemented with Duco Household Cement across the entire lower surface of the aluminum diaphragm. The mica surfaces should first be roughened with fine emery paper.

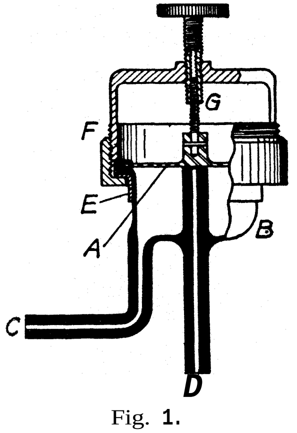

Fig. 1.

By varying the diameter of the inlet and outlet tubes, and the size and thickness of the diaphragm, this type of valve can be adapted to a wide range of gas flows. In connection with some experiments in this Laboratory, this type of valve was used successfully to regulate gas flows ranging from a few tenths of a cubic centimeter to several liters of gas per minute.

This valve is especially useful in controlling very slow flows where an ordinary stopcock is inadequate.

The writers wish to express their thanks to Mr. L. Testa for making the glass cup for the valve.

CONTRIBUTION FROM THE
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A Method of Winding Helical Quartz Springs and of Constructing Glass Sorption Buckets.—The construction and characteristics of the quartz helix sorption balance have been described in detail by McBain and Bakr[1] and the technique of its application to sorption studies by McBain and co-workers.[2] The author feels that the method of winding such helices which is presented here is an improvement upon that described by McBain and Bakr as regards ease of manipulation and uniformity of the springs produced.

The fibers are drawn from a quartz rod 3–5 mm. in diameter which is rotated in an oxyhydrogen flame until the quartz is evenly heated. The rod is then removed from the flame and drawn out immediately. The desirable fibers are about 0.2 mm. in diameter and about 100 cm. long. With some practice it is possible to draw fibers, a fair percentage of which will be of a useful diameter.

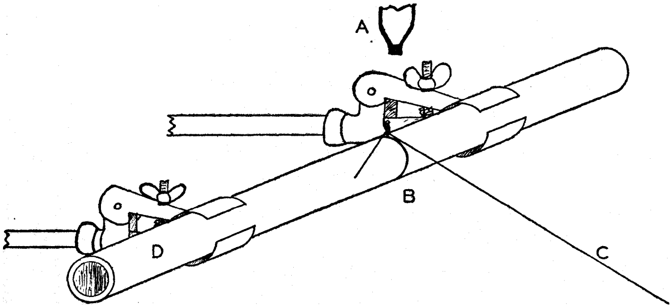

Fig. 1.

The method used in winding the helices is illustrated in Fig. 1. A section of quartz combustion tubing, D, 1.5 cm. in diameter and 30 cm. long is mounted horizontally with two buret clamps holding it loosely so that it can be moved horizontally and rotated freely. A small hand torch, A, is mounted vertically about 2 cm. above the axis of the tube. The author

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[1] McBain and Bakr, THIS JOURNAL, 48,690 (1926).

[2] McBain and Britton, *ibid.*, 52,2198 (1930); McBain, Lucas and Chapman, *ibid.*, 52,2668 (1930); McBain, Jackman, Bakr and Smith, *J. Phys. Chem.*, 34, 1439 (1930).

prepared a small glass hand torch for this purpose. A piece of heavy nichrome wire, B, is twisted around the tube to provide a point of attachment for the fiber to be wound. A gas flame about 6 cm. in length is fed an air-oxygen mixture until the inner cone does not impinge upon the tube. The end of the fiber, C, is bent and hooked around the wire post and the tube slid over so that the fiber is in the flame. The tube is then rotated with one hand and the fiber guided with the other.

The amount of oxygen fed to the flame is rather critical. Too hot a flame may melt the fiber or cause it to adhere to the tube. Too cold a flame will result in poor bending and the resulting spring will not be cylindrical. A trial or two will give the proper flame adjustment and the winding may then be quite rapid. If one tires, or if the tube overheats, the spring may be slid out from the flame, and the winding resumed at leisure.

When cold, the hook is broken off and the helix loosened from the tube by gently rotating the ends in opposite directions with the tips of the fingers. It may then be bunched up and slid off the tube. A tube with a slight taper is very advantageous.

Helical springs prepared in this manner are free from corners, and show excellent mechanical strength. The small hand torch with an air-oxygen-gas flame is very conveniently used to bend the ends of the helices to form suspension hooks. McBain and co-workers recommend that the completed helices be annealed at 400° for about forty-eight hours.

McBain and co-workers employed buckets of platinum or gold foil to hold their sorbent. The author has prepared glass buckets for the same purpose. Since these buckets cannot be used to hold weights while the springs are being calibrated, a small pan of mica may be employed. Such a pan need weigh only 0.03 g. The stages in the preparation of the glass buckets are shown in Fig. 2.

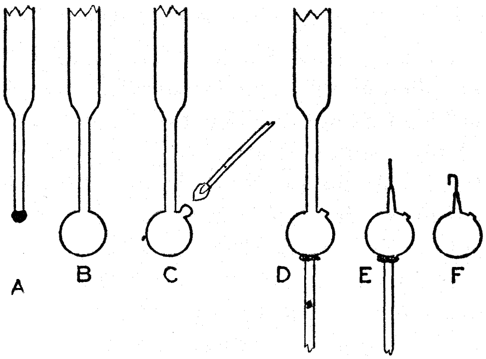

Fig. 2.

A piece of Pyrex tubing, about 1 cm. in diameter, is heated and drawn out to give a capillary about 1.5 mm. in diameter. This capillary is touched to the edge of an air-oxygen-gas flame until a small ball of glass has collected. This ball, A, is then blown out to form a bulb, B, with very thin walls. A tiny gas flame is then touched to the top as shown in C, and a small bulb blown out, broken and the edges melted down. A second capillary is then fastened to the bottom of the bulb with a drop of melted wax as shown in D, and the original capillary drawn off as rapidly as possible in a hot needle flame. The glass stem remaining is then bent into a hook, using the tiny gas flame. The wax is then melted off and the bulb cleaned with an appropriate solvent. A bituminous base wax, such as Piceïn, is recommended over a shellac wax, such as deKhotinsky, because it is readily removed with carbon disulfide or carbon tetrachloride.

Buckets prepared in this manner may be made in any desired size. The author has prepared a number which are more than 1 cm. in diameter and which weigh less than 0.1 g. The weight of such buckets is usually about 0.07 g. These buckets will withstand a baking-out temperature of 450".

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ALPHA-NAPHTHOLSULFONIC ACIDS AND DERIVATIVES. II

BY E. GEBAUER-FUELNEGG AND ECKHARD HAEMMERLE

RECEIVED FEBRUARY 12, 1931 PUBLISHED JULY 8, 1931

In a series of articles it has been shown that phenols can be converted in phenolpolysulfonyl chlorides[1] by the action of chlorosulfonic acid. It also was noticed that the reagent caused four distinct types of reaction: namely, sulfonation, sulfochlorination, chlorination and oxidation. In certain cases the hydrovyl group of the phenol was found to be esterified prior to sulfonation, while in other instances condensation products such as the sulfonylides were isolated. 'The predominance of any one of the above-mentioned reaction types will depend on the time, temperature, quantity of reagent and the nature of the phenols.

The most striking aspect of the reaction between unsubstituted phenols and chlorosulfonic acid is the fact that so far it has been impossible to obtain the respective monosulfonyl chlorides.

From these facts a reaction mechanism for the action of chlorosulfonic acid on phenols (and phenolsulfonic acids) was postulated comprising as the first step the primary formation of the phenolsulfonic acid ester, and as the second step its rearrangement to form a phenolsulfonic acid; this is followed by reesterification of the hydroxy group and a second rearrangement to form the phenoldisulfonic acid in presence of sufficient amounts of the reagent.[2] Only when the phenoldisulfonic acid is formed and further

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[1] J. Pollak and E. Gebauer-Fuelnegg, *Monatsh.*, **46, 383** (1925); **46,** 499 (1925); 47, 109 (1926); 47, 511 (1926); 49, 187 (1928); **O.** Litvay, E. Riesz and L. Landau, ***Ber*** , **62,** 1863 (1929); E. Katscher, *Monatsh.*, 56,381 (1830).

[2] E. Gehauer-Fuelnegg and **A.** Schlesinger, Ber., 61, 781 (1928).

sulfonation of the aromatic ring is more difficult, is chlorination of the phenolpolysulfonic acid accomplished with the formation of phenolpolysulfonyl chlorides. Therefore the action of the chlorosulfonic acid on phenols must be regarded as primarily a sulfonation. The chlorination of the sulfonic acid group does not occur until later. It is possible, however, to prepare phenolmonosulfonyl chlorides[2] when the phenolic hydroxy group is carbethoxylated. Other protective groups failed to give the expected results.[3]

The field which thus presented itself seemed interesting from three points of view. (I) Phenolpolysulfonyl chlorides became easily accessible, while their preparation was successful only in special cases before the experiments with chlorosulfonic acid mentioned above. Due to their reactivity they might prove to be interesting intermediates for dyestuff preparation, as well as for certain pharmaceutical purposes.

(II) The isolation and purification of the phenolsulfonyl chlorides as well as the separation of isomers, as compared to the corresponding sulfonic acids, are greatly facilitated on account of their solubility in organic solvents and the ease with which they are crystallized. Their purity can be tested by melting point determination.

(III) The relative ratio of isomeric sulfo derivatives obtained with rhlorosulfonic acid is sometimes altered as compared to sulfonations with sulfuric acid.

While in previous papers a method was developed for the sulfochlorination of various phenols[1] and naphtholmonosulfonic[4] acids, the present report will deal with results obtained with isomeric 1-naphtholdisulfonic acids.

The sulfochlorination of the isomeric a-naphtholmonosulfonic acids had resulted in the isolation of five isomeric I-naphtholtrisulfonyl chlorides, in which the position of only one of the sulfo groups was known. The position of the newly introduced sulfo radicals remained to be determined.

The 1-naphthol-2-sulfonic acid yielded a trisulfonyl chloride with a melting point of 174°. From 1-naphthol-3-sulfonic acid a product was obtained which is not yet identified but which is also believed to be a trisulfonyl chloride. The I-naphthol-4-sulfonic acid was found to form the same trisulfonyl chloride as the isomeric-2-sulfonic acid whose melting point is 174°. Upon treating the 1-naphthol-5-sulfonic acid in a similar manner, a trisulfonyl chloride with a melting point of 140" was obtained. From the 1-naphthol-6-sulfonic acid, a trisulfonyl chloride having a melting point of 203° resulted. The 1-naphthol-7-sulfonic acid yielded again the trisulfonyl chloride with a melting point of 174° and the isomeric

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[3] E. Gebauer-Fuelnegg and F. v. Meissner, *Monatsh*, **50**, 531 (1928).

[4] E. Gebauer-Fuelnegg and A. Glueckmann, *ibid.*, 53-54, 100 (1929).

8-sulfonic acid was found to give a trisulfonylchloride with a melting point of 217°. From this series of experiments the constitution of only one trisulfonyl chloride could be established: namely, that of melting point 174° which was obtained from the 1-naphthol-2, -4- and -7-acids. It therefore is the 1-naphthol-2,4,7-trisulfonyl chloride.

The present report will deal with attempts to establish the constitution of some of the other trisulfonyl chlorides described above.

Since the isomeric 1-naphtholtrisulfonic acids were not sufficiently reliable for the present study, the isomeric disulfonic acids were used. When two of them upon treatment with chlorosulfonic acid will form only one trisulfonyl chloride, the position of the three sulfonic groups is determined. This scheme was successful with the 1-naphthol-2,4- and -4,7-disulfonic acids, which both yielded the 1-naphthol-2,4,7-trisulfonyl chloride.

The constitution of a second trisulfonyl chloride was established when both the 1-naphthol-4,6- and -6,8-disulfonic acids were found to yield only one trisulfonyl chloride, which therefore has the structure of a 1-naphthol-4,6,8-trisulfonyl chloride. This was identical with the compound obtained from 1-naphthol-8-sulfonic acid.

With the given data the position of the sulfonyl groups in the trisulfonyl chloride with a melting point of 203° can be either that of a 1-naphthol-2,6,8- or 3,6,8-trisulfonyl derivative. From other indications we conclude that the 2,3,6-position probably represents its actual structure. Two other isomers theoretically equally possible are excluded because of the fact that its anilide does condense with diazotized bases (elimination of 2,4,6-position) while the 4,6,8-position was found to belong to the trisulfonyl chloride with a melting point of 217° as stated above.

The constitution of the trisulfonyl chloride of m. p. 140° for which the positions 3,5,7- or 2,5,7- *a priori* are most probable, is not yet definitely settled.

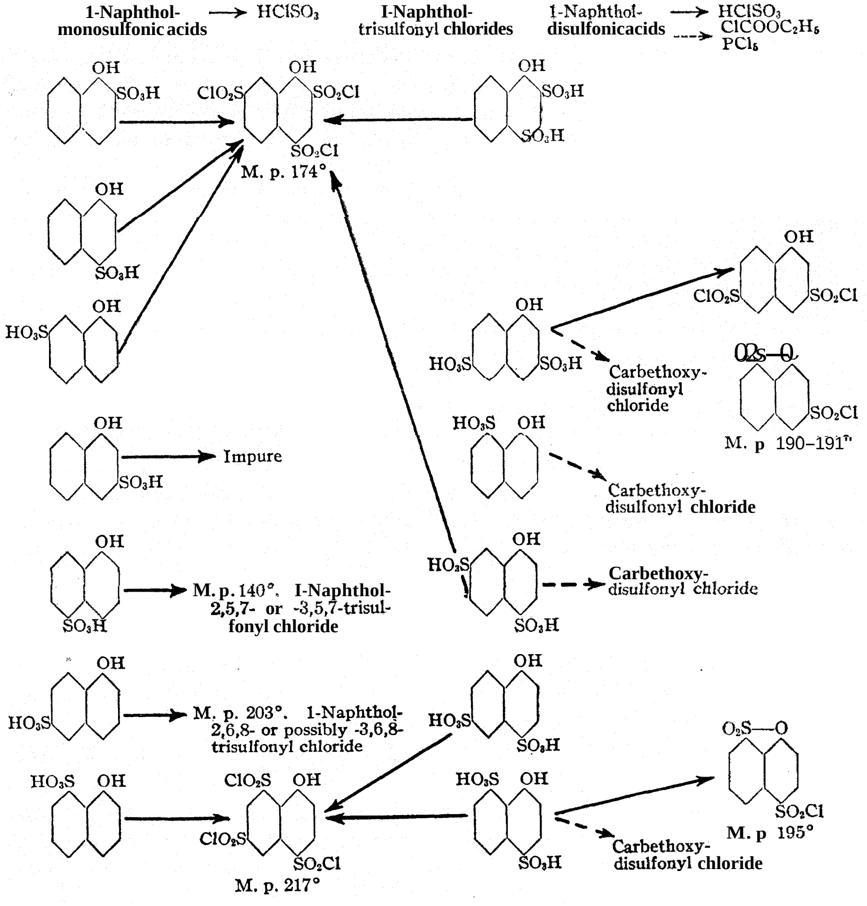
In the course of the present work, a number of new derivatives of 1-naphtholdisulfonic acids were encountered.

Upon treatment of the 1-naphthol-3,8-disulfonic acid with chlorosulfonic acid, the naphthsultone-3-sulfonyl chloride was obtained. From this acid no trisulfonyl chloride was obtained. The isomeric naphthsultone-4-sulfonyl chloride resulted under analogous conditions from the 1-naphthol-4,8-disulfonic acid.

When treated with aniline a reaction takes place, but the products obtained do not seem to be the expected naphthsultone sulfanilides. They will be studied and reported upon later.

The carbethoxy-1-naphtholdisulfonyl chlorides and some of the anilides of 1-naphthol-3,6-, -3,8-, -4,7- and -4,8-disulfonic acid have also been prepared. From the 4,6-disulfonic acid we were unable to isolate the corresponding chloride or anilide. Special care was necessary in the case of the 4,8-disulfonic acid, which was found to be easily converted by the presence of moisture into the corresponding naphthsultonesulfonyl chloride.

The chart shows the relation of the different 1-naphtholsulfonic acids and their derivatives.



Experiments

1-Naphthol **Trisulfonyl** Chlorides.—Ten grams of 1-naphthol-2,4-disulfonic acid was added to 100 g. of chlorosulfonic acid in small portions. After this had stood at room temperature for three days, crystals had formed. The yield did not seem to increase after ten days. They were filtered by suction through a funnel with a porous glass bottom, finally washed with water and dried in a vacuum. The substance was first crystallized from benzene and finally from carbon disulfide and yielded crystals melting at 174°.

The same substance may be obtained after three hours, when the reaction mixture is cautiously poured on crushed ice, carefully dried and crystallized as above. A mixture melting point proved the identity of the two preparations.

Ten grams of sodium salt of 1-naphthol-4,7-disulfonic acid were slowly added to 100 g. of chlorosulfonic acid. After fourteen days the crop of crystals was isolated and purified as above. The melting point of 174° and mixed melting point with the preparations obtained from the 1-naphthol-2,4-disulfonic acid as well as from 1-naphthol-2,4- and -7-monosulfonic acids, proved the identity of the substances. This compound also is formed after a three-hour reaction period from 1-naphthol-4,7-disulfonic acid with chlorosulfonic acid at room temperature.

Ten grams of 1-naphthol-4,8-disulfonic acid is added to 100 g. of chlorosulfonic acid, and the mixture is heated in an oil-bath for one hour at 150°. (The reaction which takes place under milder conditions will be described in a following paragraph.) After repeatedly crystallizing from carbon disulfide, the constant melting point of 217" is reached.

If 1-naphthol-4,6-disulfonic acid is treated analogously at 100 or 150° and the reaction product poured into concd. hydrochloric acid, filtered, completely dried, dissolved in benzene and crystallized from carbon disulfide to a constant melting point, crystals are obtained which melt at 217°, identical with those obtained above as well as with the compound previously obtained from 1-naphthol-8-sulfonic acid.

Anal. Calcd. for $C_{10}H_5O_7S_3Cl_3$: Cl, 24.20. Found: Cl, 24.48.

The corresponding anilide is obtained when an ether solution is refluxed with an excess of aniline on the water-bath.

Naphthsultonesulfonyl Chlorides.—Ten grams of sodium salt of 1-naphthol-3,8-disulfonic acid is added in small portions to 100 g. of chlorosulfonic acid at room temperature. The reaction mixture is cooled in the ice box, poured on crushed ice, filtered and completely dried in *vacuo*. The residue is first dissolved in benzene, crystallized and finally recrystallized from carbon disulfide, whereby crystals with a constant melting point of 190–191° are obtained. The same substance was isolated with better yields, when the reaction was prolonged for thirty days or the mixture heated to 150°.

Anal. Calcd. for $C_{10}H_5O_5S_2Cl$: Cl, 11.64; S, 21.06. Found: Cl, 11.65; S, 20.96.

Ten grams of sodium salt of 1-naphthol-4,8-disulfonic acid is slowly added to 100 g. of chlorosulfonic acid, isolated as before, m. p. 195° (a mixed melting point with the naphthsultone-3-sulfonyl chloride, m. p. 190–191°, gave a depression). The same product is obtained after prolongation of the reaction for thirty days.

Anal. Calcd. for $C_{10}H_5O_5S_2Cl$: C, 39.39; H, 1.65; Cl, 11.64. Found: C, 39.53; H, 2.11; Cl, 11.67.

The two isomeric naphthsultonesulfonyl chlorides do not react with aniline in ether solution to form the corresponding anilides. Only when boiled with aniline does a reaction ensue with the formation of products which are not the expected anilides. They will be discussed elsewhere.

Carbethoxy-1-naphtholdisulfonyl Chlorides.—Twenty grams of sodium salt of 1-naphthol-4,7-disulfonic acid is dissolved in a concd. solution of 15 g. of potassium hydroxide and well cooled, 20 g. of ethyl ester of chlorocarbonic acid is added drop by drop and the reaction mixture mechanically shaken for five to six hours. Alcohol was added to complete the precipitation and to dissolve any excess of reagent and filtered. The well dried substance was finely powdered and mixed with 1.5 molar proportions of phosphorus pentachloride and heated for one hour in an oil-bath at 130–150°. The reaction mixture was cooled to room temperature, poured on crushed ice, filtered and well washed with water. The completely dried residue was crystallized from carbon disulfide, finally giving crystals with a constant melting point of 120°.

Anal, Calcd. for $C_{13}H_{10}O_7Cl_2S_2$: Cl, 17.17. Found: Cl, 17.10.

The preparation of the carbethoxy-1-naphthol-3,8-disulfonyl chloride was analogous with the experiments described above, m. p. 180-181°.

Anal. Calcd for $C_{13}H_{10}O_7S_2Cl_2$: C, 37.76; H, 2.44; Cl, 17.17. Found: C, 38.05; H, 2.81; Cl, 17.46.

Carbethoxy-1-naphthol-4,8-disulfonyl chloride was prepared in the same way. The substance was finally obtained from carbon disulfide and melted from 177-179°. The analysis also indicates that the product is not entirely pure.

Care must be taken to avoid even traces of moisture during the reaction as well as recrystallization since the carbethoxy group is easily split off and as a result the naphthsultone-4-sulfonyl chloride, m. p. 195°, is obtained.

Anal. Calcd. for $C_{13}H_{10}O_7S_2Cl_2$: C, 37.76; H, 2.44; Cl, 17.17. Found: C, 38.52; H, 2.21; Cl, 17.80.

The carbethoxy-1-naphthol-3,6-disulfonyl chloride melted at 95° after crystallization from ether.

Anal. Calcd. for $C_{13}H_{10}O_7S_2Cl_2$: C, 37.76; H, 2.44; S, 15.52; Cl, 17.17. Found: C, 37.44; H, 2.77; S, 15.69; Cl, 17.21.

Some of the anilides of the isomeric carbethoxy-1-naphtholdisulfochlorides were prepared by boiling them with 2.5 molar proportions of aniline in ether solution for three hours. After evaporation the residue is washed with dilute hydrochloric acid and water. The carbethoxydisulfanilides were purified by carefully dissolving in dilute potassium hydroxide and precipitating with dilute hydrochloric acid.

We are indebted to the I. G. Farbenindustrie A.-G. for furnishing us with the 1-naphtholsulfonic acids.

Summary

The value of chlorosulfonic acid as a sulfochlorinating agent for phenols is emphasized.

1-Naphthol-2,4-, -2,7-, -3,6-, -3,8-, -4,6- and -4,8-disulfonic acids were sulfochlorinated with chlorosulfonic acid. 1-Naphthol-2,4- and -2,7-disulfonic acid yielded the same trisulfonyl chloride, the constitution of which therefore is determined as the 1-naphthol-2,4,7-trisulfonyl chloride. 1-Naphthol-4,6- and -6,8- also gave only one trisulfonyl chloride, which therefore must be the 1-naphthol-4,6,8-trisulfonyl chloride. Previously it had been obtained by sulfochlorination of the 1-naphthol-8-sulfonic acid. The constitution of the trisulfonyl chloride previously obtained from the 1-naphthol-6-sulfonic acid is believed to be the 1-naphthol-2,6,8- or possibly -3,6,8- derivative, while the structure of the trisulfonyl chloride derived from I-naphthol-5-sulfonic acid is either that of a 1-naphthol-2,5,7- or -3,5,7- derivative.

From the 1-naphthol-3,8- and -4,8-disulfonic acids the respective naphthsultonemonosulfonyl chlorides were obtained under proper conditions.

The carbethoxynaphtholdisulfonyl chlorides and a number of their anilides also have been prepared from the above acids.

CHICAGO, ILLINOIS

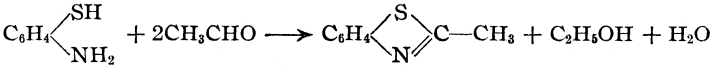
[CONTRIBUTION FROM THE SCHOOL OF PHARMACY AND THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE CONDENSATION OF ALDEHYDES WITH ORTHO-AMINOTHIOPHENOLS, BENZOTHIAZOLINES AND BENZOTHIAZOLES

BY HERMAN P. LANKELMA AND P. X. SHARNOFF

RECEIVED FEBRUARY 26, 1931 PUBLISHED JULY 8, 1931

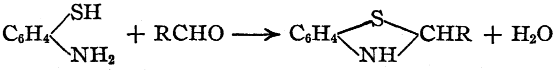
Hofmann[1] obtained benzothiazoles by the action of acids, acid chlorides and acid anhydrides upon o-aminothiophenol. Upon condensing certain aldehydes with o-aminothiophenol, he also obtained benzothiazoles.[2] He formulated the change as involving two molecules of aldehyde, one of which was reduced to the alcohol in the process.



In no case however was he able to show that an alcohol was actually formed.

Green and Perkin[3] also obtained a benzobisthiazole by condensing benzaldehyde with *p*-phenylenediamine-2,5-di-(thiosulfonic acid).

Claasz[4] condensed a number of aldehydes with o-aminothiophenol hydrochloride and obtained products which he described as benzothiazolines.



Since he obtained practically quantitative yields of product upon treating one mole of o-aminothiophenol with one mole of aldehyde, he pointed out that Hofmann's formulation of the reaction could not be correct and concluded that his products were benzothiazolines. In the cases where the corresponding benzothiazoles had previously been prepared, the melting points of Claasz' benzothiazolines were close to them and the melting points which he reported were in most cases not sharp. In no case did he establish his products as benzothiazolines by mixed melting points with the corresponding benzothiazoles.

Bogert and Stull[5] repeated a portion of Claasz' work and, upon purifying the condensation products, obtained benzothiazoles. They therefore characterized Claasz' benzothiazolines as impure benzothiazoles. In order to account for the formation of benzothiazoles from *o*-aminothiophenol and aldehydes they proposed two alternative mechanisms.

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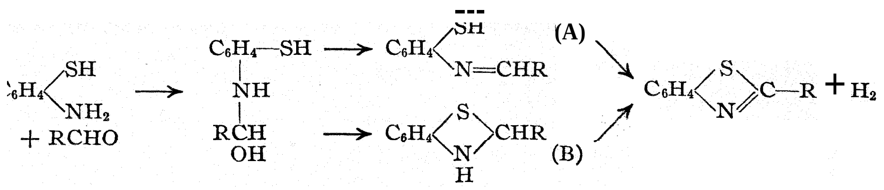
[1] Hofmann, Ber., **12,** 2359 (1879); **13,** 8 (1880).

[2] Hofmann, *ibid.*, 13,1236 (1880).

[3] Green and Perkin, *J. Chem. Soc.*, 83,1207 (1903).

[4] Claasz, *Ber.*, 45, 1031 (1912); 49, 1141 (1916).

[5] Bogert and Stull, THIS JOURNAL, 47,3078 (1925).



As evidence in favor of (A) they point out that o-aminothiophenol will not condense with ketones or their dichlorides.

In the course of an investigation in this Laboratory dealing with the use of substituted o-aminothiophenols as reagents for the identification of aldehydes, we have condensed a number of aldehydes, both aliphatic and aromatic, with 2-amino4-chlorothiophenol hydrochloride and in every case have obtained a product different from the benzothiazole obtained by the action of acid chlorides or acid anhydrides. These products were obtained as crystalline solids of sharp melting point. In some cases the melting points lay within a few degrees of the corresponding benzothiazole. In each such case a mixed melting point with the benzothiazole showed them to be different.

These substances resemble benzothiazolines as described by Claasz with the exception that they are insoluble in mineral acid. Analysis gave values required by the two possible types (A) and (B). Since they are insoluble in aqueous alkali they cannot be thiophenols as represented by (A). They are easily oxidized to benzothiazoles by warming with ferric chloride in alcohol. These facts show that these products are benzothiazolines (B).

Previous work in this field has been practically confined to the use of aromatic aldehydes. In the present work two benzothiazolines were prepared from aryl aldehydes, and both were found to be easily oxidized by the air to the benzothiazole upon crystallizing them from certain organic solvents such as alcohol or carbon tetrachloride. This would indicate that where benzothiazoles are obtained from the action of an aldehyde upon an o-aminothiophenol, a benzothiazoline is first formed and is subsequently oxidized to a benzothiazole, either in the process of preparation or purification. Whether the products which Claasz describes are benzothiazoles or benzothiazolines cannot be stated from the evidence at hand. However, in the light of our results it is quite possible that they are benzothiazolines, which in the process of purification employed by Bogert and Stull, were oxidized to benzothiazoles.

Experimental

Preparation of **Benzothiazoles.**—The action of an acid chloride or acid anhydride upon an o-aminothiophenol has been shown by several investigators to be a general method for the preparation of benzothiazoles.[1,2,6] The method employed in this work

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[6] Papers of Bogert, THIS JOURNAL (1924–1927).

had previously been used in this Laboratory for the preparation of benzothiazoles,[7] and gave very satisfactory results. A mixture of one mole of 2-amino-4-chlorothiophenol hydrochloride and one mole of the acid chloride or acid anhydride was dissolved in dimethylaniline and the solution boiled for about thirty minutes. The benzothiazole was precipitated by acidifying the cold solution. Yields from 60 to 90% were obtained, depending upon the acid chloride or acid anhydride employed.

Preparation of **Benzothiazolines.**—After trying a number of different condensing agents, the following general method was found to give the best results. One mole of

TABLE I

MELTING POINTS OF CERTAIN 2-DERIVATIVES OF 5-CHLOROBENZOTHIAZOLE AND 5-CHLOROBENZOTHIAZOLINE[8]

Name	M. p., °C.	Mixed m. p., °C.	Solvent
5-Chlorobenzothiazole	106		Alcohol
5-Chlorobenzothiazoline	168–169		Chloroform
2-Methyl-5-chlorobenzothiazole~	68– 69	40–51	Alcohol
2-Methyl-5-chlorobenzothiazoline	61		Carbon tetrachloride and ligroin
2-Ethyl-5-chlorobenzothiazole	56– 57	30–44	Alcohol
2-Ethyl-5-chlorobenzothiazoline	60		Carbon tetrachloridr and ligroin
2-Hexyl-5-chlorobenzothiazoline	51– 52		Alcohol
2-Phenyl-5-chlorobenzothiazole[7]	139	108–115	Alcohol
2-Phenyl-5-chlorobenzothiazoline	127		Chloroform and ligroin
2-(*o*-Chlorophenyl)-5-chlorobenzothiazole	136–137		Alcohol
2-(*o*-Chlorophenyl)-5-chlorobenzothiazoline	81		Alcohol

TABLE II

ANALYTICAL DATA

Name	Formula	Carbon, %		Hydrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
5-Chlorobenzothiazole	C_7H_4NClS	49.52	49.82	2.37	2.46	20.92	21.08
5-Chlorobenzothiazoline	C_7H_6NClS	48 92	49 33	3 53	3.67	20.68	20 44
2-Methyl-5-chlorobenzothiazoline	C_8H_8NClS	51.70	51.79	4.32	4.44	19.11	1874
2-Ethyl-5-chlorobenzothiazole	C_9H_8NClS	54.63	54.33	4.08	4.33	17 95	17.98
2-Ethyl-5-chlorobenzothiazoline	$C_9H_{10}NClS$	54.08	54.24	5.05	4.98	17.79	17.83
2-Hexyl-5-chlorobenzothiazoline	$C_{13}H_{18}NClS$	60.99	61.06	7.10	7.12		
2-Phenyl-5-chlorobenzothiazoline	$C_{13}H_{10}NClS$	63.03	63.10	4.04	3.91		
2-(*o*-Chlorophenyl)-5-chlorobenzothiazole	$C_{13}H_7NCl_2S$	55.71	56.12	2.52	2.29	25.32	25.46
2-(*o*-Chlorophenyl)-5-chlorobenzothiazoline	$C_{13}H_9NCl_2S$	55.28	55.14	3.21	3.35	25.14	25.14

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[7] Lankelma and Knauf, THIS JOURNAL, 53,311 (1931).

[8] The numbering suggested for the benzothiazole nucleus by Bogert and Abrahamson, *ibid.*, 44, 826 (1922), is used here for both the benzothiazole and the benzothiazoline nuclei.

2-amino-4-chlorothiophenol was dissolved in pyridine and one mole of aldehyde added dropwise to the warm solution. The mixture was finally heated from two to thirty minutes on the water-bath, the aromatic and the higher aliphatic aldehydes requiring the longer heating time.[9] The benzothiazoline was precipitated by acidifying the mixture; yields, 70–90%.

Oxidation of Benzothiazolines to **Benzothiazoles.**—The alkyl benzothiazolines could be crystallized unchanged from various solvents. 2-Phenyl-5-chlorobenzothiazoline, however, was couverted to the benzothiazole upon two or three crystallizations from alcohol. Similarly 2-(*o*-chlorophenyl)-5-chlorobenzothiazoline was converted to the benzothiazole upon crystallization from acetone or carbon tetrachloride. Any of the benzothiazolines are oxidized to the benzothiazole in good yield by warming for a few minutes with a slight excess of ferric chloride in alcohol.

Summary

1. Aldehydes condense with 2-amino-4-chlorothiophenol to give benzothiazolines.

2. Benzothiazolines are readily oxidized to benzothiazoles.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF INSULIN

BY BERTIL SJÖGREN AND THE SVEDBERG

RECEIVED MARCH 10, 1931 PUBLISHED JULY 8, 1931

The eminent physiological importance of the pancreas hormone insulin has in recent years, and especially since the isolation of crystalline insulin by Abel,[1] made it the subject of numerous chemical investigations. The experimental material so far collected decidedly indicates that insulin is of protein nature.[2] It gives several of the characteristic protein reactions,[3] its empirical composition resembles that of the proteins,[3] it is an amphoteric electrolyte possessing an isoelectric point at about PH 5,[3] which is in the same region where the isoelectric points of many proteins are situated and it shows a light absorption in the ultraviolet at exactly the same place as most of the proteins with a maximum at 270 mμ.[4]

At the suggestion of Dr. H. Jensen of The Johns Hopkins University, Baltimore, we have undertaken an ultracentrifugal study of insulin along the same lines as already followed in this Laboratory for the determination

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[9] The formaldehyde employed was a 30–35% aqueous solution; the other aldehydes used were dried in the process of purification.

[1] J. J. Abel, *Proc. Nat. Acad. Sci.*, 12, 132 (1926).

[2] H. Jensen and A. M. De Lawder, *Z. physiol. Chem.*, 190, 262 (1930).

[3] J. J. Abel, E. M. K. Geiling, C. A. Rouiller, F. K. Bell and O. Wintersteiner, *J. Pharmacol.*, **31**, 65 (1927).

[4] W. Graubner, *Z. Ges. Exp. Medizin*, 63, 527 (1928).

of molecular weight and PH-stability region of a considerable number of proteins.[5]

Material Used.—A quantity of 0.25 g. of crystalline insulin was kindly put at our disposal by Dr. Jensen and this small sample proved quite sufficient for a rather complete ultracentrifugal study. According to Dr. Jensen the material was prepared from commercial beef pancreas insulin of Squibb and Sons by the usual method of crystallization. The first crystalline product obtained had been recrystallized twice without the addition of brucine.

Specific Volume.—For the calculation of the molecular weight from ultracentrifugal data it is necessary to know the partial specific volume of the substance in solution. Two determinations were carried out at 20°, as described in previous communications. The data are given in Table I.

TABLE I

PARTIAL SPECIFIC VOLUME OF INSULIN AT 20°

Insulin concn., %	Solvent	PH of soln.	Partial sp. vol.
0.90	0.067 M in Na_2HPO_4	8.1	0.748
.45	.033 M in Na_2HPO_4 .033 M in KH_2PO_4	6.8	.750

The solution of PH 6.8 was prepared from that of PH 8.1 by addition of KH_2PO_4. The two determinations give the same result within the limits of error. As shown by the ultracentrifugal study insulin is (reversibly) dissociated at PH 8.1. This circumstance therefore does not influence the specific volume. A similar behavior has already been observed for several proteins.

The mean value 0.749 of the specific volume of insulin is the same as that of almost all the proteins so far studied in this Laboratory.

Determination of Sedimentation Constant and PH Stability Region.—The high-speed oil turbine ultracentrifuge was used for measuring the sedimentation constant in the PH range 3.5 to 12.3. The temperature of the solution was between 20 and 23° during centrifuging, the time varied from three to four hours and the speed was about 40,000 r. p. m. in all the runs. The insulin solutions were prepared from the dry material immediately before starting a run. In the PH region 6.4 to 7.4 where it is comparatively difficult to bring insulin into solution, the dry material was first dissolved by means of Na_2HPO_4 and then a suitable amount of KH_2PO_4 added. The solution of PH 4.2 was made up by dissolving insulin in acetic acid and adding sodium acetate. The determinations are summarized in Table II.

The sedimentation is independent of PH from about 4.5 to about 7.0 and has a mean value of 3.47×10^{-13}. This PH range therefore represents the stability region of insulin. Special ultracentrifugal tests showed that

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[5] Svedberg and co-workers, THIS JOURNAL, 48–52 (1926–1930).

TABLE II

SEDIMENTATION VELOCITY MEASUREMENTS ON INSULIN

	Solvent, *M*					P_H of	Concn. of	
No	HAc	NaAc	KH_2PO_4	Na_2HPO_4	NaOH	soln	insulin, %	$s_{20°} \times 10^{13}$
1[a]	0 1	..	..	..	..	3.5	0.16	1.27
2[b]	.074	0 026	..	..	..	4 2	.14	3 10
3	..	..	0086	0047	..	6.4	.12	3.46
4	..	..	.080	.053	..	6.6	.22	3.41
5	..	..	.080	.053	..	6 6	.20	3 51
6	..	..	.060	073	..	6.7	.32	3.55
7	..	..	.067	.067	..	6.8	.19	3.43
8"	..	..	.053	.080	..	7.0	.25	3.21
9[d]	..	..	.027	.107	..	7.4	.17	2.84
10[e]	..	,.	..	.133	..	8 1	.20	2.87
11[f]	..	..	..	.032	0.001	8 9	.16	2.93
12[g]	..	..	.,	..	.025	12.3	.30	0.73

[a] 20% of non-centrifugible products. [b] 10% non-centrifugible products. [c] 5% of non-centrifugible products. [d,e] 8% of non-centrifugible products. [f] 10% of non-centrifugible products; solution 1% NaCl. [g] 50–55% of non-centrifugible products; solution 1.5% in NaCl.

the dissociation of the insulin molecule into products of low molecular weight, as demonstrated by the rapid fall in the sedimentation constant outside this range, is reversible both on the acid and the alkaline side, if the PH of the solution is not too far removed from the stability region and provided that the solution is not kept too long outside the stability region. It is of interest to note that similar experiments have been made regarding the physiological activity of insulin. This fact seems to indicate that the activity is destroyed when the dissociation products lose their ability to reconstruct the insulin molecule.

The sedimentation constant is within the limits of experimental error identical with the value previously found for egg albumin[6] and for Bence-Jones protein,[7] *viz.*, 3.54×10^{-13} and 3.55×10^{-13}, respectively. The PH stability range is decidedly narrower for insulin than for egg albumin and for Bence-Jones protein. In the case of insulin it has an extension of only about 2.5 PH units, while egg albumin is stable over 5 *P*H units (PH 4 to 9) and Bence-Jones protein over 4 units (PH3.5 to 7.5). The isoelectric point of insulin is situated at a higher PH than that of egg albumin. The very low solubility of insulin near the isoelectric point has not permitted the determination of this constant accurately enough to allow of a comparison with Bence-Jones protein which, as a matter of fact, has its isoelectric point situated in the same region as insulin (PH5.2).

Determination of Molecular Weight.—When the sedimentation equilibrium method is used, the molecular weight M is given by the relation

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[6] T. Svedberg and J. B. Nichols, THIS JOURNAL, 48,3081 (1926); B. Sjögren and T. Svedberg, *ibid.*, 52, 5187 (1930).

[7] T. Svedberg and B. Sjogren, *ibid.*, 51,3594 (1929).

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2 (x_2^2 - x_1^2)}$$

where R is the gas constant, T the absolute temperature, V the partial specific volume of the solute, ρ 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.

Three equilibrium runs were performed within the stability region of insulin at a temperature of 20.1° and a speed of 10,500–11,000 r. p. m. Table III gives the complete data of a typical run and in Table IV are summarized the results of the three runs.

The mean value for the molecular weight 35,100 is within the limits of error identical with the values previously obtained for egg albumin[6] and Bence-Jones protein,[7] *viz.*, 34,500 and 35,000, respectively. Table III shows that there is no drift in the molecular weight values with distance from the center of rotation and that accordingly insulin is homogeneous with regard to molecular weight.

TABLE III

SEDIMENTATION EQUILIBRIUM RUN ON INSULIN

Concn., *0.10%;* **phosphate buffer,** *P_H 6.8 (0.067 M* **in** KH_2PO_4, *0.067* **M in** Na_2HPO_4); **V** = *0.750;* ρ = *1.012;* *T* = *293.2;* **length of col. of soln.,** *0.47* **cm.; thickness of col.,** *0.80* **cm.; dist. of outer end of soln., from axis of rotation,** *5.95* cm.; **speed,** *10,500* **r. p. m.** ($\omega = 350\pi$); **light absorption standard,** $M/1200$ **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** *90* **seconds; exposure made after** 31, 36 **and 44 hours of centrifuging**

Distances, cm. x_2	x_1	Mean concn., % c_2	c_1	Numbers of exposures	Mol wt.
5.88	5.83	0.110	0.097	10	35,900
5.83	5.78	.097	.086	10	34,600
5.78	5.73	.086	.076	10	35,900
5.73	5.68	.076	.067	10	36,900
5.68	5.63	.067	.059	8	37,600
				Mean	36,200

TABLE IV

SUMMARY OF SEDIMENTATION EQUILIBRIUM MEASUREMENTS ON INSULIN

Solvent, M KH_2PO_4	Na_2HPO_4	P_H of soln.	Concn. of insulin at start, %	Mol. wt.
0.060	0.073	6.7	0.10	33,900
.067	.067	6.8	.20	35,200
.067	.067	6.8	.10	36,200
			Mean	35,100

By means of the values for the molecular weight, M = 35,100, and the sedimentation constant, $s = 3.47 \times 10^{-13}$, we are now able to deduce the value for the molar frictional constant, $f = [M(1 - V\rho)]/s$, and find 2.54×10^{16}. The calculation of the molar frictional constant of a spherical molecule of the same molecular weight and the same specific volume as insulin calculated from the formula $f_s = 6\pi\eta N(3MV/4\pi N)^{1/3}$, where η is the viscosity of the solvent, gives the same value. Accordingly the insulin molecule must be regarded as spherical. The radius, calculated from the formula $r = (3MV/4\pi N)^{1/3}$, is 2.18 mμ. According to previous determinations[6,7] the egg albumin molecules and the Bence-Jones protein molecules are also spherical in shape with values for the radius of 2.17 and 2.18 mμ, respectively.

The fact borne out by the above investigation that the molecules of crystalline insulin are, with regard to mass, shape and size, almost identical with those of egg albumin and Bence-Jones protein and that, within the *P*H region 4.5–7.0, the insulin solutions are built up of molecules of equal mass, strongly support the view that insulin is a well-defined protein. It has a *P*H-stability region which is decidedly narrower than the stability regions for egg albumin and Bence-Jones protein, it has a much lower solubility and also in other respects differs chemically from those two proteins. These circumstances seem to indicate that we are justified in assuming that the physiologically active principle is not a low-molecular substance accidentally adsorbed on some high-molecular material but is the insulin molecule itself or some special group within it.[8]

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 insulin have been determined by means of ultracentrifugal methods.

2. Insulin is stable from a PH of about 4.5 to about 7.0 with a molecular weight of 35,100. At lower and higher *P*H values the insulin molecule is broken up into smaller units. Near the borders of the stability region this dissociation is reversible.

3. Within the stability region the sedimentation constant of insulin is 3.47×10^{-13} and the molar frictional constant 2.54×10^{16}. The molecules are spherical with a radius of 2.18 mμ.

4. The molecular weight, sedimentation constant, molar frictional constant and molecular radius of insulin are within the limits of error identical with the corresponding constants for egg albumin and Bence-Jones protein. This circumstance makes it extremely probable that insulin is a well-defined protein and that the physiological activity of this hormone is a property of the insulin molecule itself or some special group within it.

UPSALA, SWEDEN

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[8] Compare H. Jensen and A. M. De Lawder, Ref. 2.

[CONTRIBUTION FROM THE LABORATORY FOR PURE RESEARCH OF MERCK & CO., INC.]

THE PREPARATION AND PROPERTIES OF PURE DIVINYL ETHER

BY WILLIAM L. RUIGH AND RANDOLPH T. MAJOR

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The first recorded reference to divinyl ether occurs in a paper by Semmler[1] "On the Ethereal Oil of *Allium Ursinum* L." The divinyl sulfide, which was obtained from the essential oil of this plant, when treated with silver oxide yielded a low-boiling, sulfur-free liquid, the boiling point of which was about 39°. Two determinations of the molecular weight corresponded with the calculated value for divinyl ether. Semmler did not further characterize this liquid.

An attempt to prepare divinyl ether by the exhaustive methylation of morpholine was made by Knorr and Matthes.[2] A few drops of liquid were obtained but the quantity was insufficient for either an analysis or a determination of its boiling point.

Cretcher, Koch and Pittenger[3] attempted to prepare divinyl ether by the action of heated sodium hydroxide on β,β'-dichlorodiethyl ether. The reaction was carried out in an iron pot surmounted by a Crismer column. The distillate came over at 84–85°. From it they were able to isolate β-chloroethyl vinyl ether, 1,4-dioxane, acetaldehyde and a "divinyl ether" which boiled at 39°. The yield of material that boiled at 39° was 4.7% of the amount that would have been expected if the conversion of the β,β'-dichloroethyl ether into divinyl ether had been complete. These authors evidently abandoned the attempt to prepare pure divinyl ether since they gave no properties of their product except its boiling point. The acetaldehyde formed in this reaction amounted to twice the weight of the material that boiled at 39°.

Hibbert, Perry and Taylor[4] modified the method of the previous authors. They replaced the Crismer column with a reflux condenser kept at 40°; they used potassium hydroxide rather than sodium hydroxide, added the β,β'-dichlorodiethyl ether in small portions and lastly increased the time of heating. They obtained a 54.9% yield of a "divinyl ether" which boiled at 34–5°. Presumably, further details are contained in Canadian Patent Application 350,357.[5] On brominating the material that boiled at 34–5° these authors obtained a compound, tetrabromoethyl ether, which melted at 63–64° and was identical with Freundler's "tetrabromobutyraldehyde."[6] This was shown by analysis and by a mixed melting point.

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[1] Semmler, *Ann.*, 241, 111–116 (1887).

[2] Knorr and Matthes, Ber., 32, 736 (1899).

[3] Cretcher, Koch and Pittenger, THIS JOURNAL, 47, 1175–1176 (1925).

[4] Hibbert, Perry and Taylor, *ibid.*, 51, 1551 (1929).

[5] Hibbert, Canadian Patent 302,437, July 29, 1930.

[6] Freundler, *Compt. rend.*, 140, 794, 1693 (1905); Bull. *soc. chim.*, [4] **1**, 71 (1907).

We have continued the study of the reaction between β,β'-dichlorodiethyl ether and the corresponding iodo ether with heated alkalies. In confirmation of the work of Cretcher, Koch and Pittenger we have isolated acetaldehyde, β-chloroethyl vinyl ether and 1,4-dioxane as products of this reaction. We have found, however, that divinyl ether boils at 28.3 ± 0.2° at 760 mm. The small amount of "divinyl ether," b. p. 39°, obtained by these authors was presumably a mixture which they did not further investigate. In addition to these products we have found evidence of the presence of ethylene oxide among the substances formed in the reaction. Also, in our preliminary work the gaseous products of the reaction were investigated and the presence of hydrogen and traces of acetylene were demonstrated.

Although the melting points of both pure sodium and potassium hydroxides are above 300°, ordinary C. P. grades which contain water fuse at a temperature below that at which reaction between the alkali and the chloro ether takes place. The reaction was very slow at temperatures below 170°; the most satisfactory temperatures were between 200–250°.

It was found that during the course of the reaction a crust of sodium or potassium chloride formed over the surface of the fused alkali. When the alkali was well stirred and the crust formation prevented, it was found that only traces of acetaldehyde were formed. Without stirring, the amount of aldehyde was generally two to three times the amount of the divinyl ether formed. There was also considerable gas evolved during the reaction. Analysis showed that the gas consisted mainly of hydrogen with some unsaturated gases including traces of acetylene.

The yield of divinyl ether was very markedly increased by passing a slow stream of ammonia gas through the reaction system. The ammonia may either act as a true catalyst for the reaction or it may increase the yield by inhibiting the decomposition of the divinyl ether formed. A further study is being made of the function of the ammonia in promoting the reaction.

Several other reactions for the preparation of divinyl ether were studied but no other satisfactory process was found.

The important physical and chemical properties of divinyl ether have been determined and apparently for the first time it has been analyzed.

When divinyl ether was catalytically reduced with hydrogen in the presence of a platinum catalyst a 15% yield of diethyl ether was recovered. In addition to this acetaldehyde was found in the reaction mixture. This was evidently formed by hydrolysis of the divinyl ether during the reduction. Although some ethyl alcohol may have been formed by reduction of more of the aldehyde this was not determined. On the other hand, the work of Vavon, Skita and Adams on the selective reduction of olefin and aldehyde groups has shown that a platinum catalyst without a promoter such as iron is not a very effective catalyst for the reduction of aldehydes.[7]

A recent patent by Hibbert[8] has described the polymerization of "divinyl ether" in the presence of benzoyl peroxide. We have found that only 5 to 25% of our divinyl ether was polymerized when it was treated according to the directions given in this patent. Polymerization is practically completely inhibited by minute traces of ammonia.

The reactions of divinyl ether with bromine have been studied. These will be discussed in a forthcoming paper.

Experimental Part

Preliminary Study of the Reaction between β,β′-Dichloroethyl Ether and Heated Caustic Alkalies.—Considerable time was spent in attempts to prepare divinyl ether by the action of potassium hydroxide on β,β′-dichlorodiethyl ether according to the method of Hibbert, Perry and Taylor.[4] The apparatus used by these authors was later modified in most of our preliminary runs by the use of a nickel-lined copper autoclave of about 500-cc. capacity in place of a copper flask. The end of the condenser was connected through the top of the autoclave by means of a tightly fitting stuffing box packed with a mixture of asbestos and graphite. Provision was made for a gas inlet tube and a thermometer well. Ice water was circulated through the second condenser and the liquid products were collected in a flask cooled with either solid carbon dioxide and acetone or ice and hydrochloric acid mixtures.

According to the description given by these authors the copper reaction flask was "strongly heated with a Bunsen burner." In order to control the reaction more carefully, we carried out experiments over the temperature range of 150–300°. They also stated that "finely powdered caustic potash" was employed. The ordinary "C. P." grades of sodium or potassium hydroxide melt at about 140–160° depending upon the amount of water that they contain. Since these authors did not mention any particular drying of the caustic potash we assumed that their reaction mixture actually consisted of fused rather than powdered alkali. However, we varied the water content of the alkali both by the addition of water and by boiling off the excess water at slightly higher temperatures than that at which the reaction was to take place. A mixture of sodium and potassium hydroxides (and water) was also tried.

Throughout these preliminary experiments and also in later work we were never able to obtain any trace of either a compound or a true constant boiling mixture which boiled between thirty and forty degrees.

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[7] Tuley with Adams, THIS JOURNAL, 47, 3061 (1925); Skita, *Ber.*, 48, 1685 (1915); Vavon, *Compt. rend.*, 154, 359 (1912).

[8] Hibbert, Canadian Patent, 302,437, July 29, 1930.

It was found that a considerable amount of gas was evolved during the reaction. When about eight drops of β,β'-dichlorodiethyl ether was added per minute, the flow of gas varied from 5 cc. per minute at 200° to about 65 cc. at 280'.

A qualitative test with ammoniacal cuprous chloride gave a small quantity of a red precipitate which showed the presence of a small amount of acetylene. The gas also gave a strong positive test for hydrogen with Pereira's test,[9] using sodium tungstate, acetic acid and palladous chloride.

In most of the preliminary runs a small amount of material that boiled between 20 and 30" was obtained. This material contained a large amount of acetaldehyde. We also found 1,4-dioxane and β-chloroethyl vinyl ether in the distillate, in confirmation of the work of Cretcher, Koch and Pittenger.[3] However, we were unable to obtain the "divinyl ether" whose boiling point they gave as 39°.

Since they made no further study of the properties of their "divinyl ether," b. p. 39°, we presume that they abandoned further study of the compound due to the small yield obtained. We were thus forced to the conclusion that if divinyl ether was a product of this reaction it must be contained in the fraction boiling between 20 and 30°.

The low-boiling distillate from five runs using a total of about 400 g. of the chloro ether was collected and amounted to 123.5 g. This material was treated successively with solutions of sodium bisulfite, dilute alkali, sodium carbonate and hydroxylamine hydrochloride, washed several times with water, and finally dried over calcium chloride. The aldehyde-free material from this treatment weighed 37.7 g. After two fractionations, the largest cut weighing 15.9 g. boiled at 27–29' (uncorr.). The method of purification was later improved as follows: the crude low-boiling distillate was shaken with a dilute solution of ammonia, allowed to stand in the ice box for several hours in contact with an excess of the dilute ammonia and finally washed several times with water. After it had been dried over calcium chloride and then sodium, it was distilled through a Clarke column; the fraction which boiled at 28.3 to 28.5' (corr.) at 768 mm. was pure divinyl ether. The corrected boiling point at 760 mm. was 28.3 ± 0.2' (obtained on another 250-g. sample).

Properties of Divinyl Ether.—Divinyl ether rapidly decolorized bromine in carbon tetrachloride; it was also readily oxidized by an aqueous solution of potassium permanganate. The absence of any acetylenic linkage was shown by a negative test with ammoniacal cuprous chloride. Concentrated sulfuric acid reacted violently with it to give a black tarry resin and some free aldehyde. Cold concentrated hydrochloric acid gave a yellow color with divinyl ether and the odor of acetaldehyde was apparent. Dilute hydrochloric acid hydrolyzed divinyl ether rapidly to acetaldehyde (confirmed by the *p*-nitrophenylhydrazone).

A solution of p-nitrophenylhydrazine in 50% acetic acid to which a few drops of

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[9] Pereira, Chem. *Abstracts*, 7, **3284** (1913).

dilute hydrochloric acid had been added reacted rapidly with divinyl ether and gave the p-nitrophenylhydrazone of acetaldehyde, m. p. 128.5–129°. A mixed melting point with some material prepared directly from acetaldehyde also melted at 128.5–129°.

In the absence of hydrochloric acid, divinyl ether did not react with *p*-nitrophenylhydrazine in 50% acetic acid after standing for thirty minutes at room temperature.

Divinyl ether gave an immediate precipitate of iodoform when the test was applied at 0°, using the procedure of Mulliken.[10]

Tollens' reagent showed no darkening with the ether within half an hour when the mixture was kept cold. Schiff's reagent, however, gradually developed a pink color, due presumably to the acetaldehyde which was liberated by hydrolysis in the presence of the free acid.

Pure divinyl ether boiled at 28.3° = 0.2" (760 mm.); mol. wt. calcd. for C_4H_6O, 70.05; found (Victor Meyer Method): 74.43, 71.15; d_{20}^{20} 0.774; d_4^{20} 0.773; n_D^{20} 1.3989; mol. refraction, calcd. for C_4H_6O (by Lorentz–Lorenz formula),'' 21.38; found, 21.93.

Analysis.—The carbon and hydrogen analyses were performed in a modification of Reid's apparatus (Fig. 2).[12] Owing to the explosive nature of certain mixtures of divinyl ether and air, the inner tube of the apparatus was a 1-mm. Pyrex capillary tube which was loosely plugged at intervals with glass wool. This capillary tube extended to within a half centimeter of the copper oxide. A metallic wool such as silver would have probably been more efficient to prevent "backfires" because of its greater conductivity of heat. A small bulb of about 0.5-cc. capacity was blown in the capillary just below the "sample tube." Before breaking the sample bulb the lower part of the apparatus was chilled with a freezing mixture.

Anal. Calcd. for C_4H_6O: C, 68.52; H, 8.64. Found: C, 67.78, 68.44; H, 8.61, 8.61.

Reduction of Divinyl Ether.—Half a gram of a platinum oxide catalyst[13] in 75 cc. of redistilled n-butyl alcohol was reduced in a Burgess–Parr reduction apparatus.[14] A sealed ampoule containing 12.52 g. of divinyl ether was then placed in the reductor bottle. After the preliminary evacuation of the bottle, the ampoule was broken and hydrogen admitted to the system. Reduction stopped when about half the theoretical amount of hydrogen had been absorbed. The bottle and its contents were cooled in a mixture of solid carbon dioxide and acetone and opened. One tenth of a gram of catalyst and 100 cc. more of n-butyl alcohol were added and the reduction continued. After twenty-four hours 0.3 g. more of the catalyst was added as before. Reduction proceeded rapidly until about the theoretical amount of hydrogen had been absorbed, when absorption abruptly stoppcd. However, since the total reduction required eighty-eight hours, presumably some hydrogen was lost through leakage.

The butyl alcohol solution was filtered and distilled through a Clarke column. The first fraction, which boiled between 30 and 70° (practically all between 30 and 40°), weighed 4.9 g. An odor of acetaldehyde was noticeable. By treatment of 0.11 g. of this fraction with *p*-nitrophenylhydrazine in dilute acetic acid, 0.029 g. of crude acetaldehyde p-nitrophenylhydrazone (m. p. 124–125°) was obtained. The fraction of b. p. 30–70°, therefore, contained about 6.4% of acetaldehyde. This fraction was then treated with dilute hydrochloric acid for half an hour, the acid neutralized with sodium

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[10] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1914, Vol. I, p. 166.

[11] Landolt-Bronstein, "Tabellen," Julius Springer, Berlin, 1912, p. 1039.

[12] Reid, THIS JOURNAL, 34, 1033 (1912).

[13] Adams and Shriner, *ibid.*, 45,2171 (1923).

[14] Manufactured by the Burgess-Parr Company, Moline, Ill.

hydroxide, the ether layer separated, dried first over anhydrous sodium carbonate then over sodium and distilled. All this liquid boiled between 34.6–35.2° at 767 mm. and the distillate weighed 2.02 g. The refractive index was found to be $n_D^{17\ 1}$ 1.3540.[15] The yield of pure ethyl ether was thus 15.2%. Considerable loss of the product occurred during the processes of purification.

Polymerization of Divinyl Ether.—A summary of the results obtained during attempts to polymerize divinyl ether is given in Table I. The general procedure was to add the benzoyl peroxide (recrystallized, m. p. 106–107°) to a cold dry bomb tube, then add the divinyl ether and seal. The tubes were then heated in a Freas electric oven for the period stated, cooled and opened. The polymer together with the unpolymerized divinyl ether was obtained on opening the tubes. The procedure used was that given by Hibbert in a recent patent.[5]

TABLE I

POLYMERIZATION OF DIVINYL ETHER

Run	Diviuyl ether, g.	Benzoyl peroxide, mg.	Temp., °C.	Time of heating, hours	NH_3	Product, g.	Yield of polymer., %
1	5	25	90–96	24	Trace	0.073	0.96
2	5	25	90–96	24	Trace		2
3	5	50[a]	95–100[b]	25	...	1.28	24.6
4	2.5	12.5	92–94	24	...	0.32	12.4
5	2.5	25[a]	92–94	24	...	0.19	6.4
6	2.5	12.5	91–93	24.5	...	0.199	7.5
7	2	12.5	91–93	24.5	Trace	0.012	0
8	2.5	12.5	91–93	24.5	...	0.527	20.6

[a] The ratio of benzoyl peroxide to divinyl ether was twice that given in the patent of Hibbert. [b] The oven overheated for a short time to about 130" at the beginning of this run.

Ethylene Oxide as a Product of the Reaction.—Ethylene oxide was presumed to be a product of the reaction because the low-boiling fraction (15–25°) of these runs was almost completely removed by treatment with ammonia. When efficient stirring of the potassium hydroxide was maintained, very little acetaldehyde was found. Distillation of the product under these conditions showed that 20% of the material came over below 27° during the first fractionation.

To confirm the presence of ethylene oxide the test given by Mulliken was applied in conjunction with several blanks.[16] In each test about 1.5 cc. of a saturated solution of magnesium chloride and 0.1–0.3 cc. of the material to be tested was placed in a tightly stoppered 7.6-cm. test-tube. These were kept at 0° for six hours and then allowed to stand at room temperature.

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[15] "International Critical Tables," McGraw-Hill Book Co., New York, 1930, Vol. VII, p. 36, gives $n_D^{17.1}$ 1.35424.

[16] Ref. 10, p. 160.

1.	Acetaldehyde	No precipitate after 60 hours
2.	Pure divinyl ether	No precipitate after 60 hours
3.	Fraction, b. p. 15–27°	Heavy precipitate after 24 hours
4.	Pure ethylene oxide	Heavy precipitate after 12–24 hours

Reaction between β,β'-**Diiododiethyl** Ether and Fused Potassium Hydroxide.—To 150 g. of potassium hydroxide in the reaction vessel was added 100 g. of β,β'-diiododiethyl ether[17] during the course of two hours and forty-five minutes. The autoclave was kept at 190–200°. The distillate amounted to 16.7 g. and contained considerable acetaldehyde. After the treatment with ammonia, 6.7 g. of material was left of which **3.3** g. boiled between 23 and 28° (practically all at 27–28" uncorr.). The yield of divinyl ether was thus 15%.

Ammonia as a Catalyst.—The run with the diiodo ether was repeated under practically the same conditions as before except that a slow stream of dry ammonia was ran through the system. A smaller amount (75 g.) of the ether was used. The yield of divinyl ether was 5.6 g. or 34%. The use of ammonia as a catalyst increased the yield slightly more than 120%.

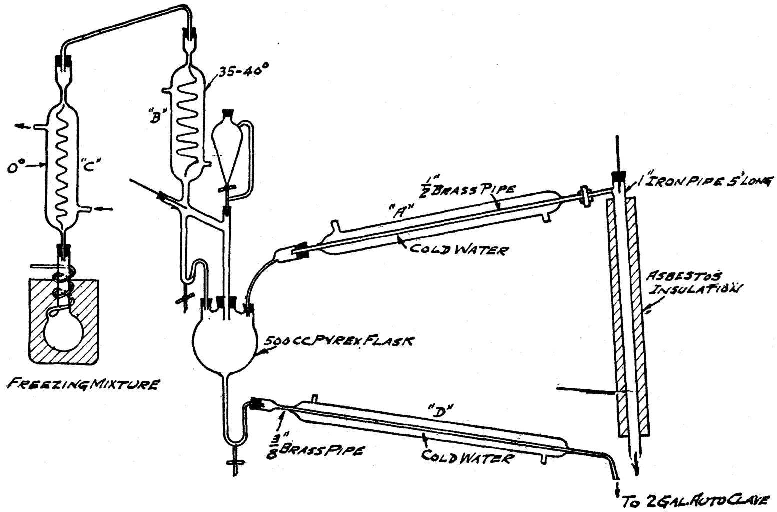

Fig. **1.**

Preparation **of** Divinyl Ether when the Molten **Alkali** was Stirred without the Use of Gaseous Ammonia.—The apparatus was set up as shown in Fig. 1. **A** charge of **7** kg. of technical lump potassium hydroxide was placed in the autoclave. *Efficient stirring of the molten alkali was found desirable.* For this reason the level of the fused alkali was well below the upper arm of the stirrer blades. If this point was disregarded, a crust of potassium chloride, etc., formed over the surface of the fused alkali. This resulted in reduced yields, production of large amounts of acetaldehyde and a very marked slowing down of the speed of reaction. When efficient stirring was maintained, practically no acetaldehyde was formed.

In the preliminary runs in which the original small scale apparatus was used without stirring, the amount of acetaldehyde formed was generally about twice the yield of divinyl ether. **A** run was made in the new apparatus with efficient stirring but without

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[17] Gibson and Johnson, *J. Chem. Soc.*, 2525 (1930).

the use of ammonia. From 923 g. of dichlorodiethyl ether was obtained 101.5 g. of distillate of which 5 g. was in an aqueous layer. Practically no aldehyde was present as was shown by tests with Tollens' and Schiff's reagents and with *p*-nitrophenylhydrazine. It may be noted here that whereas acetaldehyde formed the *p*-nitrophenylhydrazone with the hydrazine in dilute acetic acid solutions almost immediately, divinyl ether gave the hydrazone only very slowly after long standing.

Ethylene oxide was, however, a by-product of this run as shown by the previously described test.

From this reaction, 59.8 g. of material was obtained, b. p. 20–33°. This corresponds to a yield of 13.3% if this were all divinyl ether, Due to accidental loss of one of the fractions, the product was not purified by treatment with ammonia.

The reaction took place best when the temperature of the fused alkali was kept at about 200–240°; lower temperatures result in slowing up the reaction. The effect of temperatures above 250° was not determined in this apparatus.

Samples of the gas from this reaction were collected over water and then analyzed. The flow of gas varied from 400 to 500 cc. per minute and a total of four liters of gas was taken at intervals during the reaction. The analyses were made over water with a Hempel apparatus. The following results were obtained

Unsaturated	15.7%	(absorption in bromine water)
Oxygen	1.0%	(absorption in alkaline pyrogallol)
Hydrogen	78.5%	(combustion over copper oxide at 270°)
Residue	4.7%	
Total	99.9%	

The residual gas after the removal of the unsaturated gases, oxygen and hydrogen was analyzed for methane and ethane in a mercury-filled combustion pipet. Less than 0.5% of saturated hydrocarbons was found in the total sample. The 4.7% residue was thus principally nitrogen.

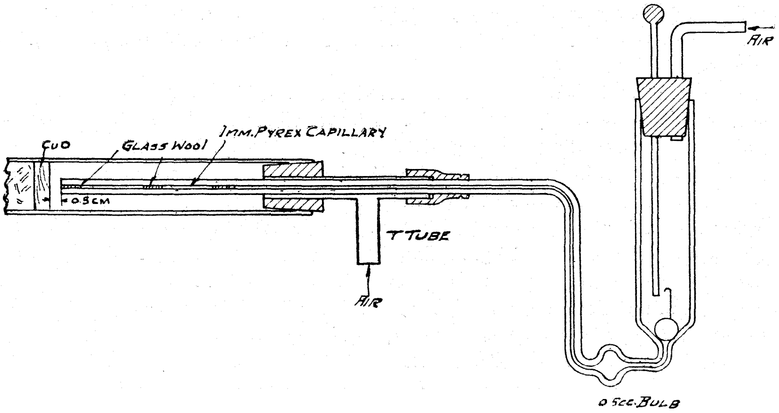

Fig. 2.

The unsaturated gas probably contained some divinyl ether since the condenser for the liquid products of the reaction was cooled only to about −15° during this run. A trace of acetylene in the gas was shown to be present by the small amount of red precipitate which was formed when the gas was passed through an ammoniacal solution of cuprous chloride.

Reaction in the Presence of Gaseous Ammonia.—When a slow stream of gaseous ammonia was passed through the system, the yield of divinyl ether was considerably increased. Using the new apparatus, the autoclave was first heated to about 230° and ammonia gas passed in through the gas inlet tube at about 1 to 3 bubbles per second. The addition of the β,β'-dichlorodiethyl ether was so regulated that condenser "B" did not become choked with the refluxing liquid. From time to time it was necessary to withdraw from the trap the excess of water, dioxane and β-chloroethyl vinyl ether which otherwise would have choked the condenser "B." The apparatus had a capacity of 1.5–2 kg. of the dichloro ether in eight hours. The capacity could have been increased by the employment of more efficient condensers. Condenser "B" in particular, being of spiral form, was rather readily choked with the refluxing liquid.

From 1850 g. of the dichloro ether in ten hours was obtained 272.8 g. of organic distillate. On fractionation, 192.5 g. of crude divinyl ether, b. p. 26.3–30° (uncorr.), was collected. The yield was thus 21%. From four runs using a total of 4750 g. of the chloro ether was obtained 478 g. of crude divinyl ether (b. p. 25–30°), or a yield of 20.3%. When the yield was corrected for losses due to a breakdown and for withdrawals of β-chloroethyl vinyl ether, the yield was about 25%.[18]

In comparing these results with the yield obtained without the use of ammonia (13.3%) it must be remembered that this yield was of relatively impure divinyl ether since it had not been purified by treatment with aqueous ammonia. In the runs using gaseous ammonia the purification consisted in washing the crude distillate several times with water, drying over calcium chloride and distilling through a Clarke column.

In order to remove all traces of ammonia, the fraction of b. p. 27–29" was washed once or twice with ice water (testing the wash water with methyl orange), dried over calcium chloride, then over sodium and redistilled.

Reaction between β,β'-Dihalogen Diethyl Ether and Sodamide.—The copper autoclave of the apparatus used in the preliminary runs was replaced by a 1-liter 3-necked distilling flask equipped with a mercury-sealed stirrer. In the flask were placed 300 cc. of dry xylene and 70 g. of very finely powdered sieved sodamide. The mixture was heated to the boiling point of the xylene and 100 g. of dichlorodiethyl ether run in during the course of four hours. Toward the end of the reaction, an additional 20 g. of fresh sodamide was added.

The product, collected in a receiver cooled with a solid carbon dioxide–acetone mixture, consisted mostly of liquid ammonia. About 1.5 g. of crude divinyl ether was obtained on fractionating this distillate; yield, 3%.

A run was made in which 50 g. of β,β'-diiododiethyl ether was used. The yield from this reaction was likewise very poor.

Action of Tertiary Amines on β,β'-Dihalogen Diethyl Ethers.—β,β'-Dichloro diethyl ether (5 g.) was refluxed with 15 g. of dimethylaniline for two hours. No reaction took place as was shown by the absence of any precipitate on the addition of dry ether.

The β,β'-diiododiethyl ether when refluxed for five minutes with dimethylaniline gave a voluminous precipitate. When recrystallized from alcohol it formed shimmering white leaflets of m. p. 220–230° (decomp.).

Anal. Calcd. for $C_{20}H_{30}I_2N_2O_2$: C, 41.28; H, 5.33; N, 4.93. Found: C, 41.47, 31.43; H, 5.53, 5.60; N, 5.12.

The material was thus the diiodide of bis-β,β'-phenyldimethylaminoethyl ether.

A mixture of 25 g. of the chloro ether and 100 g. of pure synthetic quinoline was gradually heated up to the boiling point and then refluxed for several hours. No trace

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[18] The best yield obtained, using a solid carbon dioxide–acetone mixture to cool the receiving flask, was 38%.

of divinyl ether was obtained. The reaction mixture solidified to a tarry mass when it was cooled.

Attempts to Dehydrate β,β'-Dihydroxydiethyl Ether.—Activated alumina was heated in the autoclave at 200° and β,β'-dihydroxydiethyl ether slowly added. No divinyl ether was obtained, the products being mainly aldehydes.

Phosphorus pentoxide reacted violently with the β,β'-dihydroxydiethyl ether and gave a tarry gum. The reaction was tried with xylene as a diluent but no divinyl ether was obtained.

Soda Lime and β,β'-Dichlorodiethyl Ether.—Several runs were made in an attempt to prepare divinyl ether by passing the vapor of the chloro ether over soda lime at 250–300°. Aldehydes were obtained but no divinyl ether.

We take pleasure in acknowledging the assistance of Doctor William Engels in the design of the apparatus for the preparation of divinyl ether, and of Mr. Douglass Hayman for the analysis of the diiodide of bis-β,β'-phenyldimethylaminoethyl ether.

Summary

1. Several methods for the preparation of divinyl ether have been studied, the most successful being the reaction of β,β'-dichlorodiethyl ether and caustic alkali in the presence of ammonia.

2. Divinyl ether has been prepared, analyzed and a number of its physical and chemical properties determined.

3. Pure divinyl ether was partially polymerized by the method described in a recent patent.[5] Traces of ammonia inhibited this polymerization.

4. Diethyl ether has been formed by the catalytic reduction of divinyl ether.

5. In addition to divinyl ether, the following substances were formed during the reaction between β,β'-dichloroethyl ether and caustic alkali: hydrogen, acetylene, ethylene oxide, β-chloroethyl vinyl ether, 1,4-dioxane and acetaldehyde.

RAHWAY, NEW JERSEY

[Contribution from the Chemistry Laboratory of the University of Michigan]

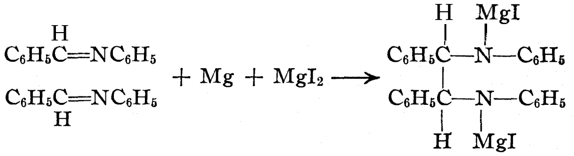
THE REDUCTION OF BENZALANILINE, BENZOPHENONE-ANIL AND BENZIL-ANIL BY THE SYSTEM MAGNESIUM + MAGNESIUM IODIDE

By W. E. Bachmann

Received April 9, 1931 Published July 8, 1931

The successful addition of the MgI group to the N=N group[1] as well as to the C=O group[2] encouraged the belief that the C=N group would take up MgI in a similar fashion. Experiment showed that benzalaniline, benzophenone-anil and benzil-anil react readily with a mixture of magnesium and magnesium iodide and in each case addition of MgI to the C=N group takes place.

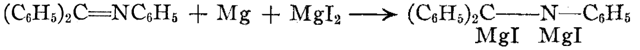
Benzalaniline is reduced by the binary system in the manner of benzaldehyde; unlike the reduction of the aldehyde, however, the reaction stops when the iodomagnesium derivative of dianilino-dibenzyl is formed.



$$\begin{matrix} C_6H_5\overset{H}{C}{=}NC_6H_5 \\ C_6H_5\underset{H}{C}{=}NC_6H_5 \end{matrix} + Mg + MgI_2 \longrightarrow \begin{matrix} C_6H_5\overset{H}{C}-\overset{MgI}{N}-C_6H_5 \\ | \\ C_6H_5\underset{H}{C}-\underset{MgI}{N}-C_6H_5 \end{matrix} \qquad (1)$$

Exactly one gram atom of metallic magnesium reacts for two gram molecules of benzalaniline. This addition of the MgI group is analogous to the addition of sodium to benzalaniline,[3] which results in the disodium derivative of dianilino-dibenzyl. Hydrolysis of the reduction product gives dianilino-dibenzyl.

Benzophenone-anil, unlike benzophenone[4] which gives a pinacol derivative, takes up two MgI groups and is reduced to the iodomagnesium derivative of N-benzohydryl-aniline.



$$(C_6H_5)_2C{=}NC_6H_5 + Mg + MgI_2 \longrightarrow (C_6H_5)_2\underset{MgI}{C}-\underset{MgI}{N}-C_6H_5 \qquad (2)$$

The amount of metallic magnesium that reacts corresponds exactly to that required by the equation. Hydrolysis of the reduction product gives N-benzohydryl-aniline. Fluorenone-anil is reduced by the binary system in the same manner. These reactions are similar to the action of sodium on benzophenone-anil[3] and on fluorenone-anil, in which cases the disodium derivatives are formed.

Benzil-anil reacts with the binary system in the manner of benzil.[5]

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[1] Bachmann, This Journal, 53, 1524 (1931).

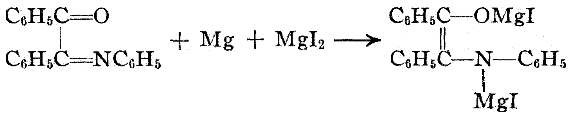
[2] See Gomberg and Bachmann, *ibid.*, 52, 4967 (1930), for principal references.

[3] Schlenk and Appenrodt, *Ber.*, 47, 473 (1914).

[4] Gomberg and Rachmann, This Journal, 49, 236 (1927).

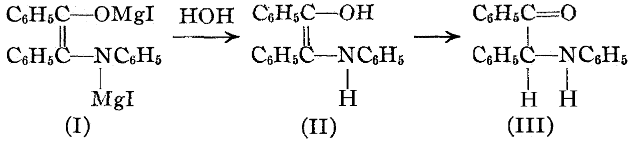
[5] Gomberg and Bachmann, *ibid.*, 49, 2584 (1927); Gomberg and Van Natta, *ibid.*, 51, 2238 (1929).

One gram atom of metallic magnesium reacts for each gram molecule of benzil-anil. It is considered that the following reaction most probably takes place



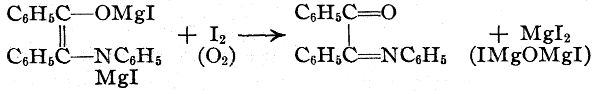
$$\begin{array}{l}C_6H_5C{=}O\\ \quad|\\ C_6H_5C{=}NC_6H_5\end{array} + Mg + MgI_2 \longrightarrow \begin{array}{l}C_6H_5C{-}OMgI\\ \quad\|\\ C_6H_5C{-}N{-}C_6H_5\\ \qquad\;\;|\\ \qquad\; MgI\end{array} \tag{3}$$

In the process of reduction the solution displays a series of intense colors which parallel those given by benzil on reduction. Hydrolysis of the reduction product (I) gives the unsaturated alcohol (II) which rapidly tautomerizes to the stable form, anilbenzoin (III).



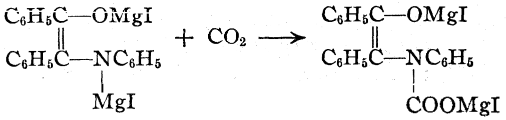
$$\underset{(I)}{\begin{array}{l}C_6H_5C{-}OMgI\\ \quad\|\\ C_6H_5C{-}NC_6H_5\\ \quad|\\ \quad MgI\end{array}} \xrightarrow{HOH} \underset{(II)}{\begin{array}{l}C_6H_5C{-}OH\\ \quad\|\\ C_6H_5C{-}NC_6H_5\\ \qquad\quad|\\ \qquad\quad H\end{array}} \longrightarrow \underset{(III)}{\begin{array}{l}C_6H_5C{=}O\\ \quad|\\ C_6H_5C{-}NC_6H_5\\ \quad|\quad\;|\\ \quad H\quad H\end{array}} \tag{4}$$

The reduction product (I) reacts rapidly with iodine and with oxygen and is converted by them to benzil-anil.



$$\begin{array}{l}C_6H_5C{-}OMgI\\ \quad\|\\ C_6H_5C{-}NC_6H_5\\ \quad\; MgI\end{array} \begin{array}{c}+ I_2\\ (O_2)\end{array} \longrightarrow \begin{array}{l}C_6H_5C{=}O\\ \quad|\\ C_6H_5C{=}NC_6H_5\end{array} \begin{array}{c}+ MgI_2\\ (IMgOMgI)\end{array} \tag{5}$$

Carbon dioxide is absorbed by the reaction mixture with the formation of the salt of an N-carboxylic acid.



$$\begin{array}{l}C_6H_5C{-}OMgI\\ \quad\|\\ C_6H_5C{-}NC_6H_5\\ \quad|\\ \quad MgI\end{array} + CO_2 \longrightarrow \begin{array}{l}C_6H_5C{-}OMgI\\ \quad\|\\ C_6H_5C{-}NC_6H_5\\ \qquad\quad|\\ \qquad\quad COOMgI\end{array} \tag{6}$$

Experimental

Reduction of **Benzalaniline.**—To a filtered solution of magnesium iodide, prepared from 8 g. of iodine in 30 cc. of anhydrous ether and 60 cc of dry benzene, were added 9.05 g. of benzalaniline and a weighed rod of magnesium. The flask was stoppered and shaken mechanically at room temperature for two days. After one day the solution contained a large amount of a light yellow solid. The rod was withdrawn from the mixture, washed with alcohol, dried and weighed: loss in weight, 0.608 g.; calcd., 0.608 g

The mixture was hydrolyzed by means of ice; dilute acetic acid was added in order to dissolve the magnesium hydroxide which was formed. The ether–benzene solution was separated and the solvents were allowed to evaporate. The residual oil crystallized completely when it was stirred with methyl alcohol. The crude product (9 g.) melted at 137–139° and was found to be identical with the dianilinodibenzyl obtained by reduction of benzalaniline by aluminum amalgam[6] as well as with the product resulting from the hydrolysis of the disodium compound prepared from benzalaniline and metallic sodium according to the directions of Schlenk and Appenrodt. Anselmino considers the product to be a mixture of stereoisomeric dianilino-dibenzyls of m. p. 139 and 164°.

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[6] Anselmino, *Ber.*, 41, **623** (1908).

By repeated recrystallizations colorless needles of m. p. 165–166° were obtained which were identical with those isolated from the amalgam reduction product.

Reduction of **Benzophenone-anil.**—Benzophenone-anil was prepared according to the directions of Reddelien[7] from benzophenone and aniline with aniline hydrochloride as a catalyst. In agreement with Reddelien we obtained 80% yields of benzophenone-anil although Gilman and Dickey[8] reported recently that they obtained yields of only 20% by this method.

A mixture of 12.85 g. of benzophenone-anil, 15 g. of magnesium iodide and a rod of magnesium in 105 cc. of ether–benzene (1:2) was shaken for several days. The reaction began immediately as was evidenced by the violet-colored streamers which came off from the surface of the rod. The solution became opaque red and finally dark reddish-brown in color: loss in magnesium, 1.21 g.; calcd., 1.21 g. The same loss of magnesium occurred when only one-quarter of the above amount of magnesium iodide was employed, indicating that the iodomagnesium derivative is able to split off magnesium iodide and thus make the latter available for further reaction as in other similar reductions.[9]

Hydrolysis of the reduction product gave a solid melting at 54–58'. When this solid was recrystallized from alcohol, a small amount of the addition complex[10] composed of a molecule each of benzophenone-anil and of benzohydryl-aniline crystallized out; from the filtrate there was obtained pure benzohydryl-aniline. Repeated crystallizations raised the melting point of the complex to 84"; the compound so obtained was found to be identical with the complex obtained by recrystallizing a mixture of equal parts of benzophenone-anil and benzohydryl-aniline from alcohol. The crude reduction product as obtained by hydrolysis was shown in the following manner to contain 90% of benzohydryl-aniline. The product was heated with concentrated hydrochloric acid until the mixture became colorless; this treatment hydrolyzed the benzophenone-anil to benzophenone and aniline and at the same time formed the hydrochloride of benzohydryl-aniline. This hydrochloride was filtered off, dried and extracted with warm petroleum ether in order to remove the benzophenone. The hydrochloride was converted to the free base by treatment with ammonium hydroxide and extracting with ether in a separatory funnel. After recrystallization from alcohol the benzohydryl-aniline melted at 57–58'; its identity was established by comparison with authentic benzohydryl-aniline.

It was found that benzohydryl-aniline can be prepared in practically quantitative yields by reduction of benzophenone-anil by means of magnesium and methyl alcohol, a method employed successfully by Zechmeister and Rom[11] for reducing nitro compounds. A mixture of 5 g. of benzophenone-anil and 1.8 g. of magnesium ribbon in 80 cc. of methyl alcohol was warmed until all of the metal had dissolved and the solution was colorless. Addition of dilute acetic acid caused precipitation of the benzohydryl-aniline.

The benzohydryl-aniline was further identified by rearranging it to *p*-aminotriphenylmethane.[12] We found that a few minutes of heating with aniline hydrochloride sufficed for complete rearrangement. One gram of benzohydryl-aniline was heated with a gram of aniline hydrochloride in 2 cc. of aniline at 180° for five minutes. The cooled mixture was shaken with 30% acetic acid in order to remove aniline and its salt, and the *p*-aminotriphenylmethane was filtered off; yield 72%, m. p. 84°. The product was

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[7] Reddelien, Ber., 46, 2720 (1913); 48, 1462 (1915).

[8] Gilman and Dickey, THIS JOURNAL, 52, 4573 (1930).

[9] Gomberg and Bachmann, *ibid.*, 49, 247, 2588 (1927).

[10] Alessandri, *Gazz. chim. ital.*, 51, 75 (1921).

[11] Zechmeister and Rom, *Ann.*, 468, 1117 (1928).

[12] Baeyer and Villiger, Ber., 37, 599 (1904).

identical with *p*-aminotriphenylmethane prepared by reduction of *p*-nitrotriphenylmethane.[12]

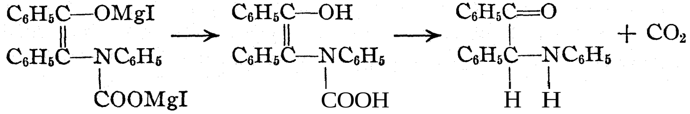
Reduction of Fluorenone-anit.—A mixture of 5.10 g. of fluorenone-anil, 6.6 g. of magnesium iodide and a magnesium rod in GO cc. of ether–benzene (1:2) was shaken for several days. As the reaction proceeded, the orange-red solution became dark green in color and a precipitate appeared. This green product is probably a complex formed from unchanged fluorenone-anil and the fully reduced product. Further shaking changed the mixture color to a bright scarlet; loss in magnesium, 0.485 g., or 100% of the theoretical value. Hydrolysis gave 9-fluorenyl-aniline. By recrystallization from a mixture of acetone and methyl alcohol, it was obtained in the form of needle-like prisms melting at 121–123°; yield, 83%. Staudinger and Gaule[13] report the value 121° and Schlenk[14] gives 124° for the melting point of 9-fluorenyl-aniline.

Reduction of Benzil-anil.—Addition of 10 g. of benzil-anil to a solution of magnesium iodide gave a dark red solution which quickly deposited a large amount of a complex in the form of orange-red crystals. After one and one-half hours of shaking with a rod of magnesium, the crystalline complex had completely disappeared and the solution was opaque reddish-brown in color. After six hours of shaking the solution was transparent yellow in color: loss in magnesium, 0.86 g.; calcd., 0.85 g. Hydrolysis was carried out in an atmosphere of carbon dioxide in order to avoid oxidation of the reduction product, and there was obtained 8.0 g. (80% yield) of anilbenzoin[15] (desylaniline), $C_6H_5CH(NHC_6H_5)CO(C_6H_5)$; after recrystallization from alcohol, the anilbenzoin melted at 97–98" and was identical with the product prepared from benzoin and aniline. Prior to hydrolysis, the reduction product did not react with phenylmagnesium bromide, indicating the absence of a free C=O group (see I, equation 4); after hydrolysis the anilbenzoin reacted readily with the Grignard reagent.

Reaction of the Reduction Product with Iodine and with Oxygen (Equation 5).—The calculated amount of iodine (2.54 g.) was added to the reduction mixture which had been prepared from 2 85 g. of benzil-anil. A considerable amount of heat was developed in the reaction that took place, and the solution became opaque reddish-brown in color. A large amount of the complex of benzil-anil and magnesium iodide precipitated. Hydrolysis gave 2.50 g. (88%) of benzil-anil.

In another experiment, dry air was passed into the transparent yellow reduction mixture obtained from 2.85 g. of benzil-anil. The solution became opaque reddish-brown and finally transparent red in color. Hydrolysis, after passing in air for four hours, gave 2.45 g. (86%) of benzil-anil.

Reaction with Carbon Dioxide.—Carbon dioxide was passed into the reduction mixture which had been prepared from 5.0 g. of benzil-anil. Within ten minutes glistening, granular crystals of the salt of the N-carboxylic acid (equation 6) appeared. After three hours the crystals were filtered off, washed with ether and dried. When this salt was treated with dilute acetic acid, carbon dioxide was evolved (collected in barium hydroxide solution) and the solid that remained was found to be pure anilbenzoin; weight, 3.6 g. (71%). The reactions that take place are undoubtedly the following



$$\begin{array}{l} C_6H_5C{-}OMgI \\ \quad\| \\ C_6H_5C{-}NC_6H_5 \\ \quad | \\ \quad COOMgI \end{array} \longrightarrow \begin{array}{l} C_6H_5C{-}OH \\ \quad\| \\ C_6H_5C{-}NC_6H_5 \\ \quad | \\ \quad COOH \end{array} \longrightarrow \begin{array}{l} C_6H_5C{=}O \\ \quad | \\ C_6H_5C{-}NC_6H_5 \\ \quad |\quad | \\ \quad H\quad H \end{array} + CO_2 \qquad (7)$$

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[13] Staudinger and Gaule, *Ber.*, 49, 1956 (1906).

[14] Schlenk, *Ann.*, 463, 318 (1928).

[15] See Cameron, *Trans.* Roy. *Soc. Can.*, *[3]* 23, Sect. 3, 53 (1929), *Chem. Abstracts*, 24, 610 (1930), for the structure of anilbenzoin.

Summary

Benzalaniline is reduced by a mixture of magnesium and magnesium iodide to the iodomagnesium derivative of dianilino-dibenzyl.

Benzophenone-anil is reduced by the binary system to the iodomagnesium derivative of N-benzohydrylaniline.

Benzil-anil takes up two MgI groups to give a stilbene derivative which is very reactive to iodine, oxygen and carbon dioxide. Hydrolysis of the reduction product yields anilbenzoin.

The results of this investigation substantiate the hypothesis that the active reducing agent is MgI.[16]

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY AND THE ELI LILLY LABORATORIES]

THE ACTIVATION OF ERGOSTEROL WITH RADIUM EMANATION

BY RICHARD B. MOORE[1] AND THOS. DEVRIES

RECEIVED APRIL 13, 1931 PUBLISHED JULY 8, 1931

Introduction

The existence of an antirachitic vitamin (D) has been recognized for some time. Recently, however, it has become possible to prepare an antirachitic substance by "irradiative" or "activating" ergosterol with ultraviolet radiation. Such a product is called viosterol and is considered by some to be vitamin D.

To Huldschinsky[2] perhaps should go the credit for first using ultraviolet light on children afflicted with rickets. Two years later in 1924, Steenbock reported on his work[3] with rats cured by the use of activated cholesterol. He took out patents that same year. The high-speed electrons from a Coolidge tube have been used by Knudsen.[4] He and C. N. Moore activated cholesterol in a few minutes with 200,000 volt electrons, such that 0.0050 g. per day was the minimum dosage required to cure rachitic rats, whereas 0.00002 was the minimum dosage using ultraviolet activated cholesterol.

The activation of cholesterol or ergosterol with radium has not been

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[16] In a recent article [*Z. physik. Chem.*, *153*, 83 (1931)], Sven Bodforss reports results obtained from a study of magnesium potentials in aqueous salt solutions, which are best explained by considering that magnesium metal can send into solution univalent ions, Mg^+.

[1] Deceased Jan. 20, 1931.

[2] Hess, "Rickets, Osteomalacia and Tetany," p. 107.

[3] Steenbock, *J. Biol. Chem.*, 61, 405 (1924); 64, 263 (1925).

[4] Knudsen, *Proc. Soc. Exptl. Biol. Med.*, 24, 366 (1927); *J. Biol. Chem.*, *81*, 49 (1929).

reported. Chick and Tazellar[5] used radium emanation in a study of vitamin A deficiency in rats. Their results were negative. Kofman and Chizet[6] demonstrated that radium emanation through x-rays made sterols photoactive even as ultraviolet had done.

In this investigation ergosterol was activated with radium emanation and the results as given below show that a reasonably active viosterol can so be produced.

Experimental Methods and Results

Reasonably pure ergosterol was activated with radium emanation on four different occasions under different experimental conditions and with two varieties of ergosterol. The one sample, prepared at the Eli Lilly Laboratories, had *a* melting point of 148°, and a specific rotation of −100° in chloroform solution. The other sample, sent from Germany by C. H. Boehringer Sohn, had a more crystalline appearance, a melting point of 157" and a specific rotation of −121° in chloroform.

The activated samples were tested on white rachitic rats by C. R. Eckler of the Eli Lilly Laboratories under the direction of Mr. H. W. Rhodehamel. A modification of the line test[7] was employed for the determination of the antirachitic potency. The extent of healing is designated in the tables by the following notation:

– – – – no healing
+ – – – very slight healing
+ – – slight healing
+ – healing (calcification line not continuous)
\+ healing (calcification line continuous)
++ moderate healing
+++ marked healing
++++ complete healing

There is also included in the tabulation of results a quantity called "millicurie hours per cubic centimeter" (mch/V) which is a measure of the concentration of radium emanation multiplied by the time of its action on the ergosterol and is therefore a measure of the amount of radiation to which different samples were exposed and so can be used in the comparison of samples. The quantity millicurie hours is given by the definite integral

$$mch = \int_{t_1}^{t_2} Q\,dt \qquad (1)$$

where

$$Q = Q_0 e^{-kt} \qquad (2)$$

which is the radioactivity decay formula. If the units of time are in hours or days, the relations become

$$\log Q = \log Q_0 - 0.00326\, t \text{ (hours)} \qquad (3)$$

$$\log Q = \log Q_0 - 0.0782\, t \text{ (days)} \qquad (4)$$

$$mch = 133.2\,(Q - Q_0) \qquad (5)$$

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[5] Chick and Tazellar, *Biochem.* J., 18, 1346 (1924).

[6] Kofman and Chizet, Compt. *rend.*, **189,** 45 (1929).

[7] Bills, J. *Biol. Chem.*, **51,** 41 (1922).

In each of the four series, the radium emanation was mixed with air in a Ramsay style gas buret over mercury and admitted to the evacuated tube containing a known amount of ergosterol. In Series I, approximately one gram of the Eli Lilly sample was placed in each of three tubes, with stopcocks attached. Each tube had a volume of about 15 cc. About 0.2, 0.3 and 0.5 of 60 millicuries of radium emanation was admitted to each tube, and left in contact for three and one-half, eighteen and seventy-two hours and labeled as R-1, R-2 and R-3, respectively. At the end of seventy-two hours there was no visible sign of decomposition except a pale yellow color. The results given in Table I show that for a 0.0001 g. dosage, 20 millicurie hours per cc. is sufficient to activate ergosterol. For a 0.00001 g. dosage it is necessary to submit it to about 100 mch per cc.

Sample R-3 was retested after three months and also after five months, at which time the results were practically identical. This would indicate that the activated samples were permanent.

TABLE I

AMOUNT OF IRRADIATION AND EXTENT OF HEALING FOR SAMPLES OF SERIES I

$Q_0 = 12$, 18 or 30 millicuries, respectively. Vol. of containers, 15 cc.

Sample no.	Withdrawn after	*mch/V*	*Dosage* in grams *per* day				
			0.0002	0 0001	0.00001	0.000001	0.0000001
R-1	3.5 hours	2.7	(2) ++ (3) +− (1) −	lost weight	died	−	
R-2	18 hours	20.2	(6) ++	++	−	−	
R-3	72 hours	110.1	(8) +++ (2) ++	++	++	+−−	
Ultraviolet treated					(6) +++	(2) +++ (1) ++	+−−

The numbers in parentheses indicate number of rats giving the indicated results. No figure means only one rat used.

Series 11.—The second set of samples was prepared with the purpose of determining whether prolonged radiation would modify the antirachitic properties of the ergosterol. For this experiment, 114 millicuries of emanation was available and after mixing with air in the usual way, it was placed with 7 g. of ergosterol in a 30-cc. tube, fitted at one end with a rubber tube (one end closed) and a pinch clamp, so that samples could be withdrawn without loss of emanation or admitting any undue amount of air. Five samples were withdrawn, the first after seventeen hours, the last after having been in contact with the emanation for two hundred eleven hours. The results (see Table II) substantiated those of the first series. The lowest radiation this time was 50 mch per cc., and was more than sufficient to activate lor dosages of 0.0001 g. For dosages of 0.00001 g. per day, more than 100 units of radiation were required. The results also indicated that there was no noticeable deleterious effect due to the prolonged irradiation; in fact, such samples were more efficient, as shown by the results when dosages of 0.000001 g. were used.

The result for X-5 with the 0.000001 g. dose was perhaps not as conclusive as might be desired. The rat which gave this negative result seemed to be a poorer specimen than usual.

TABLE II

AMOUNT OF IRRADIATION AND EXTENT OF HEALING FOR SAMPLES OF SERIES II

Q_0 = 114 millicuries. Vol. of container, 30 cc.

Sample no.	Withdrawn after	mch/V	Dosage in grams per day 0.0001	 0.00001	 0.000001	 0.0000001
X-1	17 hours	47	(2) +++	(2) –	(2) –	–
X-2	41 hours	134	(2) +++	(2) + – – –	(2) –	–
X-3	**93** hours	254	(2) ++++	(2) + –	(2) –	–
					–	
X-4	162 hours	356	(2) ++++	(2) ++	+ – – –	–
X-5	211 hours	400	(2) ++++	+ – – –	–	–
				+		–

Series III.—The third series of samples was prepared using the ergosterol prepared by Boehringer Sohn in Germany. It was also our belief that the active rays from the emanation did not penetrate very deeply into the ergosterol, so that by crushing the material, fresh surfaces would be exposed to the rays and so increase the potency of the product. For the latter a specially designed Pyrex tube, filled half full with glass rods, was constantly rotated at the rate of twelve revolutions per minute. The effective volume of this apparatus was 56 cc. About 4 g. of ergosterol was put in with 31 millicuries of emanation. As a comparison experiment with Series I and II, about 2 g. of the German ergosterol was placed in the 30-cc. tube used for Series II with 16 millicuries of emanation. (The emanation was first mixed with air and this mixture subdivided itself between the two containers in the ratio of their volumes.)

It should be mentioned that Sample R-19 was the ergosterol which had caked on the inside of the rod mill and was dissolved out with alcohol. Upon evaporation of the solvent, there was evidence that organic decomposition products were present. There was only a small amount of yellow product at the crystallizing edge, however.

In Table **3A** are listed the results for the control samples and in 3B the results for the stirred samples.

Series IV.—The fourth series of samples was prepared to obtain a check on the previous results and to compare the efficiency of stirring with Eli Lilly product in place of the German material.

The samples were activated in substantially the same way as in Series III. A smaller rod mill was made, with 23-cc. capacity. The A-1 to A-7 samples were prepared in it. The B-1 to B-7 samples were activated in the 30-cc. tube used previously. At the start 120 millicuries of emanation

TABLE III

AMOUNT OF IRRADIATION AND EXTENT OF HEALING FOR SAMPLES OF SERIES III

A—German ergosterol, not stirred

Q_0 = 16 millicuries. Vol. of container, 30 cc.

Sample no.	Withdrawn after	mch/V	Dosage in grams per day 0.0001	 0.00001	 0.000001
S-1	2 hours	1.0	(4) −	(2) −	(2) −
S-2	3 hours	1.6	(2) −		
S-3	7 hours	3.6	(2) −		
S-4	17 hours	8.1	(2) −	(2) −	
S-5	41 hours	18.8	(2) −	(2) −	
S-6	93 hours	35.7	(2) −	(2) −	
S-7	165 hours	50.3	(4) − (2) +−	(2) −	(2) −
S-8	310 hours	64.0	Broken in mail		

B—German ergosterol, stirred

Q_0 = 31 millicuries. Vol. of container, 56 cc.

Sample no.	Withdrawn after	mch/V	Dosage in grams per day 0.0001	 0.00001	 0.000001
R-11	1 hour	0.5	(4) −	(2) −	
R-12	3 hours	1.6	(2) −		
R-13	7 hours	3.7	(2) +		
R-14	17 hours	8.7	(2) ++	(3) −	
R-15	41 hours	19.5	(2) ++	(2) +− (1) −	
R-16	93 hours	37.0	(2) +++	(1) + (4) +−−	
R-17	165 hours	52.3	(2) +++	(4) +−−− (3) −	(2) −
R-18	310 hours	66.8	(2) ++	(4) +− (4) −	(2) −
R-19	310 hours	66.8	(2) +++	(4) +− (4) −	(2) −

was available, and admitted into the evacuated apparatuses connected in series. The concentration of emanation was therefore 2.8 m.c. per cc., since the ergosterol occupied about 10 cc. of the total volume.

TABLE IV

AMOUNT OF IRRADIATION AND EXTENT OF HEALING FOR SAMPLES OF SERIES IV

A—German ergosterol, not stirred

Q_0 = 70 millicuries. Vol. of container, 30 cc.

Sample no.	Withdrawn after	mch/V	Dosage in grams per day 0.0001	 0.00001
B-1	20 minutes	1.0	(2) −	
B-2	65 minutes	3.0	(1) −	
B-3	160 minutes	7.5	(2) −	
B-4	330 minutes	15	(2) +−	(2) +−−−
B-5				
B-6	39.6 hours	96	(2) ++ to +++	(2) + to ++

TABLE IV (Concluded)

B—Lilly ergosterol, stirred

Q_0 = 50 millicuries. Vol. of apparatus, 23 cc.

Sample no.	Withdrawn after	mch/V	Dosage in grams per day 0 0001	0 00001	0 000001	0 0000001
A-1	23 minutes	1.0	(2) –			
A-2	65 minutes	3 0	(2) –			
A-3	160 minutes	7 5	(1) –			
A-4	330 minutes	15	(2) +–		(1) –	
A-5	15.7 hours	42	(2) ++		(2) –	
A-6	39.5 hours	96		(2) ++	(2) –	
A-7	184.0 hours	280		(2) ++	(2) +–––	(2) –

The results of previous series were well confirmed (see Tables IVA and IVB) although the results with 0.0001 g. doses seem to indicate that the German product activates slightly faster, being capable of producing moderate healing after 10 mch per cc. of radiation, while the Eli Lilly ergosterol required 40 units of radiation. At TO, both gave results of "marked healing." The 0.00001 dosage also indicated that the German product had only a slightly higher degree of potency.

Acknowledgment.—The authors wish to express their gratitude to Dr. S. C. Lind and to Dr. C. F. Burnam who were so generous in donating the radium emanation, and to Mr. H. W. Rhodehamel of the Eli Lilly Laboratories for his generous advice, cooperation and experimental aid with the rat-feeding experiments.

Summary

1. Ergosterol can be activated with radium emanation to a degree of potency perhaps 0.01 of that of a good grade of ultraviolet irradiated ergosterol.

2. Stirring the sample while under the influence of the emanation increases the speed of activation but does not increase the potency appreciably.

3. There is no appreciable loss in potency if the activation is carried on to even as much as a twenty-fold excess. There are some decomposition products formed in all cases.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE SULFUR DERIVATIVES OF THE SIMPLE AMINES. I. AMINE HYDROSULFIDES[1]

BY MARVIN ACHTERHOF,[2] ROLLIN F. CONAWAY[2] AND CECIL E. BOORD

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During the preparation of the polysulfides of certain organic bases it was noted that a white crystalline deposit was formed in the upper part of the reaction chamber and in the inner tube of the condenser. Since, under the conditions of the experiment, the principal constituents of the vapor phase were free amine and hydrogen sulfide, it seemed probable this deposit was the amine hydrosulfide. An examination of the literature revealed the fact that the hydrosulfides of the simple amines have not been definitely described.

As some of our more prominent theories on the mechanism of the activation of sulfur[3] assume the formation of amine hydrosulfides and polysulfides, it has seemed altogether worth while to examine more carefully into the nature of these products.

Very early in the history of amines Wurtz[4] observed a reaction between ethylamine and hydrogen sulfide when the two gases were brought together in a reaction chamber immersed in an ice-bath. The product was a white crystalline compound which soon turned yellow but no analysis or other descriptive details were given. Isambert[5] in his vapor pressure studies measured the vapor pressure of ethylamine and diethylamine sulfhydrates but did not separate the free compounds. Kindler[6] has assumed the formation of dimethylamine hydrosulfide and attributed to it the function of a catalyst in the addition of hydrogen sulfide to benzonitrile. Peters,[7] on the other hand, has studied the action of hydrogen sulfide upon several simple amines at the temperature of the carbon dioxide-ether bath. He concluded that under these conditions the normal sulfides were formed. The products were obtained as white crystalline powders all decomposing below 0°.

Bineau[8] more than ninety years ago studied the interaction of ammonia and hydrogen sulfide by volume. He came to the conclusion that the

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[1] Presented, in part, before the Division of Organic Chemistry of the American Chemical Society, at the meeting in Detroit, September 8, 1927.

[2] This paper is abstracted from a part of the dissertation of Marvin Achterhof 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, August, 1926 and from the Master's Thesis of Rollin F. Conaway at the same institution, in June, 1927.

[3] Scott and Bedford, *J. Ind. Eng. Chem.*, 13, 126 (1921).

[4] Wurtz, *Ann.*, 76, 331 (1850).

[5] Isambert, *Jahresb.*, 81 (1883).

[6] Kindler, *Ann.*, 431, 201 (1923).

[7] Peters, *Ber.*, 40, 1479, 1481 (1907).

[8] Bineau, *Ann. chim. phys.*, 67, 230 (1838); 68, 435 (1838); 70, 261 (1839).

normal sulfide is stable only at very low temperatures, the usual form of the salt being the hydrosulfide. The work of Bloxam[9] on ammonium hydrosulfides, sulfides and polysulfides is almost the only detailed study in the field. Although Bloxam obtained many of the sulfides of ammonium in the solid state, his reactions and analyses were almost wholly made on aqueous solutions. Ammonium hydrosulfide was obtained in colorless needles and scales but chiefly as a porcelain-like deposit by leading ammonia and hydrogen sulfide simultaneously into a bottle cooled with ice. The preparation of the pure hydrosulfide was found to depend upon having the hydrogen sulfide always in excess.

Using a procedure somewhat analogous to that of Wurtz, Peters and Bloxam, the hydrosulfides of twelve of the simple amines have been prepared. The successful preparation of these products may be accomplished by bringing together the dry, free amine and an excess of dry hydrogen sulfide at a temperature below 0°, and in the complete absence of air. The formation, filtering, washing and drying must be done in an atmosphere of hydrogen sulfide.

The solid amine hydrosulfides are rapidly decomposed on exposure to air. Those of low molecular weight show an appreciable vapor pressure of free amine and hydrogen sulfide, but the chief cause of their instability arises from a rapid decomposition by oxidation. The hydrosulfides of the more volatile amines are spontaneously oxidized with an almost quantitative deposition of free sulfur. Those of the less volatile amines are oxidized under the same conditions to give large yields of the corresponding thiosulfate. All of these changes occur without the product taking on a color deeper than the tinge of yellow characteristic of free sulfur.

In the light of the above facts it would seem necessary to adopt a mechanism for the oxidation of these solid hydrosulfides different from that used by Bloxam in explaining the transformations characteristic of ammonium hydrosulfide in aqueous solution. He says: "These changes may be explained as follows. In the first stage, polysulfide alone is formed. . . . At the surface of the liquid some of the aqueous solution of ammonium hydrosulfide is resolved into ammonia, water and hydrogen sulfide, the latter undergoing oxidation and yielding water and sulfur. This sulfur then acts on ammonium hydrosulfide forming polysulfide. . . . There is not the slightest ground for supposing ammonium disulfide to be formed.

"In the second stage, the polysulfides are acted on by oxygen, sulfur being liberated.

$$(NH_4)SS_x + O = 2NH_3 + H_2O + S,S_x$$

"In the third stage, the sulfur acts upon ammonia as follows

$$4NH_3 + 4H_2O + S_3 = (NH_4)_2SO_3 + 2NH_4SH + H_2O$$

resulting in the production of ammonium sulfite and hydrosulfide.

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[9] Bloxam, *J. Chem. Soc.*, 67, 277 (1895); 77, 753 (1900).

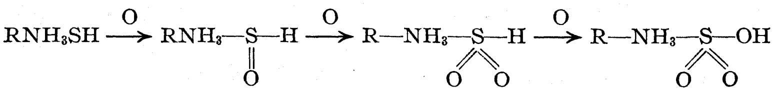
"In the fourth stage it will be observed that there are now two modes in which sulfur may combine, namely, by union with ammonium sulfite, thereby transforming it into thiosulfate or by acting on ammonium hydrosulfide whereby more polysulfide is formed."

It is true that stages (I) and (II) would account for the quantitative deposition of sulfur by the oxidation of the lower amine hydrosulfides except for the fact that the mechanism requires the intermediate formation of the polysulfide. This seems a doubtful explanation in view of the fact that the product during these changes never takes on a color deeper than a faint yellow.

The mechanism indicated is objectional also from another point of view. Bloxam assumes a dissociation of the hydrosulfide previous to any oxidation. In solution this assumption offers no difficulty. But for the solid hydrosulfide such an assumption would mean a dissociation into gaseous amine and hydrogen sulfide. It seems scarcely logical to believe gaseous hydrogen sulfide will oxidize leaving approximately a quantitative deposition of sulfur at the point of generation. Experiment has shown that dimethylamine hydrosulfide is spontaneously oxidized in air with a deposition of more than 97% of its total sulfur.

By the same reasoning the mechanism as given seems inadequate to explain the formation of thiosulfates. It is true the amine hydrosulfides when confined in a closed space, as in the bottom of a test-tube or in a loosely stoppered bottle, decompose slowly with partial liquefaction of the product. Under these conditions the mass takes on the blood-red color indicative of polysulfide formation. But if the solid hydrosulfide is exposed as a mass of loose crystals or spread out in a thin layer, thus insuring a free circulation of air, the oxidation proceeds to the formation of thiosulfate with no evidence of polysulfide formation.

Since the amine hydrosulfides pass through the initial stage of the oxidation previous to dissociation, and since the oxidation can continue to the formation of thiosulfate without the polysulfide stage as an essential step in the process, a mechanism quite analogous to that commonly used to explain the oxidation of mercaptans to sulfonic acids or of thio ethers to sulfones would seem to be applicable to the present case.



$$RNH_3SH \xrightarrow{O} RNH_3{-}\underset{\overset{\|}{O}}{S}{-}H \xrightarrow{O} R{-}NH_3{-}\underset{O\;\;O}{S}{-}H \xrightarrow{O} R{-}NH_3{-}\underset{O\;\;O}{S}{-}OH$$

I II III

T. M. Lowry[10] has shown that the oxygen acids of sulfur corresponding to I and II must be expected to show marked instability when considered from the standpoint of their electronic structure.

The quantitative deposition of sulfur by the spontaneous oxidation of

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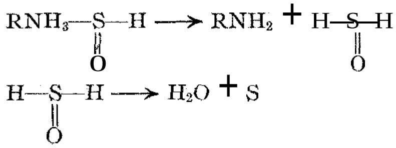
[10] Lowry, *Trans. Faraday Soc.*, 18,289 (1923).

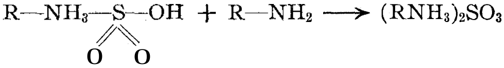
the lower amine hydrosulfides will be sufficiently accounted for by the dissociation of I according to the scheme



$$\text{(a)}\quad RNH_3\text{—}\underset{\underset{O}{\|}}{S}\text{—}H \longrightarrow RNH_2 + H\text{—}\underset{\underset{O}{\|}}{S}\text{—}H$$

$$\text{(b)}\quad H\text{—}\underset{\underset{O}{\|}}{S}\text{—}H \longrightarrow H_2O + S$$

In the case of the hydrosulfides of the less volatile amines the dissociation of I will not be so rapid or if dissociation does take place the dissociation products may remain in juxtaposition for a sufficient length of time for the oxidation to proceed through stage II to III. The bisulfite, III, being more acid in character than I or II, will take up an additional molecule of amine to form the normal sulfite.



$$R\text{—}NH_3\text{—}\underset{O\;\;O}{\underset{/\,\backslash}{S}}\text{—}OH + R\text{—}NH_2 \longrightarrow (RNH_3)_2SO_3$$

The formation of thiosulfate may then be accounted for by the well-known fact that sulfites readily take up free sulfur to form thiosulfates.

$$(RNH_3)_2SO_3 + S \longrightarrow (RNH_3)_2S_2O_3$$

The formation of polysulfides, when the hydrosulfide is permitted to decompose in the presence of a limited quantity of oxygen as in a closed tube or in solution, may be equally well explained if, after the initial stage in the oxidation, "active" (monatomic) sulfur is assumed to play the role of oxygen in the above transformations. From this point of view it would seem the formation of polysulfide and thiosulfate may be regarded as concurrent as well as consecutive phenomena. That the polysulfides of organic bases are spontaneously oxidized by air to thiosulfates is an easily demonstrated fact. The mechanism of this transformation will be discussed in a later communication.

Experimental Part

The successful preparation of the amine hydrosulfides depends upon the entire series of operations being carried out in the absence of oxygen or air. The apparatus shown in Fig. 1 was devised for this purpose. For those amines which are liquid at ordinary temperatures two grams of the anhydrous amine was dissolved in 50 to 60 cc. of anhydrous ether and placed in the separatory funnel, **A.** Hydrogen sulfide, dried over calcium chloride, was passed through the large test-tube, T, until the air had been expelled. The amine solution was then allowed to flow into the reaction chamber, which was immersed in a bath of ice and salt. The passage of the hydrogen sulfide was continued until the deposition of the crystalline hydrosulfide was complete. The wide delivery tube, D, which fitted loosely in the stopper, was then thrust downward into the reaction mixture and the crystalline suspension of the amine hydrosulfide filtered by suction into the Gooch crucible, C. After washing with an additional portion of anhydrous ether, the crystalline product was dried in a current of dry hydrogen sulfide.

For those amines which are gaseous at room temperatures, the amine and hydrogen sulfide gases were admitted simultaneously into the reaction chamber, care being taken to keep the latter always in excess of an equimolecular amount. The hydrosulfide was deposited as an encrusted mass upon the walls of the reaction tube and suspended as feathery crystals. After a suitable deposit had been formed, the passage of the amine vapor was discontinued and 50–60 cc. of anhydrous ether admitted from the funnel A. The feathery crystals were loosened by shaking the tube and the suspension filtered into the crucible and dried as described above. The encrusted mass adhering to the walls of the reaction chamber was dried *in situ*.

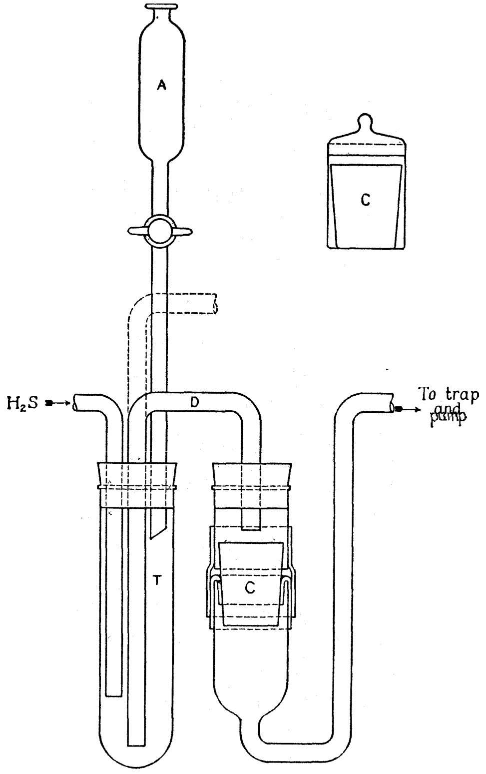


Fig. I.—Apparatus for the preparation of amine hydrosulfides.

The amine hydrosulfides were usually obtained as white needle-shaped crystals, less frequently as clear colorless plates. Melting points taken in an open tube were quite indefinite since the products melted with decomposition over wide ranges of temperature. The molten hydrosulfides decomposed rapidly, with marked ebullition, as the hydrogen sulfide was expelled. Melting points taken in a sealed tube were higher and more clearly defined, but still were not sharp. The crystalline products in sealed tubes frequently sublimed below their melting points. Methylamine hydrosulfide melts at 90–92° in a sealed tube. The melting points of the higher members decrease with increasing carbon content. The hydrosulfide of *n*-butylamine was obtained as a colorless, viscous liquid, which only partially solidified on cooling in a bath of ice and salt. Tri-n-butylamine hydrosulfide could not be induced to crystallize but on the other hand the isoamyl derivative melted at 62–67°.

The rapid decomposition of the amine hydrosulfides upon exposure to air necessitated that for analysis the samples be freshly prepared for each determination. The experimental conditions were set so as to provide a sample of from 0.2–0.5 g. in the crucible C. When the sample was thoroughly dried it was quickly transferred to the weighing bottle, W, and rapidly weighed.

The sulfur determinations were made by oxidizing the hydrosulfides in sodium peroxide solution, acidifying and precipitating as barium sulfate. The nitrogen determinations were for the most part made by the Kjeldahl method but in a few cases it was determined as the amine hydrochloride by adding an excess of hydrochloric acid and evaporating to dryness.

The physical characteristics and analyses of twelve amine hydrosulfides, prepared as described above, are shown in Table I.

TABLE I

THE AMINE HYDROSULFIDES

		Melting point, °C.		Analysis, S, %			Analysis, N, %		
Formula	Crystal form	Open tube	Closed tube	Calcd.	Found		Calcd.	Found	
CH_3NH_3SH	Needles	40–44	90–92	49 15	49 19	49 08	21 51	21 51	21.54
$(CH_3)_2NH_2SH$	Needles and leaves	34–40	...	40 51	39 85	40 58	17.69	17 62	17 72
$(CH_3)_3NHSH$	Leaves and plates	15-20	28–30	34 37	33 90	33 81	15 04	14 94	14 92
$C_2H_5NH_3SH$	Needles	50–55	55–57	40 51	41 01	40 92	17.69	17.76	17.94
$(C_2H_5)_2NH_2SH$	Needles	...	55–62	29 91	29 90	29 91	13.07	13.02	13.00
$(C_2H_5)_3NHSH$	Needles	25-27		23 64	23.54	23 58	10 36	13.37	10.32
n-$C_3H_7NH_3SH$	Needles	38–42	40–42	34 37	34 45	34 44	15.04	15.09	15.02
(n-$C_3H_7)_2NH_2SH$	Needles	58–62	76–78	23 64	23 30	23 44	10 36	10.42	10.29
n-$C_4H_9NH_3SH$	(Oil)	18–20	...	29 91	28 52	28 65	13 07	13 51	13.30
(n-$C_4H_9)_2NH_2SH$	....	25–30	28–32	19 52	19 08	19 07	8 59	8 63	8 70
i-$C_5H_{11}NH_3SH$	Plates	62–67 80–85	...	26 42	27 00	26 62	11.56	11.53	11 52
$(C_6H_5CH_2)_2NH_2SH$	....	32–34		13.84	13.85	13.83	6.06	6.15	6.14

The amine hydrosulfides are readily soluble in water and alcohol but only slightly soluble in ether and benzene. The solubility in water decreases and the stability increases with increasing molecular weight. The freshly prepared water solutions precipitate yellow cadmium sulfide and black lead sulfide from solutions of the respective acetates. The aqueous solutions soon become yellow on standing and will dissolve free sulfur, taking on a blood-red color indicative of the formation of polysulfides.

Oxidation of Dimethylamine Hydrosulfide.—A sample of **0.3418** g. of dimethylamine hydrosulfide was placed on a watch glass and exposed to the air for two days. The residue was dried and weighed. The weight of the residual deposit was **0.1344** g. and an examination showed it to be entirely free sulfur. This yield corresponds to 97.1% of the total sulfur content of the original sample.

Oxidation of Isoamylamine Hydrosulfide. Preparation of Isoamylamine Thiosulfate.—A quantity of the isoamylamine hydrosulfide was exposed to the air for several days. The product took on a slightly yellowish tinge. At no time did the product assume the blood-red color indicative of polysulfide formation. The major product was purified from the small quantity of free sulfur by recrystallization from water. The purified product was crystalline, stable and free from water of crystallization.

Analysis for nitrogen by the Kjeldahl method and titration by standard iodine solution gave the following results. Subs., **0.3000, 0.3000: 10.06, 10.03** cc. of **0.20845** N HCl. Found: N, 9.79, 9.76. Calcd. for $(C_5H_{11}NH_3)_2S_2O_3$: **N, 9.78.** Subs., 0.1000, 0.1000, **0.1000: 34.80, 34.60, 34.62** cc. of $N/100$ iodine. Calcd. for $(C_5H_{11}NH_3)_2S_2O_3$: **34.73 cc.**

Isoamylamine thiosulfate partially sublimes when heated to 176° and melts with decomposition at 192–196°. Its aqueous solution decolorizes permanganate, precipitates sulfur when acidified with hydrochloric acid and gives a white precipitate, which slowly changes through brown to black, when treated with silver nitrate solution. These reactions are characteristic of the thiosulfate ion.

Several residues, formed by the spontaneous oxidation of a number of amine hydrosulfides, had been standing in open tubes for eight months. The residue from *n*-butylamine hydrosulfide was large in comparison with the others at hand. Recrystallization of this product from water yielded a white crystalline compound which began to sublime at 175" and melted with decomposition and charring at 180–193°.

Analysis for nitrogen and titration with standard iodine gave the following results. Subs., 0.3000, 0.3000: 11.23, 11.20 cc. of 0.2485 N HCl. Found: N, 10.93, 10.90. Calcd. for $(C_4H_9NH_3)_2S_2O_3$: N, 10.85. Subs., 0.1000: 38.86 cc. of *N*/100 iodine. Calcd. for $(C_4N_9NH_3)_2S_2O_3$: 38.90 cc.

The residues from n-propyl and methylamine hydrosulfides were extracted with water and the solutions evaporated to dryness. The amount of product in each case was too small to be analyzed quantitatively, but qualitative tests were positive for the thiosulfate ion. The residues from trimethyl and trimethylamine hydrosulfides proved to be entirely free sulfur.

Summary

The hydrosulfides of twelve of the simple amines have been described. These include the hydrosulfides of methyl-, ethyl-, n-propyl-, n-butyl-, *i*-amyl-, dimethyl-, diethyl-, di-*n*-propyl-, di-n-butyl-, dibenzyl-, trimethyl- and triethylamines.

The amine hydrosulfides undergo rapid oxidation upon exposure to air. Those derived from the more volatile amines leave an almost quantitative deposition of sulfur. Those derived from the less volatile amines are oxidized to the corresponding thiosulfates. These oxidation reactions take place without evidence of polysulfide formation. A mechanism is suggested for the oxidation reactions which fully accounts for all the facts observed.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

RHODANINES. I. DERIVATIVES OF β-PHENYLETHYLAMINES

BY JOHANNES S. BUCK AND CLIFFORD S. LEONARD

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Apparently no rhodanine derivatives of β-phenylethylamines have been described previously in the literature. The pharmacological properties of such compounds may prove interesting on account of their relation to compounds such as adrenaline, epinine, etc. On the other hand, they also contain the rhodanine (keto-thioketo-thiazolidine) ring, which, when alkylated in the methylene carbon, has been shown by Leonard[1] to possess pharmacological properties of the same type as the barbituric acid derivatives. The compounds described in the present paper contain an unsubstituted or an ether-substituted benzene ring and a non-alkylated

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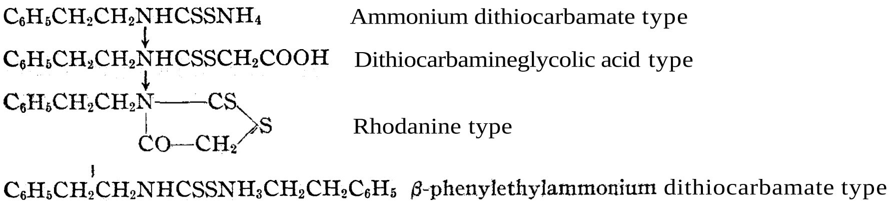
[1] Leonard, Medd. Vetenskapsakad. *Nobelinst.*, Bd. 4, No. 14 (1921).

rhodanine ring. On account of their low solubility in water, they would probably not be of practical use in pharmacology. The authors are endeavoring to remedy this defect in solubility by (a) introducing hydroxyl groups in place of the ether groups, and (b) by modifying the rhodanine ring. The introduction of hydroxyl groups into the benzene ring would bring the compounds very close to the chemical type of epinine.

The preparation of the compounds here described is a relatively simple matter. The β-phenylethylamine is condensed with ammonia and carbon bisulfide to the ammonium dithiocarbamate[2] and this is then condensed, by means of potassium chloroacetate, to the dithiocarbamineglycolic acid.[3] This, on warming with dilute acetic acid, gives the rhodanine. The isolation of the dithiocarbamineglycolic acid may be omitted, and the rhodanine obtained directly by heating the dithiocarbamate with potassium chloroacetate, acidified with acetic acid.

Another method is to form the phenylethylammonium dithiocarbamate by treating the amine with carbon bisulfide. On heating this with potassium chloroacetate acidified with acetic acid, the rhodanine is produced. The steps may be shown as follows



$C_6H_5CH_2CH_2NHCSSNH_4$ Ammonium dithiocarbamate type

$\downarrow$

$C_6H_5CH_2CH_2NHCSSCH_2COOH$ Dithiocarbamineglycolic acid type

$\downarrow$

$C_6H_5CH_2CH_2N \begin{matrix} —CS \\ | \\ CO—CH_2 \end{matrix} > S$ Rhodanine type

$\uparrow$

$C_6H_5CH_2CH_2NHCSSNH_3CH_2CH_2C_6H_5$ β-phenylethylammonium dithiocarbamate type

Four series of compounds, derived from β-phenylethylamine, homoanisylamine, homopiperonylamine and homoveratrylamine are described. One compound, the dithiocarbamineglycolic acid from homoveratrylamine, could not be obtained in the pure state, as it spontaneously passes into the rhodanine.

Experimental

Ammonium Dithiocarbamates.—One mole of the amine, dissolved in twice its volume of absolute alcohol, is treated with one mole of ammonia (satd. aqueous soln.). Slightly more than one mole of carbon bisulfide is then slowly added, the mixture being cooled in ice throughout the above operations. After standing for a few hours the solid is filtered off and washed on the filter with alcohol and ether, and is then sufficiently pure. Recrystallization may be carried out by adding ether to a cold alcoholic solution, when the compound is obtained in the form of shiny leaves. Recrystallization, however, is not advisable on account of the instability of the compounds in solution. The yields are good. The ammonium dithiocarbamates are well-crystallized compounds, soluble in the cold in water, alcohol, acetic acid and ammonium hydroxide. They give colorless solutions in cold sulfuric acid, with the exception of the homopiperonyl derivative, which

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[2] Hann, THIS JOURNAL, 47, 1998 (1925).

[3] Holmberg, *J. prakt. Chem.*, [2] 79, 253 (1909).

gives a deep claret color. The compounds are sparingly soluble in warm chloroform and moderately soluble in warm acetone. On melting, they froth violently.

β-Phenylethylammonium Dithiocarbamates.—The amine, dissolved in twice its volume of absolute alcohol, is cooled in ice, and one-half its volume of carbon bisulfide added slowly, with stirring. After standing for a few hours, the product is filtered off and washed with alcohol and ether and recrystallized by adding ether to the cold alcoholic solution. The compounds form well-defined crystals, soluble in warm water, alcohol, chloroform and acetone and soluble in the cold in acetic acid and in sulfuric acid. Only the homopiperonylamine derivative gives a color with the latter (deep red). The yields are excellent. On melting, pronounced frothing takes place.

Dithiocarbamineglycolic Acids.—The preparation of these compounds is simple. The ammonium dithiocarbamate is dissolved in a little warm water, and treated with a solution of an equal weight of chloroacetic acid which has been accurately neutralized with potassium bicarbonate. A white magma rapidly forms. After one hour the mixture is diluted with water and made slightly acid with acetic acid. The white, crystalline precipitate which forms is filtered off and washed on the filter with water. Although stable when dry, it is not possible to recrystallize the compounds. The dithiocarbamineglycolic acids are fairly soluble in water, the solution decomposing when heated. They are soluble in cold alcohol, acetic acid, ammonium hydroxide and ether and moderately soluble in cold chloroform. With cold concd. sulfuric acid, only the homopiperonyl compound gives a color (deep crimson). All attempts to prepare a homoveratryl derivative resulted in the isolation of products containing the corresponding rhodanine, formed by loss of water and cyclization. On melting, the acids froth violently.

Rhodanines.—The rhodanines are readily obtained by heating an aqueous solution of the ammonium or phenylethylammonium dithiocarbamate with an aqueous solution of potassium chloroacetate, made acid with acetic acid, on the water-bath for thirty minutes. They are also formed by warming the dithiocarbamineglycolic acid with dilute acetic acid. The rhodanines are best recrystallized from alcohol, in which they are moderately or readily soluble when heated. They are practically insoluble in water, very soluble in cold chloroform and acetone, soluble in warm acetic acid and insoluble in ammonium hydroxide. The rhodanines, when pure, are quite stable, but liquors and impure solutions soon develop red colors. For brevity, the individual compounds are tabulated.

TABLE I

AMMONIUM DITHIOCARBAMATES

Ammonium ( )-dithiocarbamate	Formula	Appearance	M. p., °C.	Formula	Analyses, N, % Calcd.	Analyses, N, % Found
N-β-phenylethyl-	$C_6H_5CH_2CH_2NHCSSNH_4$	Large, transparent plates	132, froth.	$C_9H_{14}S_2N_2$	13.08	19.72
N-[3,4-dimethoxy-β-phenylethyl]-	$(CH_3O)_2C_6H_3CH_2CH_2NHCSSNH_4$	White, stout irreg. prisms	138, froth.	$C_{11}H_{18}O_2S_2N_2$	10.21	10.17
N-[4-methoxy-β-phenylethyl]-	$CH_3OC_6H_4CH_2CH_2NHCSSNH_4$	White, pearly leaves (plates)	139, froth.	$C_{10}H_{16}OS_2N_2$	11.47	11.66
N-[3,4-methylenedioxy-β-phenylethyll-	$CH_2O_2C_6H_3CH_2CH_2NHCSSNH_4$	White, cryst. powder (prisms)	138, froth.	$C_{10}H_{14}O_2S_2N_2$	10.85	10.96

TABLE II

β-PHENYLETHYLAMMONIUM DITHIOCARBAMATES

Name and structure, ( )-dithiocarbamate	Appearance	Formula	M. p., °C.	Analyses, N, % Calcd.	Analyses, N, % Found
β-Phenylethylammonium-N-β-phenylethyl- $C_6H_5CH_2CH_2NHCSSNH_3CH_2CH_2C_6H_5$	White, tiny, glittering plates	$C_{17}H_{22}S_2N_2$	130. froth.	8.81	8.85
3,4-Dimethoxy-β-phenylethylammonium-N-[3,4-dimethoxy-β-phenylethyl]- $(CH_3O)_2C_6H_3CH_2CH_2NHCSSNH_3CH_2CH_2C_6H_3(OCH_3)_2$	White, powdery crystals	$C_{21}H_{30}O_4S_2N_2$	124, froth.	6.39	6.66
4-Methoxy-β-phenylethylammonium-N-[4-methoxy-β-phenylethyl]- $CH_3OC_6H_4CH_2CH_2NHCSSNH_3CH_2CH_2C_6H_4OCH_3$	White, felted needles	$C_{19}H_{26}O_2S_2N_2$	135, froth.	7.41	7.37
3,4-Methylenedioxy-β-phenylethylammonium-N-[3,4-methylenedioxy-β-phenylethyl]- $CH_2O_2C_6H_3CH_2CH_2NHCSSNH_3CH_2CH_2C_6H_3CH_2O_2$	Faint buff, tiny prisms	$C_{19}H_{22}O_4S_2N_2$	133, froth.	6.90	7.09

TABLE III

DITHIOCARBAMINEGLYCOLIC ACIDS

-Dithiocarbamineglycolic acid	Structure	Appearance	M. p., °C.	Formula	Analyses, N, % Calcd.	Analyses, N, % Found
N-[β-Phenylethyl]-	$C_6H_5CH_2CH_2NHCSSCH_2COOH$	Felted, pearly leaves	125, froth.	$C_{11}H_{13}O_2S_2N$	5 49	5.43
N-[3,4-Dimethoxy-β-phenylethyl]-	$(CH_3O)_2C_6H_3CH_2CH_2NHCSSCH_2COOH$	Not isolable in pure state	......	$C_{13}H_{17}O_4S_2N$	..	..
N-[4-Methoxy-β-phenylethyll-	$CH_3OC_6H_4CH_2CH_2NHCSSCH_2COOH$	Bulky, tiny leaves	128, froth.	$C_{12}H_{15}O_3S_2N$	4.91	5.14
N-[3,4-Methylenedioxy-β-phenylethyll-	$CH_2O_2C_6H_3CH_2CH_2NHCSSCH_2COOH$	Chalky, cryst. mass	132, froth.	$C_{12}H_{13}O_4S_2N$	4 68	4.88

TABLE IV

RHODANINES

-2-Thioketo-4-keto-thiazolidine	Structure	Appearance
3-[β-Phenylethyl]-	$C_6H_5CH_2CH_2\underline{NCSSCH_2CO}$	Pale yellow flat needles
3-[3,4-Dimethoxy-β-phenylethyl]-	$(CH_3O)_2C_6H_3CH_2CH_2\underline{NCSSCH_2CO}$	Pale yellow pearly leaves
3-[4-Methoxy-β-phenylethyll-	$CH_3OC_6H_4CH_2CH_2\underline{NCSSCH_2CO}$	Pale yellow flat needles
3-[3,4-Methylenedioxy-β-phenylethyl]-	$CH_2O_2C_6H_3CH_2CH_2\underline{NCSSCH_2CO}$	Pale flesh-colored tiny nodules

TABLE IV (Concluded)

M. p., °C.	Cold H_2SO_4	Formula	Analyses, % Calcd. C	H	S	N	Found C	H	S	N
107	No color	$C_{11}H_{11}OS_2N$	55.67	4.67	27.00	5.91	55.82	4.68	27.35	6.05
154	Intense yellow	$C_{13}H_{15}O_3S_2N$	52.50	5.09	21.55	4.71	52.56	5.25	21.52	4.92
106	No color	$C_{12}H_{13}O_2S_2N$	53.91	4.91	23.97	5.24	54.06	4.98	23.71	5.47
126	Intense yellow	$C_{12}H_{11}O_3S_2N$	51.23	3.94	22.77	4.98	51.15	4.09	22.82	5.31

The authors are indebted to Mr. W. S. Ide for the analyses (all micro) given above.

Summary

The ammonium dithiocarbamates, phenylethylammonium dithiocarbamates, dithiocarbamineglycolic acids and rhodanines derived from β-phenylethylamine, homoanisylamine, homopiperonylamine and homoveratrylamine are described, together with their preparations.

TUCKAHOE, NEW YORK

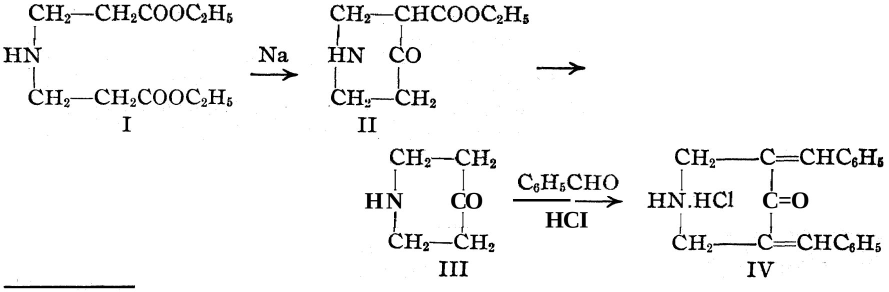
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OR WISCONSIN]

PIPERIDINE DERIVATIVES. XI. 3-CARBETHOXY-4-PIPERIDONE AND 4-PIPERIDONE HYDROCHLORIDE

BY GLEN M. KUETTEL AND S. M. MCELVAIN

RECEIVED APRIL 18, 1931 PUBLISHED JULY 8, 1931

In an effort to prepare 4-piperidone, Ruzicka and Fornasir[1] carried out an internal acetoacetic ester condensation of β,β[1]-dicarbethoxydiethylamine. No attempt was made to isolate the intermediate 3-carbethoxy-4-piperidone. The reaction mixture containing this latter compound was subjected directly to reaction conditions which would bring about its hydrolysis and decarboxylation. The resulting 4-piperidone was not obtained in the form of a crystalline salt and since the free base appeared to be quite unstable it was isolated in the form of the hydrochloride of the dibenzal derivative. These transformations may be illustrated as follows



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[1] Ruzicka and Fornasir, *Helv. Chim. Acta*, **3,806** (1920).

A considerable number of the 1-alkyl-4-piperidones have been prepared in excellent yields and isolated as crystalline hydrochlorides[2] in this Laboratory from the corresponding 1-alkyl-3-carbethoxy-4-piperidones. These latter compounds were obtained by a condensation similar to that shown above from the β,β'-dicarbethoxy diethyl alkyl amines and were isolated and purified in the form of the hydrochlorides.[3] It seemed quite probable from this work that if the intermediate 3-carbethoxy-4-piperidone (II) could be isolated and purified, the 4-piperidone (III) resulting from its hydrolysis and decarboxylation might be obtained in a useful form as a crystalline salt, since its purification would not be complicated by the association of side-reaction products resulting from the condensation of the β,β'-di-carbethoxydiethylamine (I). The carbethoxy compound (II) would appear to offer better opportunities for purification on account of its amino-β-ketonic ester structure which causes it to be soluble in acids and alkali hydroxides, but not in alkali carbonates. The present paper reports the results of this effort.

The β,β'-dicarbethoxydiethylamine which was used in the condensation was obtained from the hydrochloride which had been carefully purified by recrystallization. Whereas the di-esters of type (I) containing the various alkyl groups attached to the nitrogen instead of hydrogen are condensed by sodium to give 55–75% yields of the corresponding 1-alkyl-3-carbethoxy-4-piperidone, only a 11% yield of (II) was obtained by the condensation of β,β'-dicarbethoxydiethylamine (I). The major portion of the reaction product is a yellow gum which appears to be derived from a further condensation of (II) with itself. The 3-carbethoxy-4-piperidone was easily isolated and purified as the hydrochloride.

The hydrolysis and decarboxylation of (II) in the form of the hydrochloride took place quite readily and a crystalline hydrochloride of the piperidone (III) was obtained. Recrystallization of the latter compound from an alcohol–ether mixture gave an apparently pure product which melted at 138–140°, but gave chlorine analyses which were considerably lower than that calculated for the piperidone hydrochloride (calcd. 26.15% Cl; found, 17.41, 17.45%). All attempts to alter these values by drying the product under diminished pressure were unsuccessful. If this 138–140" melting material were dissolved in water and the solvent then evaporated off under diminished pressure, a product melting at 92–94' and containing 23.00% Cl was obtained. The analyses in the case of the product from the alcohol crystallization correspond to the piperidone hydrochloride with 1.5 C_2H_5OH of crystallization and in the case of the

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[2] (a) Bolyard and McElvain, THIS JOURNAL, 51, 922 (1929); (b) Bolyard, *ibid.*, 52, 1030 (1930).

[3] McElvain, *ibid.*, 46, 1721 (1924); 48, 2179 (1926); Thayer and McElvain, ibid., 49, 2862 (1927).

water crystallization the analysis corresponds to the piperidone hydrochloride with $1H_2O$ of crystallization.

Similar abnormal analyses were obtained with certain of the 1-alkyl-4-piperidone hydrochlorides.[2] In these cases it was shown that these analyses were of no fundamental significance, since by reduction and benzoylation these 1-alkyl-4-piperidones were converted into the corresponding 1-alkyl-4-benzoyloxypiperidines. In the case of the 4-piperidone hydrochloride obtained in the present work a similar conclusion may be drawn from the fact that it was readily converted into the hydrochloride of the dibenzal-4-piperidone (IV), the structure of which has been established by Ruzicka and Fornasir.[1]

Experimental

All melting points and boiling points herein given are corrected.

β,β'-Dicarbethoxydiethylamine (I).—This compound was prepared by Ruzicka and Fornasir by the action of ethyl β-iodopropionate on ethyl β-aminopropionate and was purified by fractional distillation. The following procedure seems to be simpler and in general much more satisfactory. To a mixture of 308 g. of β-bromopropionic acid ("Organic Syntheses," Vol. III, p. *25)* in 300 cc. of water, was added a suspension of 168 g. of sodium bicarbonate in 500 cc. of water. After complete neutralization and solution, 1100 cc. of ammonium hydroxide (sp. gr. 0.90) was added and the solution allowed to stand in a stoppered bottle at room temperature for four days with occasional stirring. The solution was then evaporated on a steam-bath to a volume of about 600 cc., and made acid to Congo red with dilute hydrochloric acid, using a small excess of the acid. The acidified solution was then evaporated to dryness under diminished pressure. The amino acid hydrochlorides were extracted from the gummy residue by thorough shaking with two 400-cc. portions of alcohol. After the inorganic salt was filtered off, this alcoholic solution was evaporated to dryness under reduced pressure over a steam-bath. The residue obtained after the removal of the alcohol was then esterified by refluxing with 1500 cc. of a 4% solution of dry hydrogen chloride in absolute alcohol for twelve hours. The alcohol was then completely removed under reduced pressure from a steam-bath. The thick residue was poured into a one-liter beaker and allowed to cool to room temperature. The distillation flask was rinsed with 50 cc. of water and the rinsings added, together with 70 g. of ice, to the mixture of the amino acid ester hydrochlorides. The beaker was placed in an ice–salt mixture, 200 cc. of ether was added and the contents stirred until the temperature of the liquid was below 10°. Then 100 cc. of cold concentrated potassium hydroxide solution (45% by weight) was added slowly and with rapid stirring. The temperature of the mixture was kept below 10° during the addition of the alkali. The ether layer, which now had assumed a brownish coloration, was removed and 200 cc. more of ether was added. A 50-cc. portion of the potassium hydroxide solution was then added. The ether layer was separated and the aqueous layer extracted with another 100 cc. of ether. The combined ether extracts were evaporated on a steam-bath and the residue immediately distilled under diminished pressure from an oil-bath.

The distillate was collected in two fractions. The first fraction, consisting of primary and secondary amino esters, distilled from 70–130° (10 mm.) and the second fraction, consisting of comparatively pure β,β'-dicarbethoxydiethylamine, distilled at 130–140" (10 mm.). The first fraction, upon refractionation, yielded a portion of ethyl β-aminopropionate which distilled at 70–80° (10 mm.), and a portion of the secondary amino-ester. The total yield was 15–20 g. (6–8%) of the primary amino ester and 51–57 g. (23–26%) of the β,β'-dicarbethoxydiethylamine fraction.

The secondary amino ester so obtained is best purified by recrystallization of the hydrochloride to constant melting point as described below. The pure β,β'-dicarbethoxydiethylamine is then obtained by the decomposition of the hydrochloride with potassium hydroxide in the manner described above for the liberation of the crude primary and secondary amino esters from their hydrochlorides. The pure β,β'-dicarbethoxydiethylamine boils at 137–138° (12 mm.); n^{25}_{D} 1.43802, d^{20}_{20} 1.0462. A recovery of 88–93% of the free secondary amino ester is possible from its hydrochloride. On account of the fact that the free secondary amino ester slowly undergoes self-condensation it is advisable to keep it as the hydrochloride.

β,β'-Dicarbethoxydiethylamine Hydrochloride.—The secondary amino ester fraction which boiled at 130–140° (10 mm.) was dissolved in 150 cc. of dry ether and any insoluble material filtered off. Dry hydrogen chloride was slowly passed into this ethereal solution. The hydrochloride, which formed readily in white flaky crystals, was filtered and washed several times with small portions of dry ether. These ether washings were similarly treated with hydrogen chloride and a second crop of crystals was obtained. In a like manner a third crop of crystals was obtained but succeeding ether washings and hydrogen chloride treatments yielded only a small amount of an oil that failed to crystallize. The secondary amine hydrochloride, upon first precipitation from the ether solution, must be thoroughly washed with ether, or be immediately recrystallized because the impure ester hydrochloride, upon standing a short time, assumes a reddish coloration that is difficult to remove. The hydrochloride after several recrystallizations from an alcohol–ether mixture melted at 79.5–80.5°.

Anal. Calcd. for $C_{10}H_{20}O_4Cl$: Cl, 14.02. Found: Cl, 13.98, 13.90.

3-Carbethoxy-4-piperidone Hydrochloride (II).—The pure β,β'-dicarbethoxydiethylamine (b. p. 137–138°, 12 mm.) as obtained from the decomposition of its hydrochloride in the manner described above was used in the preparation of the carbethoxypiperidone. To a mixture of 40 cc. of xylene and 3.9 g. of powdered sodium was added 37 g. of the secondary amino ester and the mixture warmed to 85° in an oil-bath until the reaction started. The condensation started in gradually but soon became sufficiently vigorous to cause the xylene to boil. After this initial reaction subsided, the mixture was cooled and treated with 200 cc. of ice water and the xylene extracted with ether. The water layer was made acid with hydrochloric acid and the free carbethoxy-piperidone base liberated with excess potassium carbonate. The free base was immediately extracted with ether and precipitated as its hydrochloride with dry hydrogen chloride. A yield of 4.0 g. (11%) was obtained.

The hydrochloride crystallized in the form of fine white needles and after recrystallization from alcohol-ether mixture melted at 168–169° with decomposition. It produced the characteristic deep red coloration with ferric chloride.

Anal. Calcd. for $C_8H_{14}O_3NCl$: Cl, 17.28. Found: Cl, 17.10, 17.10

The greater portion of the reaction product consisted of a yellow gum insoluble in ether. This was dissolved in alcohol, the alcohol evaporated and the gum dried in a vacuum desiccator over sulfuric acid. It was then dissolved in 20% hydrochloric acid. A drop of the solution produced a distinct coloration with ferric chloride. Evolution of carbon dioxide resulted when this solution was refluxed and after thirty minutes' boiling no coloration was shown by ferric chloride. After removal of the water and excess hydrochloric acid under diminished pressure, an uncrystallizable gum was obtained. The original gummy reaction product appears to be a further condensation product of 3-carbethoxy-4-piperidone.

4-Piperidone Hydrochloride (III).—To 2.33 g. of 3-carbethoxy-4-piperidone was added 80 cc. of 20% hydrochloric acid and the solution refluxed until it showed no coloration with ferric chloride (about thirty minutes). The carbon dioxide which was evolved was carried by a current of carbon dioxide-free air from the reaction flask through a series of drying tubes and absorbed in a weighed ascarite bulb. A yield of 0.4451 g. (90%) of carbon dioxide was obtained. The acid solution was then evaporated to dryness under diminished pressure The resulting solid after recrystallization from an alcohol–ether mixture weighed 1.1 g. and melted at 139–141° with decomposition. After drying at 100° and 10 mm. it was analyzed.

Anal. Calcd. for $C_5H_{10}ONCl$ (4-piperidone hydrochloride): Cl, 26.15; calcd. for $C_5H_{10}ONCl \cdot 1.5C_2H_5OH$: Cl, 17.34. Found: Cl, 17.41, 17.45.

An attempt was made to free the hydrochloride from the associated solvent by recrystallization from other solvents, such as acetone, which have been found (*cf.* Ref. 2b) to give analytically pure piperidone hydrochlorides. These efforts were unsuccessful on account of the insolubility of the hydrochloride in these solvents. However, a solution of the 139–141° melting piperidone hydrochloride in water yielded a product after evaporation to dryness that melted at 92–94°. This product was found to contain 23.00% of chlorine; calcd. for $C_5H_{10}NCl \cdot H_2O$, 23.10.

3,5-Dibenzal-4-piperidone Hydrochloride (IV).—The identity of the 4-piperidone hydrochloride, melting at 138–140°, was established by converting it into the dibenzal-4-piperidone hydrochloride which has been characterized by Ruzicka and Fornasir.[1] A solution of 0.08 g. of the piperidone hydrochloride in 3 cc. of glacial acetic acid saturated with dry hydrogen chloride was treated with 0.15 cc. of benzaldehyde. After standing for twenty-four hours, a mass of yellow needle-like crystals had separated which after decantation of the acetic acid and recrystallization from alcohol weighed 0.069 g. (58%) and melted at 276–277° with decomposition. Ruzicka and Fornasir reported this compound as melting at 275–277°.

Summary

1. The preparation of 3-carbethoxy-4-piperidone hydrochloride and its hydrolysis and decarboxylation to 4-piperidone hydrochloride are described. The latter compound could not be obtained free from solvent used in its recrystallization but was characterized by its conversion into the known dibenzal-4-piperidone hydrochloride.

2. An improved method for the preparation of β,β'-dicarbethoxydiethylamine is given.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]

MERCURY DERIVATIVES OF CYCLOHEXYL- AND BENZYLPHENOLS[1]

BY JOHN W. HAUGHT,[2] C. E. GARLAND AND H. A. H. PRAY

RECEIVED APRIL 22, 1931 PUBLISHED JULY 8, 1931

Only a few references to the mercuration of compounds similar to the cyclohexyl- and benzylphenols have been found.

Dimroth[3] prepared mercury derivatives of *p*-cresol by heating with alcoholic mercuric acetate at 90° for half an hour. About equal quantities of the mono- and di-mercurated products were formed but the latter, being less soluble, separated out almost pure. The mono-acetoxymercuri-*p*-cresol was rather difficult to crystallize on account of its solubility, so it was precipitated from solution in the form of chloromercuri-p-cresol by the addition of sodium chloride solution. He dissolved chloromercuri-p-cresol in sodium hydroxide and precipitated the anhydride by passing carbon dioxide into the solution. The di-acetoxymercuri-*p*-cresol as crystallized from the reaction mixture contained one molecule of water of crystallization. When the compound was heated to drive off this water it was converted into hydroxymercuriacetoxymercuri-*p*-cresol.

Henry and Sharp[4] have mercurated several alkyl phenols and alkylphenol aldehydes and studied their bactericidal properties. They found that the bactericidal action of organo-mercury compounds was not entirely dependent on the number of mercury groups present, but was largely influenced by the configuration of the organic part of the molecule. They prepared both mono- and di-mercurated derivatives of *p*-tertiary butyl phenol by refluxing the alcoholic solution of the phenol with mercuric acetate dissolved in alcohol containing a small quantity of acetic acid. When this solution was diluted with water the acetoxymercuri compounds were precipitated. The mono- and di-acetoxymercuri compounds were also prepared from *p*-isoamylphenol, carvacrol and thymol. The acetoxymercury groups assumed the ortho position to the hydroxyl group in the mono derivatives and the ortho, ortho prime positions in the di-substituted compounds. These positions were determined by converting the mercury groups to nitro groups by treatment with cold nitric acid.

Mameli[5] found that o-cresol could be mercurated in either hot or cold

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[1] This communication is an abstract of part of a thesis submitted by John W. Haught in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at West Virginia University.

[2] D. A. Burt Fellow in Chemistry, 1929–1930.

[3] Dimroth, Ber., 35, 2856 (1902); Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, pp. 275–277.

[4] Henry and Sharp, J. *Chem. Soc.*, 2432 (1926).

[5] Mameli, Gazz. *chim. ital.*, 56, 948 (1926); *Chem. Abstracts*, 21, 1252 (1927).

alcohol or acetic acid solution. The best results were obtained for mono-acetoxymercuri-o-cresol in cold dilute acetic acid and for di-acetoxymercuri-*o*-cresol in hot dilute acetic acid. Both the mono- and di-acetoxymercuri-o-cresols dissolved in sodium hydroxide, from which mono- and di-chloromercuri-o-cresols were precipitated by the addition of sodium chloride solution.

Either 95% alcohol slightly acidified with acetic acid or glacial acetic acid may be used as a solvent for the mercuration of ortho and para cyclohexyl and benzyl phenols. The acidified alcohol was found to be more satisfactory because there was less coloration of the product in this solvent. If the mercuration was carried out in dilute acetic acid, the product separated on cooling as a sticky mass which could not be crystallized.

The di-acetoxymercuri compounds of both ortho and para cyclohexyl phenol and ortho and para benzylphenol were so soluble in the acidified alcohol that they could not be crystallized from solution even by evaporation to a small volume. They were precipitated by slowly diluting the alcoholic solution with water.

Much difficulty was encountered in freeing these compounds of water. They slowly decomposed at 100° so they were heated for twenty-four hours in an oven at 50° but without effect. They were further heated in a vacuum oven at 60° for twenty-four hours. This treatment removed the water from the mercurated para cyclohexyl and benzyl phenols but not entirely from the similar ortho compounds. This was especially true of the chloromercuri and hydroxymercuri derivatives of ortho benzylphenol.

An effort was made to prepare the anhydromercuri or hydroxymercuri derivatives by treatment of the chloromercuri compounds with hot concentrated sodium carbonate solution but the conversion was not complete. Sodium hydroxide solution was substituted for the sodium carbonate solution and complete conversion resulted.

The hydrogen in the hydroxyl group of the phenols used seems to have only very slight acid properties, because the mercury derivatives of the para cyclohexyl and benzyl phenols were not soluble in sodium hydroxide and the similar derivatives of ortho cyclohexyl and benzyl phenols only slightly soluble. This is in marked contrast to the action of the mercury derivatives of phenol and the cresols.

The acetic acid in the acetoxymercuri derivatives was determined by the method of Brieger and Schulemann, as described by White,[6] which is based on the decomposition of the compound with phosphoric acid in water solution, followed by distillation and titration of the acetic acid. The acetoxy compounds analyzed in this work were so insoluble that it was found necessary to use a larger quantity of phosphoric acid and to collect more of the distillate than indicated by White.

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[6] White, THIS JOURNAL, **42**, 2355 (1920).

All of the preparations were dissolved for mercury determination by the method described by Hart and Hirschfelder.[7] The mercury was then determined by the method of Jamieson.[8]

The ortho cyclohexylphenol and para cyclohexylphenol used in preparing these mercuration products were supplied through the courtesy of Dr. R. **R.** Read, of Sharp and Dohme, Baltimore, to whom the thanks of the authors are due.

Experimental Part

Di-acetoxymercuri derivatives of cyclohexyl and benzyl phenols were prepared by reacting 0.025 mole of the phenol dissolved in 15 cc. of ethyl alcohol with 0.05 mole of mercuric acetate dissolved in 100 cc. of ethyl alcohol acidified with 5 cc. of glacial acetic acid. The two solutions were mixed and heated on a steam-bath for two hours, after which time the reaction mixture did not give a test for inorganic mercury with sodium hydroxide. The resulting solution was evaporated to a volume of 50 cc. and the mercury derivative either crystallized from this solution or precipitated by dilution with a large volume of water. The precipitate was filtered, washed, dried at 50° and then in a vacuum oven at 60°. The numerical data appear in Table I.

TABLE I

PREPARATION, DATA AND ANALYSES

Compound, -phenol	Yield, %	Dec. at	Formula	Analyses Mercury, % Calcd.	Analyses Mercury, % Found		Analyses OAc, % Calcd.	Analyses OAc, % Found	
Diacetoxymercuri-									
-*p*-Benzyl-	95	110–115	$C_{17}H_{16}O_5Hg_2$	57.22	56.81	57.02	16.83	16.31	16.70
-*o*-Benzyl-	92	115–125	$C_{17}H_{16}O_5Hg_2 \cdot H_2O$	55.78	55.35	55.67	16.40	16.02	16.16
-*p*-Cyclohexyl-	95	105–110	$C_{16}H_{20}O_5Hg_2$	57.86	57.15	57.59	17.02	16.52	16.25
-*o*-Cyclohexyl-	95	135–140	$C_{16}H_{20}O_5Hg_2 \cdot H_2O$	56.4	56.07	55.92	16.41	16.02	15.95
Dichloromercuri-									
-*p*-Benzyl-	97	128-134	$C_{12}H_{10}OHg_2Cl_2$	61.34	61.66	61 57			
-*p*-Cyclohexyl-	93	225–230	$C_{12}H_{14}OHg_2Cl_2$	62.10	61 93	61.76			
-*o*-Cyclohexyl-	92	155-160	$C_{12}H_{14}OHg_2Cl_2 \cdot H_2O$	60.41	59 96	60 00			
Anhydromercuri-hydroxymercuri-									
-*p*-Benzyl-	90	245-250	$C_{13}H_{10}O_2Hg_2$	66.95	66 96	66.27			
Dihydroxymercuri-									
-*p*-Cyclohexyl-	90	255–260	$C_{12}H_{16}O_3Hg_2$	65.88	65.85	65.37			
-*o*-Cyclohexyl-	85	230–235	$C_{12}H_{16}O_3Hg_2 \cdot H_2O$	63.16	62.94	63.16			

Di-chloromercuri derivatives were prepared from the corresponding acetoxymercuri compounds by dissolving them in glacial acetic acid and adding the solution so obtained to a saturated sodium chloride solution. The insoluble di-chloromercuri compounds were precipitated as white powders. These were washed free of sodium chloride and dried in the same way as the acetoxymercuri derivatives. It was not found possible to free the di-chloromercuri-o-benzylphenol of water without decomposi-

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[7] Hart and Hirschfelder, THIS JOURNAL, 42,2678 (1920).

[8] Jamieson, *J. Ind. Eng. Chem.*, 11,296 (1919).

tion, so a satisfactory analysis of this material was not obtained and therefore it does not appear in the above table.

Anhydromercuri-hydroxymercuri and di-hydroxymercuri derivatives were obtained by moistening the di-chloromercuri compounds with ethyl alcohol and treating with hot (10%) sodium hydroxide solution. The mixture was filtered and the sodium hydroxide washed from the residue which was dried in a vacuum oven. In the case of the di-hydroxymercuri-o-benzylphenol and the di-hydroxymercuri-o-cyclohexylphenol, it was found necessary to neutralize with dilute hydrochloric acid in order to cause precipitation. Due to the difficulty of drying the former, a satisfactory analysis of this material was not obtained.

Summary

The following ten mercury derivatives of ortho and para cyclohexylphenol and ortho and para benzylphenol have been prepared and analyzed: di-acetoxymercuri-*p*-benzylphenol, di-acetoxymercuri-o-benzylphenol, di-acetoxymercuri-p-cyclohexylphenol, di-acetoxymercuri-o-cyclohexylphenol, di-chloromercuri-*p*-benzylphenol, di-chloromercuri-*p*-cyclohexylphenol, di-chloromercuri-o-cyclohexylphenol, anhydromercuri-hydroxymercuri-p-benzylphenol, di-hydroxymercuri-*p*-cyclohexylphenol, and di-hydroxymercuri-o-cyclohexylphenol.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALABAMA]

FORMIC ACID FROM HYDROLYSIS OF CELLULOSE OXALATE[1]

BY JACK P. MONTGOMERY

RECEIVED APRIL 30, 1931 PUBLISHED JULY 8, 1931

One of the usual laboratory methods for making formic acid is to prepare glyceryl mono oxalate, convert it to glyceryl mono formate by heating, and hydrolyze by adding more crystallized oxalic acid, the water of the crystallized acid serving as that required for the hydrolysis. Finally, steam distillation completes the hydrolysis and delivers all the formic acid produced.[2]

It has been found that cellulose in the form of absorbent cotton can be substituted for glycerine with some changes in the technique of the process.

Procedure.—Eighty grams of crystallized oxalic acid, 100 g. of absorbent cotton and 100 cc. of concentrated hydrochloric acid are required. The oxalic acid is melted in its water of crystallization in a 1000-cc. round-bottomed flask over the water-bath and the cotton, torn into small bits, thoroughly shaken with it. The hydrochloric acid is added and the flask

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[1] Presented before the Division of Cellulose Chemistry of the American Chemical Society at the Indianapolis Meeting, March 30–April 3, 1931.

[2] Cohen, "Practical Organic Chemistry," 3rd ed , The Macmillan Co., Preparation 47, p. 130.

connected for steam distillation in the usual manner, the flask being supported on gauze and tripod and not on the water-bath. Before the admission of steam, the flask is heated by the burner flame and kept boiling until about 50 cc. of distillate is obtained. The distillate is returned to the flask, 100 cc. of water added and the mixture steam distilled until about 150 cc. of distillate is collected.

Lead oxide is added to the distillate in slight excess and the liquid filtered. The filtered liquid is evaporated to small bulk and allowed to crystallize. The yield is 65 g. of lead formate, equivalent to 20 g. of formic acid. If it is assumed that one mole of oxalic acid gives one mole of cellulose mono formate and that the cellulose mono formate is completely converted to formic acid, it follows that one mole of oxalic acid in this procedure should yield, theoretically, a maximum of one mole of formic acid. On this basis 126 g. of crystallized oxalic acid will give 46 g. of formic acid.

$$126 : 46 : : 80 : X$$
$$X = 27.2$$

The theoretical yield of formic acid is therefore 27.2 g. If desired, the formic acid is recovered by dissolving the lead formate, precipitating the lead with hydrogen sulfide and distilling off the formic acid.

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[CONTRIBUTION PROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE NATIONAL INSTITUTE OF HEALTH, UNITED STATES PUBLIC HEALTH SERVICE]

THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. II. THE PREPARATION AND PROPERTIES OF GOLD–CARBON COMPOUNDS OF THE TYPE R_2AuX AND $RAuX_2$[1]

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Introduction

In 1902 Pope and Gibson[3] published a paper on the preparation of diethyl auric bromide and ethyl auric dibromide. Diethyl auric bromide was prepared by the action of ethylmagnesium bromide upon an ethereal solution of auric bromide. Ethyl auric dibromide was prepared by subjecting diethyl auric bromide, dissolved in chloroform, to the action of bromine.

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[1] Published by permission of the Surgeon-General.

[2] This work, as well as the other papers on organo–gold compounds in this series, was submitted by H. S. Isbell in 1926 to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Pope and Gibson, J. Chem. *Soc.*, 91, 2061 (1902). This early work was recently repeated and confirmed by Gibson and Simonsen (*ibid.*, 2531 (1930)), who prepared, in addition, diethyl gold iodide and diethyl gold acetylacetone.

These ethyl gold compounds are the only ones whose preparation is described in the literature. This fact appears remarkable if one examines the numerous compounds of arsenic, antimony, mercury, lead, tin and the organo-metallic derivatives of other metals which have since been described. The lack of organo-gold compounds is certainly not due to unfamiliarity of the organic chemist with the element, for gold salts have found considerable application in the identification of many organic substances, particularly amines.

In 1926 Feldt reviewed the subject of organic gold compounds. This investigator, whose research in the field of gold chemotherapy covered a period of fifteen years, had evidently overlooked the paper of Pope and Gibson and wrote as follows in the "Klinische Wochenschrift," summarizing his experience in the synthetic preparation of gold carbon compounds. "Organische Goldverbindungen waren nicht bekannt. Gold besitzt keine Verwandschaft zum Kohlenstoff. Komplexe organische Goldverbindungen in denen das Gold unmittelbar am C sitzt, sind nicht existenzfahig, zum mindesten nicht isolierbar. Monatelange dahingehende versuche schlugen daher fehl."[4] (("Organic compounds of gold are unknown. Gold has no affinity for carbon. Complex organic compounds of gold in which the gold is directly attached to carbon are incapable of existence, or at least cannot be isolated. This has been shown by prolonged experimentation.")

The Significance of the Properties of Auric Salts in the Synthesis of Organic Gold Compounds.—The failure to synthesize organic compounds may have been due to a lack of consideration of the following salient facts regarding auric salts: first, the tendency of auric salts to form compounds of the aurate type (i.e., $HAuX_4$); second, the insolubility of auric salts in most organic solvents; third, the interaction of auric salts with solvents that are commonly employed in the Grignard syntheses.

The tendency of auric salts in solution toward compound formation has been known for a long time. Thus it is postulated that if a water solution of gold chloride is acidified with hydrochloric acid, the solution contains hydrochloroauric acid, $HAuCl_4$. Again, when auric chloride is added to a water solution of sodium chloride, the sodium chloroaurate is supposed to be formed. Furthermore, a water solution of sodium chloroaurate contains fewer auric ions than a water solution of auric chloride which presumably exists in the form $H^+(AuCl_3OH)^-$. Whether this difference is merely a common ion effect or the formation of a more stable chloroaurate complex is impossible to determine from the available data, but it can be brought out in a very striking manner by the following experiment. If a water solution of auric chloride is treated with sulfanilic acid, an instant precipitation of gold results. On the other hand, if to

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[4] *Feldt, Klinische Wochenschrift,* Feb. 19, *1926.*

another sample of the same solution of gold chloride one or two moles of sodium chloride are added, followed by sulfanilic acid, it takes fifteen or more minutes (depending upon the concentration of the solution) before any precipitation of gold becomes noticeable. This experiment indicates that the concentration of auric ion, or the active oxidizing ion, has been suppressed. The change in the intensity of color of a water solution of auric chloride upon addition of sodium chloride is also quite significant.

Naturally it is to be expected that anhydrous gold chloride would also combine readily with many organic substances. The proof of the validity of this statement will be taken up in other papers.[5] For the present, suffice it to say that except for nitrobenzene and aliphatic hydrocarbons, most substances either react or form double compounds with anhydrous auric chloride or bromide. In the case of ether this combination can be illustrated by the following experiment. It was found by us that anhydrous auric chloride, under well controlled conditions, reacts with anhydrous benzene to form phenyl auric dichloride.[5] However, if we suspend the anhydrous auric chloride in anhydrous ether, or some other oxygen-containing substance, or add any of these substances to anhydrous benzene, no phenyl auric dichloride is formed.

With the above facts in mind it is not at all surprising to find that auric chloride does not react smoothly with a Grignard reagent, and that the yields of the gold carbon–compounds are very small.

Criteria Regarding Types of Gold-Carbon Compounds That May Be Prepared by the Grignard Reagent.—The facts cited above are of fundamental importance in interpreting the low yields of gold–carbon compounds by the Grignard reagent. However, in addition to the limiting factors mentioned previously, there are still others of equally vital importance. Our experience regarding these additional limitations of the use of the Grignard reagent in the preparation of organ—gold compounds may be summarized as follows.

(1) Gold–carbon compounds in which the gold is directly attached to three carbon radicals, *i. e.*, AuR_3, cannot be prepared by the Grignard reagent; at least our numerous efforts, under a variety of conditions, with a variety of radicals have been totally unsuccessful. Other indirect methods were also of no avail. We have prepared numerous compounds of the type $R_2Au(CN)$, but do not consider them, in the absence of definite proof, as compounds in which the three valences of the gold are attached directly to the carbon atoms.

(2) There appears to be a definite limitation to the use of the Grignard reagent in that it is impossible (at least we were unable to accomplish the synthesis) to prepare by that method gold-carbon compounds of the

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[5] Kharasch and Isbell, unpublished work: IV, Direct Auration; III, Gold–Nitrogen Compounds

type R_2AuX, if the radical R is a strongly electronegative radical. This limitation is forced upon us by our laboratory experiences: first, our inability, after many trials and under a variety of experimental conditions, to prepare by the use of the Grignard reagent any gold–carbon compounds of the phenyl radical and those radicals which are above the phenyl radical in the table of electronegativity of radicals[6] (the tolyl, naphthyl, *p*-methoxyphenyl, etc.); second, the successful isolation of the gold-carbon compounds of the ethyl radical and radicals below the ethyl radical in the above-mentioned table.[7] Thus, the gold-carbon compounds of the type R_2AuX of the following radicals were readily prepared: ethyl, n-propyl, isopropyl, n-butyl, isobutyl, isoamyl, cyclohexyl, benzyl and phenylethyl.

That the electronegativity of the radical as a whole is of prime importance in determining whether a stable gold–carbon compound will be formed becomes apparent from the fact that such radicals as benzyl and phenylethyl, although they contain phenyl nuclei, yielded extremely stable gold-carbon compounds. The explanation is that both of these radicals are extremely weak electronegative radicals compared with the phenyl radical and are to be found at the bottom of the table of electronegativity of radicals. The gold compounds of the benzyl and phenylethyl radicals were sufficiently stable to enable us to sulfonate the benzene ring with the aid of fuming sulfuric acid. The table of radicals thus served as an excellent guide in the preparation of gold-carbon compounds, for it enabled us to pick out successfully the range of radicals which yielded stable gold-carbon compounds.

General Properties and Stabilization of Gold–Carbon Compounds.—It has been found feasible to synthesize the compounds of the type R_2AuCl and R_2AuBr by starting with the organomagnesium halide and treating that with the corresponding gold halide. It is to be noted that irrespective of whether one starts with gold chloride and an organomagnesium bromide or gold bromide and an organomagnesium chloride, the bromides of the gold-carbon compounds were formed in each case.

The gold-carbon compounds R_2AuCl or R_2AuBr have characteristic odors, suggestive of pine needles or of bromocamphor. The odors are decidedly nauseating. The gold-carbon compounds are soluble in pyridine, benzene and chloroform, less readily soluble in ether and petroleum ether, difficultly soluble or insoluble in acetone and alcohol and practically insoluble in water. Most of them are somewhat soluble in olive oil. They are all light sensitive and are readily decomposed by heat.

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[6] Kharasch and Marker, This Journal, 48, 3130 (1926); Kharasch and Flenner (unpublished work); Kharasch and Legault (unpublished work); Kharasch and Pines (unpublished work).

[7] The gap between the phenyl and ethyl radicals still remains to be filled.

The diethyl gold chloride and bromide are well-defined crystalline solids, but as the length of the chain is increased the melting point first decreases to a minimum, while subsequent lengthening of the chain increases the melting points again. In addition to the difficulties involved in the isolation of many of the gold–carbon compounds because of their low melting points, their instability in general was a quite troublesome feature. Thus, most of the compounds R_2AuCl could be kept without decomposition for but a few days—the only compounds which may be kept for some time without appreciable decomposition are those of extremely weakly electronegative radicals, such as the benzyl and cyclohexyl radicals.

Organo–Gold Cyanides.—We were extremely fortunate in that both of the above difficulties, *i. e.*, low melting point and instability, were overcome by the replacement of the halogen by the (CN) radical.[8] This was accomplished by shaking an ether or benzene solution of the compound $R_2AuCl(Br)$ with silver cyanide. An examination of the table reveals the fact that the cyanides have the highest melting points, followed by bromides, and that the chlorides have the lowest melting points. The advantages that accrue from the fact that the decomposition points of the cyanides are so much higher than the chlorides are quite obvious.

TABLE I

STABILITY OF COMPOUNDS OF THE TYPE R_2AuX

	Chloride		Bromide		Cyanide	
Compound	Melts, °C.	Dec., °C.	Melts, °C.	Dec., °C.	Melts, °C.	Dec., °C.
Diethyl	48	48	58	58	92 Slight dec.	92–160 Shows dec.
Di-*n*-propyl	Liq.	107 Gas 120	Liq.	95	84	128–147
Di-isopropyl	Dec.	95 Gas 120	Dec.	100-130	88–90	121–133
Di-n-butyl		.....	Liq.	65	Dec.	125–130
Di-isobutyl		.....	Liq.	.....	112–113	160
Di-isoamyl		.....	Liq.	.....	70	135–140
Dicyclohexyl		180–190 Dec.	148	Dec. 140–148	152, s.d.	155
Dibenzyl	Dec.	70–110	Dec.	77 Detonates 85	Dec.	122
Diphenylethyl		.....	112–115	105–115	.....	.....

Furthermore, the cyanides of most of the compounds can be kept in brown bottles without darkening. The compounds $R_2Au(CN)$ when freshly prepared are soluble in benzene. Many of these compounds, particularly the compounds from the benzyl radical, upon standing for a period of time become insoluble in benzene, although the empirical formula of the compound remains the same.

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[8] The halogen can evidently be replaced by any negative radical. Thus, shaking the organo–gold bromides with silver sulfate gave the corresponding organo–gold sulfates.

The above-mentioned behavior of the organo–gold halides toward silver cyanide is of considerable interest if one bears in mind that auric chloride reacts with silver salts to give compounds of the chloroaurate type. The tendency toward formation of chloroaurate complexes is entirely absent under anhydrous conditions in the organic gold compounds of the type R_2AuX. However, they still form complexes with various nitrogenous substances such as pyridine, hexamethylenetetramine, etc.

Organo–Gold Sulfur Compounds.—Very striking also is the behavior of gold-carbon compounds of the type R_2AuX toward thio compounds. Thus it is well known that when an auric salt is treated with a mercaptan, the auric ion is reduced to the aurous state and the mercaptan salt of the aurous compound is formed.

$$AuCl_3 + 3HS{-}R \longrightarrow AuSR + 2RSSR + 3HCl$$

However, when gold is firmly attached to two organic radicals, it is possible to prepare the corresponding sulfur compounds

$$R_2AuX + HSC_6H_4COOH \longrightarrow R_2AuSC_6H_4COOH + HX$$

The mercaptides of these compounds while readily soluble and stable in alcohol are easily hydrolyzed in water containing less than 33% of alcohol.

Behavior of Organo-Gold Compounds toward Reducing Agents.—Gold–carbon compounds of the type R_2AuX are much more stable toward reducing agents than auric salts. Thus, while stannous chloride, sodium hydrosulfide and hydroquinone instantly reduce auric chloride, the organic gold compounds react with these reagents much more slowly. Of interest is the observation that while mercury diphenyl and diethyl when treated with dibenzyl auric bromide precipitate metallic gold, mercury dibenzyl is without any effect on that substance.

Sulfonation of Organo–Gold Compounds.—As previously indicated, the stability of organo–gold compounds toward various chemical agents increased as the electronegativity of the radical attached to the gold decreased. Notable among these properties of gold-carbon compounds of the weakly electronegative radicals is their stability toward acids. Thus, the dibenzyl and diphenylethyl auric salts were readily sulfonated under properly controlled conditions. The type of the inorganic radical X, attached to the molecule R_2AuX, made little difference in the ease of sulfonation, for the chlorides, bromides and cyanides as well as the sulfates were sulfonated by the use of fuming sulfuric acid (25% excess SO_3). It was noticed, however, that in the case of the bromides some free bromine was formed, which caused the decomposition of some of the gold compound. The sulfonated organoauric salts were usually isolated first in the form of their calcium salts. The latter by double decomposition with sodium sulfate were converted into the sodium salts.

The calcium salts of the sulfonated gold compounds are fairly soluble in water and very stable toward reducing agents. Hydroquinone, sodium formate or sodium stannite have no immediate effect, and it is only by prolonged boiling that gold can be detected in the compounds by the above reagents.

Gold–Carbon Compounds of **the Type $RAuBr_2$.**—A number of organo-gold dibromides were prepared by treatment of the compounds R_2AuBr with bromine in chloroform. The benzyl, phenylethyl and cyclohexyl gold dibromides were thus prepared. All of these substances as well as the ethyl compound described by Pope and Gibson[3] were obtained as ruby-red needles.

The organo–gold dibromides are in general much less stable than the di-organo–gold bromides. Thus, while the latter substances are quite stable toward reducing agents, the treatment of the organo-gold dibromides with stannous chloride or hydroquinone leads to the formation of metallic gold in a few minutes, while with sodium hydrosulfite an immediate separation of gold takes place.

Solutions of the organo–gold dibromides in organic solvents such as benzene, chloroform and carbon tetrachloride are intensely colored. Strikingly, however, in solvents which contain unsaturated groups, such as olive oil, oleic acid, methyl cyclohexene, etc., these ruby-red compounds yield colorless solutions. This change in color of the solution is suggestive not of a true solution of the compounds $RAuBr_2$ but rather of an addition to the double bond, yielding substances of the type R_2AuBr.

Experimental Part

The Preparation of Organo–Gold Compounds of the **Type R_2AuX.**—The general method employed for the preparation of organic gold compounds of the type R_2AuX, which gave the most satisfactory results, is given below in detail for the preparation of di-phenylethyl auric bromide. Modifications of this method whenever desirable are indicated under the respective compounds in the main table.

The Preparation **of** Di-phenylethyl Auric Bromide.—An ether solution of phenylethylmagnesium bromide was prepared from 42.8 g. of phenylethyl bromide, 6.6 g. of magnesium turnings and 500 cc. of anhydrous ether. Thirty grams of auric chloride was added to 500 cc. of anhydrous ether which previously had been cooled to −15°. To this latter solution, vigorously stirred with a mechanical stirrer, a filtered solution of the phenylethylmagnesium bromide was added dropwise.

The addition of the Grignard reagent required about fifty minutes. Although the reaction appears to be almost instantaneous, a period of ten minutes was allowed before the addition of about 50 g. of finely crushed ice. The precipitated magnesium hydroxide was dissolved in 500 cc. of 2% acetic acid and after the addition of about 200 cc. of benzene the ether–benzene solution was separated and successively washed with portions of a 5% aqueous sodium bromide solution until all gold was removed from the ether–benzene layer. The use of a dilute sodium bromide solution instead of pure water facilitated the removal of auric bromide from the ether layer. Finally, the ether–benzene solution was washed with distilled water, separated and evaporated to a small volume at room temperature in *vacuo*. Di-phenylethyl auric bromide crystallized on evaporation. The filtrate was diluted with ten volumes of 95% ethyl alcohol, which

TABLE II

ORGANIC GOLD HALIDES

Di-substituted auric halide	Yield AuCl$_3$, g. ⟶ g.	M. p.,[a] °C.	Dec. p., °C.	Gold analyses, % Calcd.	Gold analyses, % Found	Remarks
Di-ethyl chloride	2 ⟶ 0.3	48 V.s.d.	48	67.80	67.45	Dec., few days
Di-ethyl bromide	30 ⟶ 2.2	58 V.s.d.	58	...	...	AuCl$_3$, 45 g. ⟶ 5.5 g. of subst.
Di-*n*-propyl chloride	6 ⟶ 0.2	Lt. yel. oil	107, gas 120	See cyanide		
Di-*n*-propyl bromide	Small	Lt. yel. oil	95	54.42	51.7	Pine needle odor
Di-isopropyl chloride		D.	95, gas 120	See cyanide		Sl. sol. EtOH; cryst. solid, liq. at 75–80° with gold sepn.
Di-isopropyl bromide		D.	100–130	See cyanide		Cryst. solid. Dec. to liquid and gold metal
Di-*n*-butyl bromide	2 ⟶ 0.3	Liquid	65	50.40	50.19	Diff. sol. EtOH. Pine odor
Di-isobutyl bromide	2 ⟶ *ca.* 0.2	Liquid		See cyanide		Colorless oil. Diff. sol. EtOH, easily sol. pet. ether
Di-isoamyl bromide	2 ⟶ 0.2	Liquid		47.03	47.00	
Diacetyl bromide. A compound with the characteristic odor of these compounds was obtained. It contained gold and had the correct properties						
Di-benzyl chloride	2 ⟶ 0.3	D.	70–110	47.54	47.50	Diff. sol. Et$_2$O, sol. Bz, BzCH$_2$Cl
Di-benzyl bromide	2 ⟶ 0.476	D.	77, det. 85	42.94	43.44 41.70	Diff. sol. org. solv. incl. ether; more sol. Bz, BzCH$_2$Cl
Di-cyclohexyl bromide	2 ⟶ 0.081	D. 148	140–148	44.49	44.49	Sol. Bz, Et$_2$O, CHCl$_3$; olive oil, 0.113 g. in 13 cc.
Di-cyclohexyl chloride	60 ⟶ 5.5		180–190	49.49	49.53	
Di-phenylethyl bromide	30 ⟶ 3.77	112–115	105–115	40.47	40.49	
Di-phenylethyl sulfate		D.	105–108	43.30	43.21	

[a] V.s.d., very slight decomposition; D., decomposes without melting.

precipitated an additional quantity of di-phenylethyl auric bromide. The combined precipitates were crystallized from a chloroform–ligroin mixture.

Di-phenylethyl auric bromide is easily soluble in chloroform and benzene, less soluble in ether, ligroin, and almost insoluble in alcohol. It crystallizes from benzene or chloroform in long, branching needles. In a melting point tube it begins to darken at 105° and melts with decomposition at 112–115°.

TABLE III

ORGANO-GOLD CYANIDES

Auric cyanide	M. p., °C.	Dec. p., °C.	Gold analyses, % Calcd.	Found
I Di-ethyl	92	Sl. dec. 92–160	See chloride	
2 Di-n-propyl	84	128–147	63.75	63.63
3 Di-isopropyl	88-90	121–133	63.75	63.71
4 Di-*n*-butyl	Dec.	125–130	See bromide	
5 Di-isobutyl	112–113	160	58.45	58.44
6 Di-isoamyl	70	135–140	See bromide	
7 Di-benzyl	Dec.	122	48.65	48.11 48.67" 48.84[b]
8 Di-cyclohexyl	152 sl. dec.	155	50.64	50.57

[a] Benzene-soluble product. [b] Benzene-insoluble product.

Remarks

1 Cryst. solid. Sol. pet. ether, Bz, olive oil, when new; insol. on standing
2 Easily sol. olive oil. $AuCl_3$, 6 g. ⟶ 0.124 g.
3 Stable. Easily sol. olive oil, Bz, Et_2O, $CHCl_3$
4 Sol. to 0.7 *M*/100 in olive oil. Au, 6 g. ⟶ 0.35 g. Crystalline solid, but diff. to obtain in cryst. form
6 Easily sol. Et_2O, Bz, pet. ether. Faint odor
7 Dec. pt. same after six weeks. Sol. warm NH_4OH
8 Insol. EtOH, EtOAc, Me_2CO; very diff. sol. Et_2O; sol. Bz, $CHCl_3$

Preparatian of Di-phenylethyl Auric Sulfate.—A benzene solution of di-phenylethyl auric bromide was mixed with a large excess of silver sulfate and shaken until a test portion of the filtrate gave a negative test for halogen. The filtrate was evaporated in *vacua.* A white crystalline residue remained which was dried to constant weight in vacuo at 40°.

Anal. Subs., 0.0766: Au, 0.0331. Calcd. for $C_{32}H_{36}Au_2SO_4$: Au, 43.30. Found: Au, 43.21.

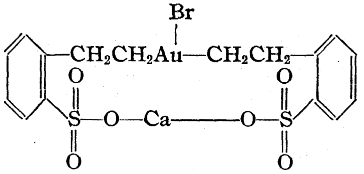
Di-phenylethyl auric sulfate is easily soluble in chloroform, less soluble in benzene, ether and low boiling ligroin and very slightly soluble in ethyl alcohol. It is insoluble in water. In a melting point tube it begins to darken at about 105" and decomposes violently at about 108°.

Sulfonation of Di-phenylethyl Auric Bromide.—To 1.25 g. of di-phenylethyl auric bromide dissolved in 10 cc. of chloroform and cooled to −15°, 6.25 cc. of cold fuming sulfuric acid (25% excess SO_3) was slowly added while the mixture was kept in an ice-salt bath at −15°. After the solutions were thoroughly mixed the temperature was allowed to rise by removing the flask from the ice-bath. The temperature was allowed to rise to about 10°. That the reaction had proceeded to completion was ascertained by the facts that evaporation of a few drops of the chloroform layer did not give a residue of unchanged di-phenylethyl auric bromide and that the acid layer when poured into water gave a clear solution. The mixture was then cooled again to about −10° and slowly poured with stirring into a mixture of 50 g. of crushed ice containing 1.25 g. of calcium bromide. The resulting solution was kept cold and, as soon as possible, neutralized with 25 g. of calcium carbonate. The solid that separated was collected on a small Büchner funnel and washed with a small amount of water. The residue showed only a faint test for gold while the filtrate gave a very strong test.

The filtrate was then mixed with about five volumes of absolute alcohol. A precipitate of calcium sulfate formed which was collected on a filter. The filtrate was then evaporated in vacuo at 20° to a volume of about 10 cc. It was then diluted again with three volumes of absolute alcohol and the small amount of calcium sulfate which formed was collected on a filter. The resulting filtrate was practically free from calcium sulfate and upon the addition of 500 cc. of absolute alcohol a very fine white precipitate separated. After standing overnight in the ice box the precipitate was collected on a filter, washed with alcohol and dried *in vacuo*. The weight of the dry material was 0.84 g.

The compound was further purified by dissolving it in the smallest possible quantity of water and precipitating it by the addition of absolute alcohol. The resulting precipitate was very fine and the solution filtered slowly. It was dried in *vacuo* over phosphorus pentoxide to constant weight.

Anal. Subs., 0.2064: Au, 0.0596; subs., 0.1088: 2.9 cc. of 1.098 *N*/20 KSCN; 0.1511: 4.0 cc. of 1.116 *N*/10 $KMnO_4$. Calcd. for $C_{16}H_{16}O_6S_2CaAuBr$: Au, 28.77: Br, 11.66; Ca, 5.85. Found: Au, 28.88; Br, 11.69; Ca, 5.92. This corresponds to the formula[9]



The calcium salt when heated turns dark and begins to decompose at about 130". It is insoluble in alcohol and organic solvents. It is fairly soluble in water. Strikingly, it is much more soluble in solutions of calcium chloride, bromide or sodium bromide than in pure water, thus recalling to mind the characteristics noted for ammonium succinimide aurate.

A water solution of the calcium salt is not reduced by hydroquinone, stannous chloride or sodium formate, thus indicating an extremely low ionization of the gold from the carbon atoms.

The following points are of importance in the sulfonation of the gold compounds. (1) There was some decomposition of the organo–gold bromide by the fuming sulfuric acid, which resulted in the formation of some free bromine. This bromine decomposed some of the organic gold–carbon compound and led to the formation of some auric bromide. Thus, it would appear that the use of the organ—gold chlorides might be more advantageous than the use of bromides.

(2) Calcium bromide was added to the ice prior to pouring in the sulfonated mixture because it was found that the addition of calcium bromide or chloride at this point prevented the formation of much metallic gold.

(3) The success of the sulfonation depends to a large extent upon the technique. The following additional points are of importance. The period during which the fuming sulfuric acid is allowed to react must be regulated. A few drops of solution may be

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[9] It is understood, of course, that a molecular weight determination is essential before one could state with certainty that the simple formula given for the calcium salt of the sulfonated di-phenylethyl auric bromide is correct or whether a number of the sulfonated molecules are linked together through the calcium atom.

tested in water or the chloroform layer may be sampled and its residue on evaporation noted.

The concentration of the solution? in vacuo is usually attended with some decomposition unless a low temperature is maintained.

The precipitated calcium salt of the gold compound is very fine and may be best separated by the use of a centrifuge.

Sulfonation of Di-phenylethyl Auric Sulfate.—One gram of di-phenylethyl auric sulfate was gradually stirred into 4 cc. of fuming sulfuric acid (25% excess SO_3) kept at −15". After thorough mixing, the temperature was allowed to rise to about 15°, when the di-phenylethyl auric sulfate seemed to be completely in solution. The mixture was then cooled to −10° and poured on 50 g, of finely crushed ice. A nearly clear solution resulted. The acid was neutralized by adding calcium carbonate. The calcium sulfate and excess calcium carbonate was collected on a filter and the filtrate poured into 15 volumes of absolute alcohol. A flocculent precipitate resulted which consisted of the calcium salt of the sulfonated organic gold compound and a small amount of calcium sulfate. The precipitate was collected upon a filter. As the filtrate contained only a trace of gold, it was discarded. The precipitate was extracted with a few cc. of water. The gold compound went into solution leaving an insoluble residue of calcium sulfate. The water solution of the calcium salt of the sulfonated di-phenylethyl auric sulfate was poured into ten volumes of absolute alcohol. A very fine white precipitate resulted which was collected on a filter.

The compound corresponded in properties to that obtained by the sulfonation of the di-phenylethyl auric bromide. Thus it did not give the usual gold test with stannous chloride or hydroquinone but after decomposition by either heat or bromine a strong test for gold was obtained. Qualitative tests for calcium and sulfate ion were also obtained. The compound was water soluble.

Dibenzyl auric chloride and dibenzyl auric cyanide were also sulfonated in a manner similar to the di-phenylethyl auric bromide. The reaction proceeded smoothly and a solution was obtained which was not reduced by hydroquinone and exhibited similar properties to the corresponding di-phenylethyl gold compounds.

Organo–Gold Sulfides

The Preparation of **Dicyclohexyl** Auric **Thiosalicylate.**—A quantity of dicyclohexyl auric chloride (1.9935 g.) was dissolved in 20 cc. of benzene, mixed with 0.7520 g. of thiosalicylic acid dissolved in 30 cc. of ethyl alcohol and the calculated equivalent of an alcoholic solution of potassium hydroxide ($N/2$) necessary to react with the hydrochloric acid formed was added. The mixture was evaporated to dryness and the residue was washed free from chlorides with cold water followed by several washings with cold alcohol. The product was easily and completely soluble in one equivalent of sodium hydroxide dissolved in 50% alcohol, from which it was precipitated by the addition of acid. The product thus obtained was dried to constant weight over phosphorus pentoxide.

Anal. Subs.: 0.1170: Au, 0.0446. Calcd. for $(C_6H_{11})_2AuSC_6H_4COOH$: **Au,** 38.18. Found: Au, 38.12.

The compound decomposed at 173–180°. It is quite stable when kept in brown bottles, as indicated by the fact that even after several months the salt of the compound was still completely soluble in dilute alcohol.

The Preparation of Phenylethyl Auric **Dibromide.**—A chloroform solution of diphenylethyl auric bromide was mixed with a chloroform solution of bromine which contained approximately two equivalents of bromine. Upon spontaneous evaporation of the solvent ruby-red needles which formed in fan-like clusters were obtained. These were washed first with a small quantity of chloroform, then ether, and dried in *vacuo* at 40° to constant weight over phosphorus pentoxide.

Anal. Subs., 0.0542: Au, 0.0231. Calcd. for $C_8H_9AuBr_2$: Au, 42.67. Found: Au, 42.62.

The compound is difficultly soluble in chloroform, almost insoluble in ether, benzene, petroleum ether and water. Phenylethyl auric dibromide decomposes at 150–160°.

Preparation of Ethyl Auric **Dibromide.**—This compound was prepared by the method used by Pope and Gibson. Three grams of di-ethyl auric bromide was dissolved in 25 cc. of chloroform and 1.5 g. of bromine dissolved in 30 cc. of chloroform was added. The mixture was allowed to stand overnight in an open beaker. All of the chloroform had evaporated and a reddish black residue remained. This was extracted successively with 15 cc. of cold chloroform and with five portions of petroleum ether. A quantity of unchanged diethyl auric bromide was thus recovered. The residue was washed with water and finally crystallized from chloroform; 0.95 g. of ethyl auric dibromide was thus obtained. The compound forms red needles difficultly soluble in chloroform and easily soluble in alcohol.

Reactions of Ethyl Auric Dibromide: Behavior with Unsaturated Derivatives.—Solutions of ethyl auric dibromide in all saturated organic solvents are intensely colored. However, solutions of this substance in unsaturated solvents are practically devoid of any color. Thus, the ethyl auric dibromide dissolves to a colorless solution in olive oil, methylcyclohexene, cyclohexene, etc. This phenomenon is probably due to the addition of ethyl auric dibromide to the double bond, giving rise to compounds of the type R_2AuBr which have very little color.

Preparation of Benzyl Auric **Dibromide.**—To 0.202 g. of di-benzyl auric bromide dissolved in 10 cc. of chloroform, 12 cc. of 0.0962 N bromine dissolved in carbon tetrachloride was added. After standing for two days the solvent was evaporated and the residue was washed with water and finally crystallized from chloroform.

Anal. Subs., 0.0745: Au, 0.0327. Calcd. for $C_6H_5CH_2AuBr_2$: Au, 44.01. Found: Au, 43.89.

The compound separates from chloroform in the form of dark needles. It is soluble in acetone and alcohol, imparting to these solvents a yellow color, while red solutions are obtained in chloroform and benzene. The compound is rather insoluble in carbon tetrachloride, petroleum ether and ether. Benzyl auric dibromide decomposes at about 140°. The change in appearance was slight and gradual over a considerable temperature range.

The Preparation **of Cyclohexyl** Auric **Dibromide.**—To 0.9 g. of di-cyclohexyl auric bromide dissolved in 20 cc. of chloroform, 48 cc. of 0.09 N bromine solution in chloroform was added. The mixture was allowed to stand overnight. The residue upon evaporation of the chloroform was washed with water and crystallized from chloroform.

Anal. Subs., 0.1025: Au, 0.0456. Calcd. for $C_6H_{11}AuBr_2$: Au, 44.81. Found: Au, 44.53.

The compound is obtained from chloroform in the form of dark red needles which decompose without melting at 150°. It is soluble in benzene, chloroform and carbon tetrachloride with a red coloration. However, yellow solutions are obtained in alcohol and ethyl acetate. Similar to the ethyl compound, cyclohexyl gold dibromide gives colorless solutions when dissolved in unsaturated solvents, like olive oil or methylcyclohexene.

Summary

1. The limitations of the Grignard reagent in the preparation of gold-carbon compounds, of the type R_2AuX, are discussed.

2. It is pointed out that the table of electronegativity of radicals serves as an excellent guide in the preparation of gold compounds R_2AuX. Thus it has been found that gold compounds of the ethyl radical and all the radicals below the ethyl radical in that table can be readily prepared from the appropriate Grignard reagents and auric chloride. However, no stable gold–carbon compounds R_2AuX of the phenyl radical, or radicals more strongly electronegative than the phenyl radical, can be prepared by that method.

3. The stabilization of gold–carbon compounds R_2AuX through the preparation of the corresponding cyanides is described.

4. It is shown that although no inorganic sulfides of trivalent gold are known, when two of the valences of the gold are attached to organic radicals as in R_2AuX, it is possible to prepare compounds of the type $R_2Au—S—R$. It is further shown that these substances are hydrolyzed in water solution, a behavior characteristic of the amphoteric elements of the third group.

5. The stability toward acids of gold compounds R_2AuX of weakly electronegative radicals is discussed, and the sulfonation of di-phenylethyl auric bromide and di-benzyl auric chloride is described.

6. The gold compounds R_2AuX have been found to be extremely stable toward powerful reducing agents.

7. The preparation of a number of gold compounds $RAuX_2$ is described.

8. It is shown that compounds of the type $RAuX_2$ are extremely unstable toward reducing agents.

9. The fact is emphasized that compounds $RAuX_2$, while insoluble in water, dissolve readily in sodium chloride solution. This fact is explained upon the assumption that complexes of the chloroaurate type are thus formed.

10. It is shown that gold compounds $RAuX_2$ are intensely colored in chloroform solution, but that their colors disappear instantly when substances containing ethylene bonds are added to them. Direct addition of the gold complex to the double bond is postulated.

11. The preparation of a large number of organo-gold compounds is described and their behavior toward many reagents is given.

CHICAGO, ILLINOIS

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTIONS OF ACETALDEHYDE OVER ZINC CHROMITE UNDER A PRESSURE OF 210 ATMOSPHERES

BY HOMER ADKINS, KARL FOLKERS AND MAURICE KINSEY

RECEIVED MAY 1, 1931 PUBLISHED JULY 8, 1931

The formation of esters and the higher alcohols by the hydrogenation of carbon monoxide or from the lower alcohols under similar conditions may well depend upon the behavior of aldehydes which are first formed. It was thus of interest to ascertain the nature and ratio of products formed from acetaldehyde under the experimental conditions used for the reactions referred to above. A rather extensive study of the condensation of acetaldehyde over a zinc chromite catalyst at 360° under a pressure of 200 atmospheres of hydrogen has therefore been made.[1]

The zinc chromite catalyst used in this work was prepared in the same way as has been previously described for copper chromite,[2] except that a mole of zinc nitrate was substituted for a mole of copper nitrate. The general process used in preparing the zinc chromite catalyst was first described by Lazier.[3]

The liquid product from the reactions of acetaldehyde over the zinc chromite catalyst is a mixture of water and saturated and unsaturated alcohols, esters, aldehydes, lactones, hydrocarbons and acids. All attempts to separate this mixture into its components by fractionation were unsuccessful. On this account and because of the tendency for the unsaturated compounds to condense it was necessary to reduce the carbonyl and alkene linkages and to saponify the esters prior to further attempts for the isolation of pure compounds.

All of the significant findings in connection with these attempts to isolate, identify and estimate the products from the condensation of acetaldehyde over a zinc chromite catalyst may be illustrated by describing the results of a single experiment in which the methods used were the resultant of the experience in many similar experiments carried out on a smaller scale. In this experiment a mixture of two parts of acetaldehyde and one part of ethanol was pumped at the rate of 270 cc. per hour over 30 cc. (30 g.) of

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[1] A paper having to do in part with material herewith presented was published in *Industrial and Engineering Chemistry*, 22, 1046 (1930). The previous paper was prepared as an outline of an oral report given before a symposium at the Cincinnati (1930) meeting of the Society, and was not intended for publication. It was in proof before the authors were aware that it had been submitted to the Editor by the Secretary of the Symposium.

[2] Adkins and Connor, THIS JOURNAL, 53, 1091 (1931).

[3] Lazier, British Patent 301,806, June 12, 1926; *Chem. Abstracts*, 23, 4306 (1929); U. S. Patent 1,746,783, February 11, 1930; *Chem. Abstracts*, 24, 1649 (1930).

pellets of zinc chromite in a steel bomb held at 360±5°, under a pressure of 210±10 atmospheres of hydrogen. The apparatus and procedure used for this purpose have been previously described.'

The general scheme followed in working up the reaction product was as follows. The reaction product weighing 4732 g. was fractionated giving fraction A (2941 g.), b. p. from 21 to 85°; fraction B (762 g.), b. p. from 85 to 170°; fraction C (519 g.), b. p. 50–160° (2 mm.); and fraction D (419 g.), which was not distilled. Widmer fractionating columns with glass spirals were used for all fractionations except that a Claisen flask was used in obtaining fraction C. One of the Widmer columns had a spiral 50 cm. in length while the other contained a spiral 15 cm. in length. When necessary the columns were heated externally in a shield containing spirals of nichrome wire.

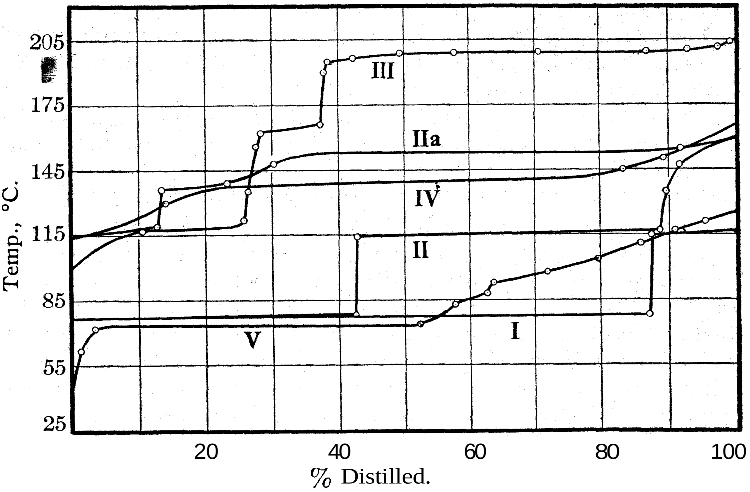

Fig. 1.—Distillation curves obtained in the fractionation of products from the condensation of acetaldehyde.

Fraction A contained 6 millimoles of aldehyde per gram according to the sodium sulfite method of analysis. An aliquot of 260 g. was hydrogenated at 150–175° under a pressure of 150 atmospheres over a nickel catalyst by the method previously described.[4] Six millimoles of hydrogen per gram of fraction A was absorbed and the hydrogenated product contained 1.34 millimoles of ester per gram. The hydrogenated aliquot was saponified and the alcohols dried. These alcohols (203.7 g.) were fractionated with the result shown in Curve I of Fig. 1.

Fraction B was washed with a 5% sodium hydroxide solution in order to remove acids. The neutral compounds were recovered from the wash water by distillation and salting them out from the distillate. The neutral compounds so obtained were returned to fraction B which was hydrogenated after being partially dried over magnesium sulfate. The hydrogen absorption was 6.7 millimoles per gram and the ester content was

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[4] Adkins and Cramer, This Journal, 52, 4349 (1930).

2.23 millimoles per gram. The fraction was then saponified and 246.7 g. of neutral compounds obtained. The fractionation of 211 g. of this material is shown in Curve II, there being a residue of 35.7 g. The portion boiling at 117–160° was refractionated as shown in Curve IIa. The acids originally washed out of fraction B were added to the acids obtained from the saponification and after drying over magnesium sulfate 117.6 g. of acids was obtained. The fractionation of 104.8 g. of acids is shown in Curve III, there being 12.8 g. of residue.

Fraction C upon hydrogenation absorbed 7.6 millimoles of hydrogen per gram. It had an average molecular weight of 195 as determined by the depression of the freezing point of benzene and contained 0.5 millimole of acids, 2.9 millimoles of esters and 1.3 millimoles of alcohols per gram. This latter value was calculated from the saponification value of the fraction as compared with the value after it had been acetylated through the use of acetic anhydride. Fraction C after hydrogenation was saponified and there was obtained after drying 237.7 g. of neutral compounds, and 112 g. of acids. The fractionation of 24 2 g. of the neutral compounds is shown in Curve IV of Fig. 1. The residue weighed 213.4 g. Ninety per cent. of the acids was taken for fractionation at 3 mm. Forty-six grams distilled as shown in Curve V, leaving a residue of 54.7 g.

The Identification of Products.—Curve I. This fraction was made up exclusively of ethanol and n-butanol, which were identified by the boiling points and by the preparation of the 3,5-dinitrobenzoates.

Curve *II*. The fractions boiling 77–78° and 115–116° were identified as ethanol and butanol as above. The fraction 117–160" was a mixture of butanol and hexanol which were refractionated as indicated below.

Curve *IIa*. The fraction 115–119° was butanol and that from 136–148° contained p-xylene and is referred to again under Curve IV. The main portion of this fraction (b. p. 148–154°) was identified as n-hexanol by comparing the melting point of its 3,5-dinitrobenzoate with that from an authentic sample of n-hexanol.

Curve *III*. The lower fraction was acetic acid, the middle one was butyric acid and the highest and chief fraction was caproic acid. These were identified by their boiling points and also by the preparation of the *p*-toluidide of acetic acid and *p*-bromoanilides of butyric and caproic acids, and the determination of mixed melting points with authentic specimens. However, the caproic acid was not pure, since a 1.000-g. sample at 25° required 8.26 ml. of 1 N alkali for its neutralization but when refluxed with an excess of alcoholic alkali 8.63 ml. of alkali reacted. From these data it may be calculated that the sample was 95.8% caproic acid and 4.2% *a* lactone having a saponification equivalent of 113.3. This value is almost identical (114) with that for caprolactone. The caproic acid fraction was shown to contain none of the isomeric diethylacetic acid by the following experiment. The p-bromoanilide of caproic acid, m. p. 103–104°, was obtained in a 60% yield from a sample of caproic acid of known purity, while a 61% yield of the derivative of m. p. 104–105° was obtained from the sample of acid referred to above. Recrystallization of these two preparations of the p-bromoanilide of caproic acid raised the melting points to 105–105.5° and reduced the yields to 55 and 58%, respectively.

Curve *IV*. The lower-boiling portions of this material was n-butanol while the highest was n-hexanol with perhaps some octyl alcohol. The chief fraction of 136–145° was identical with that indicated on Curve IIa and was shown to be p-xylene. This fraction after treatment with sodium and distillation had the following physical characteristics: b. p. 137–138°, n_{25} 1.4910, d_{25}^{25} 0.8595, mol. wt. by lowering of freezing point of benzene, 105.9, 100.5. The trinitro derivative after two recrystallizations melted at 138–140°, which was not changed when the unknown substance was mixed with the trinitro derivative of an authentic sample of p-xylene supplied by Dr. Carl S. Marvel.

p-Xylene has a molecular weight of 106 and has been described[6] as boiling at 137.5° and as having d_{25}^{25} 0.8593. The trinitro-*p*-xylene is reported to melt at 138.5–139°.[6] The identification of *p*-xylene in the reaction mixture was so unexpected that the whole experiment on the condensation of acetaldehyde was repeated on the same scale as before. *p*-Xylene was again obtained in a similar quantity, so that there can be no doubt as to its formation in these experiments. The fact that *p*-xylene did not undergo hydrogenation when fraction C was subjected to the action of nickel and hydrogen is due no doubt to the effect of water in the reaction mixture inhibiting the hydrogenation of the benzenoid ring.[7]

***Curve** V.* About 79% of the material boiling 72–74° (3 mm.) was caproic acid as identified by its *p*-bromoanilide, mixed melting points being taken.

There remained to be identified the neutral compound boiling above 160" and the acids boiling above 205°. No specific compound except perhaps octyl alcohol has been identified among these mixtures so it is possible only to describe their general character. The neutral compounds boiling above 160° are mixtures of alcohols and hydrocarbons. This is indicated by the fact that the acetylation values are always greater than the average molecular weight as determined cryoscopically. Further, by the treatment of the mixtures with phthalic anhydride a residue was obtained which apparently contained no more than 4% of any alcohol, yet which had a boiling point of 55–75° (8 mm.), approximately the same as the alcohol mixture from which it was separated and an average molecular weight of 144. This residue was not entirely soluble in cold concentrated sulfuric acid. Attempts to separate these inert compounds completely from the alcohols by means of metallic sodium were uniformly unsuccessful. However, an alcohol boiling in the temperature range (190–191.5°) for n-octyl alcohol was obtained by the hydrolysis of the sodium alkoxides so obtained. The 3,5-dinitrobenzoate ester of this alcohol melted 4–7° lower than the ester of an authentic sample of n-octyl alcohol. The saponification equivalent of the acetate of this alcohol indicated a molecular weight of 184 as compared with a value of 172 for octyl acetate. Glycols were apparently absent from the neutral compounds for the saponification equivalent from the acetylated neutral compounds was always considerably more than the average molecular weight as determined by the cryoscopic method. A comparison of acetylation values obtained before and after hydrogenation indicated no increase in hydroxyl groups, so that aldehydes and ketones must have been absent from fraction C.

The acids of fraction C from the saponification of the esters always contained lactones or acyloxy acids after they had been subjected to distillation. This is evidenced by the fact that 25 to 50% more alkali was required for the neutralization of a sample of these fractions at 100" than was required at 25°. Further, .it was found that after acetylation twice as much alkali was required to saponify a fraction at 100° as was required to titrate the sample at 25°.

There are given in Table I the weights of products calculated to be present in the reaction mixture after hydrogenation. For convenience in calculation and tabulation the assumption is made that acetic, butyric and caproic acids were in the form of ethyl esters, while the butyl, hexyl and higher alcohols were present as such. This assumption ignores the fact that in a mixture of acids, esters and alcohols, alcoholysis will occur so

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[5] Perkin, J. *Chem. Soc.*, 69, 1193 (1876).

[6] Nulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 202.

[7] *Cf.* Adkins, Zartman and Cramer, THIS JOURNAL, 53,1425 (1931).

that all possible esters will be formed. The figures in Table I are calculated for the data given in Fig. 1, and elsewhere in this paper.

TABLE I

THE WEIGHT OF THE PRODUCTS (G.) AFTER HYDROGENATION

Ethyl alcohol	1800	Higher alcohols	180
Ethyl alcohol (from acetaldehyde)	593	Inerts (hydrocarbons)	77
Ethyl acetate	420	Ethyl butyrate	17
n-Butyl alcohol	456	Ethyl caproate	143
n-Hexyl alcohol	14	Higher acids and lactones	127
p-Xylene	19	Residue	419

Hypothesis Concerning the Formation of Alcohols and Esters from Acetaldehyde.—We are now in a position to consider the reactions by which alcohols and esters of higher molecular weight may be synthesized from acetaldehyde. The formation of ethyl acetate can hardly be explained except as a result of an autoxidation–reduction reaction (equation I) in which the zinc chromite plays the Same role as the metallic alkoxide in the well-known Tischtschenko reaction.

$$2CH_3CHO = CH_3COOC_2H_5 \qquad (I)$$

The similar autoxidation–reduction of alcohols over oxide catalysts has recently been observed.[8] The formation of butanol and its possible precursors crotonyl alcohol, crotonic aldehyde and butyraldehyde, would result from a combination of the reactions shown in equations II to VIII, inclusive.

$$2CH_3CHO = CH_3CHOHCH_2CHO \qquad (II)$$
$$CH_3CHOHCH_2CHO = CH_3CH{=}CHCHO + H_2O \qquad (III)$$
$$CH_3CH{=}CHCHO + C_2H_5OH = CH_3CH_2CH_2CHO + CH_3CHO \qquad (IV)$$
$$CH_3CH{=}CHCHO + H_2 = CH_3CH{=}CHCH_2OH \qquad (V)$$
$$CH_3CH{=}CHCH_2OH = CH_3CH_2CH_2CHO \qquad (VI)$$
$$CH_3CH_2CH_2CHO + H_2 = CH_3CH_2CH_2CH_2OH \qquad (VII)$$
$$CH_3CH_2CH_2CHO + C_2H_5OH = CH_3CH_2CH_2CH_2OH + CH_3CHO \qquad (VIII)$$

There is no direct evidence that reaction II occurs over oxide catalysts, but the aldol reaction is known to occur under such a wide variety of conditions that its tentative assumption seems justifiable. G. T. Morgan[9] has formulated the formation of the higher alcohols from carbon monoxide as depending upon the aldol reaction. The dehydration of an alcohol (equation III) has long been known to occur over a variety of oxide catalysts. Reaction IV was recently shown to take place over oxide catalysts[10] while reactions V and VII are hydrogenations of a type for which zinc

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[8] Adkins and Folkers, THIS JOURNAL, 53, 1420 (1931).

[9] Morgan, *Proc. Roy. Soc.* (London), 127A, 247 (1930).

[10] Adkins and Wcston, THIS JOURNAL, 51, 2430 (1929).

chromite is quite active.[11] The occurrence of reaction VI in the case of allyl alcohol was also recently observed.[12]

The formation of small amounts of butyrates (or crotonates) would be expected as the result of a reaction similar to equation I except that butyraldehyde or crotonic aldehyde played the role of acetaldehyde

$$2CH_3CH{=}CHCHO = CH_3CH{=}CHCOOCH_2CH{=}CHCH_3 \qquad (IX)$$

The formation of caproates (or their unsaturated precursors) can hardly occur exclusively as a result of a similar reaction, for the amount of hexyl alcohol in the reaction mixture is very much less than molecularly equivalent to the acid. This is not surprising in view of the great excess of acetaldehyde which would be present at any reaction surface and thus favor a reaction of the type indicated in equation X.

$$CH_3CH{=}CHCH{=}CHCHO + CH_3CHO = CH_3CH{=}CHCH{=}CHCOOC_2H_5 \qquad (X)$$

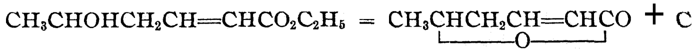
The formation of the hexadienal represented in equation X would result from a repetition of the aldol reaction followed by dehydration in which crotonaldehyde reacted with acetaldehyde as in equation XI.

$$CH_3CH{=}CHCHO + CH_3CHO = CH_3CH{=}CHCH{=}CHCHO + H_2O \qquad (XI)$$

Hydroxy acids as esters would result if a partly undehydrated aldol would react as in equation XII in a fashion similar to that indicated in equation X.

$$CH_3CHOHCH_2CH{=}CHCHO + CH_3CHO = CH_3CHOHCH_2CH{=}CHCO_2C_2H_5 \qquad (XII)$$

Esters of such hydroxy acids would readily give lactones as indicated in equation XIII.



$$CH_3CHOHCH_2CH{=}CHCO_2C_2H_5 = CH_3\underbrace{CHCH_2CH{=}CHCO}_{O} + C_2H_5OH \qquad (XIII)$$

Morgan in a discussion of the formation of higher alcohols and aldehydes from carbon monoxide and hydrogen states that "the aldolization hypothesis accounts for the products hitherto isolated, but it also postulates the transitory existence of intermediate hydroxyaldehydes and glycols which have not so far been detected." The detection in the present investigation of esters of hydroxy acids which would be derived from such hydroxy aldehydes thus lends strong support to the aldolization hypothesis.

The xylene was chiefly obtained from fraction C of the hydrogenated and saponified reaction mixture which boiled above 170". It could not have been there as such because its boiling range (136–139°) is too low and *n*-hexanol, which boils higher (151–154°), was readily obtained from the fraction B boiling below 170". That it was chiefly formed during the distillation of fraction C is further evidenced by the fact that water, which was not originally present in the mixture undergoing distillation, appeared

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[11] Adkins and Connor, THIS JOURNAL, 53,1091 (1931).

[12] Constable, *Proc. Roy. Soc.* (London), **113A,** *254* (1926); Adkins and Weston, THIS JOURNAL, 51,2430 (1929).

in the distillate. It is probable then that xylene resulted from the dehydration accompanied by cyclization of an unsaturated octyl alcohol or aldehyde.

Summary

The reactions of acetaldehyde over a zinc chromite catalyst at 360° under a pressure of 210 atmospheres of hydrogen resulted in the formation of a complex mixture of saturated and unsaturated alcohols, aldehydes and esters. After hydrogenation of this product over nickel the following products were identified and estimated: *n*-butanol, *p*-xylene, n-hexanol and the esters of acetic, butyric and caproic acids. The chief components of the mixture were ethyl acetate, butyl acetate and ethyl caproate. There were also produced in considerable amounts higher alcohols, lactones, hydrocarbons and acids. The synthesis of these products may be accounted for as the result of aldol and Tischtschenko-like reactions accompanied by such dehydrations, hydrogenations, autoxidation–reductions and intramolecular rearrangements as have been demonstrated previously to occur over oxide catalysts.

MADISON, WISCONSIN

[CONTRIBUTION NO. 71 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE PREPARATION OF FLUORENONE FROM FLUORENE AND FROM DIPHENIC ACID

BY E. H. HUNTRESS, E. B. HERSHBERG AND I. S. CLIFF

RECEIVED MAY 1, 1931 PUBLISHED JULY 8, 1931

In the extension of various studies in progress in this Laboratory[1] it became necessary to secure an adequate supply of fluorenone. Of the numerous reactions in which the formation of fluorenone has been noted, the most promising seemed to be the oxidation of fluorene. Since the published methods do not indicate the best results, we have studied the process in detail. Our results are expressed in the specific directions and accompanying notes in the Experimental Part.

During the course of the work, however, it was observed that fluorenone could be obtained in substantially quantitative yield merely by the action of heat upon diphenic acid. Since the latter is readily preparable from commercial anthranilic acid, this mode of formation of fluorenone has the advantage of starting with conventional intermediates. Careful search of the literature yielded no reference to the action of heat alone upon diphenic acid save the statement[2] that when heated 10° above its melting point, (*i.e.*, at 238°) for half an hour, no diphenic anhydride was isolated. The

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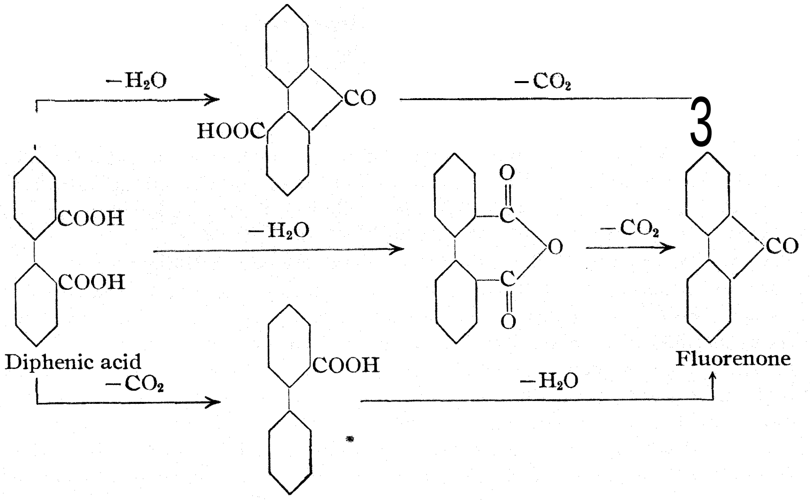
[1] Moore and Huntress, THIS JOURNAL, 49, 1324–1334, 2618–2624 (1927).

[2] Underwood and Kochmann, *ibid.*, 45, 3071–7 (1923).

formation of fluorenone and carbon dioxide at higher temperature might be accounted for by several possible mechanisms, as follows:



Although our purpose was not to study the mechanism of the reaction, we have observed that the same result is obtained whether the starting material be diphenic acid, fluorenone-4-carboxylic acid or diphenic anhydride. Since a trace of diphenyl was found in the product, decarboxylation of diphenic acid evidently occurs very slowly as compared with ring closure. It seems probable, since the keto acid and diphenic anhydride can be interconverted under certain conditions, that both types of ring closure are involved.

By means of following the yields of carbon dioxide obtained upon heating fluorenone-4-carboxylic acid, it was found that a temperature of 360" sufficed for quantitative splitting out of carbon dioxide. Application of similar conditions to diphenic acid gave similar results. Acting on this preliminary study, runs were carried out on a larger scale, measuring the resultant fluorenone directly. It was found also that good results were obtained using a crude diphenic acid not subjected to the usual zinc dust-acetic acid purification.

Experimental Part

Fluorenone by Oxidation of **Fluorene.**—Equip a 3-liter ring-necked flask with an addition tube carrying a 500-ml. dropping funnel and a water condenser. Place in the flask 200 g. (1.2 moles)[2a] of technical fluorene (Note 1), add 400 ml. of technical glacial

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[2a] Since acceptance of this paper for publication, Mr. W. W. Hartmann, Department of Synthetic Chemistry, Eastman Kodak Company, has found that these directions may be applied to ten times the quantities here given, the oxidation being carried out in a 22-liter flask, and the final yield of pure recrystallized fluorenone amounting to 1450 g., or 66.8% of the calculated yield.

acetic acid and heat to gentle boiling. In another flask dissolve 600 g. of technical crystals of sodium bichromate (Note 2) in a warm mixture of 800 ml. of glacial acetic acid and 200 ml. of water. By means of the dropping funnel (Note 3) add this warm oxidizing solution in a slow steady stream to the boiling fluorene solution, so that boiling is never interrupted (Note 4) and no precipitation of lumps occurs. This will require about half an hour, as at first the reaction is quite vigorous. The mixed solutions are then refluxed for two and one-half hours more. The deep green liquid is then poured into 4 liters of ice water, allowed to stand for at least two hours and finally filtered through cloth on a 120-mm. Büchner funnel. The first wash water should contain a little sulfuric acid to avoid possible hydrolysis of the chromium salts, but the residue on the filter is presently washed free from all trace of chromic ion with pure water. If air dried at this point the bright yellow residue weighs 190–200 g.

Place the air-dried crude fluorenone in a 500-ml. Claisen distilling flask arranged to distil into an ordinary 300-ml. distilling flask, the Claisen side-arm serving as the only condenser. The Claisen flask is provided with the usual tube for the admission of air in vacuum distillations. The upper part of the Claisen may advantageously be wound with asbestos paper or twine. The flask is preferably heated with an electric cone heater as this facilitates smooth distillation. The receiver is connected to a vacuum pump (suitably protected from vapors and preferably arranged with pressure regulator) and the fluorenone distilled under reduced pressure. Toward the end of the distillation the clear bright yellow liquid will commence to acquire an orange tinge, the appearance of which serves as a convenient signal to stop distillation. The temperature range of distillation is not particularly important because its purpose is merely to remove rubicene and other highly colored impurities which cannot be separated by crystallization. Fluorene, if still present, is removed during the subsequent recrystallization.

The clear bright yellow distillate is dissolved in that number of ml. of benzene numerically equal to its weight in grams, this solution is warmed and to it is slowly added twice the benzene volume of petroleum ether, b. p. 30–60°, in such a way that no permanent separation of precipitate occurs. On allowing this solution to stand, extraordinarily beautiful crystals of fluorenone separate. These are filtered off, washed with petroleum ether and dried in the air. The yield based on the original crude fluorenone is 60–70% of crystals melting at 83.0–83.5°, uncorr.

Notes on the Preparation of Fluorenone

1. The purification of the technical fluorene prior to oxidation has no advantage. When fluorene which had been four times recrystallized from alcohol to a freezing point of 113° was used in this process, 70% of pure fluorenone was ultimately obtained. Precisely similar treatment of unrecrystallized hydrocarbon gave repeatedly 60–65% of final pure product. This slight difference in yield does not warrant the time and trouble required for preliminary purification. In this connection the recommendation of Thiele and Henle[3] that fluorene is best purified by recrystallization from alcohol containing sodium ethylate was tested, but the color and freezing points of the product from alcohol with or without sodium ethylate were substantially the same.

2. The use of a higher proportion of sodium dichromate is without advantage, since it does not affect either the yield or purity of the final product. The proportion here recommended is that originally proposed by Graebe and Rateanu and appears to represent about the minimum. Substitution of the equivalent quantity of potassium dichromate makes no difference in the yield or purity of the product, and because of the much smaller solubility in the aqueous acetic acid it does not completely dissolve and is therefore inconvenient to handle. Fanto's recommendation that 10% of sulfuric acid

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[3] Thiele and Henle, *Ann.*, 347, 296 (1906).

be added to the oxidizing mixture was tested but since tar formation resulted its use was abandoned.

3. Since the solution of sodium dichromate in acetic acid and water crystallizes at room temperature, it is recommended that the stock oxidizing solution be kept warm in the second flask and added to the dropping funnel in small increments.

4. During the first part of the oxidation external heating may not be required. Care should be taken, however, to see that constant vigorous ebullition of the liquid is not interrupted, as otherwise an impenetrable lump of hydrocarbon precipitates which redissolves only with difficulty, and generally leads to much unchanged fluorene. With vigorous boiling, however, the use of a motor stirrer is unnecessary.

5. In the literature the recrystallization of fluorenone from alcohol is usually recommended for purification. This has the disadvantages, however, that the ketone separates first as liquid phase, and that any unchanged hydrocarbon is not completely removed. The precipitation of fluorenone from benzene by means of petroleum ether not only serves to remove every trace of hydrocarbon but also yields magnificent crystals. From the mother liquor additional fluorenone can be precipitated by more petroleum ether. An extensive crystallographic examination of fluorenone from alcohol has been made by Fittig and Schmitz.[4]

6. Distillation of the crude oxidation product prior to recrystallization is imperative. The process removes highly colored substances such as rubicene which otherwise follow the ketone through the purification process. Under atmospheric pressure fluorenone boils at **341.5°**.

Fluorenone from Heating Diphenic Acid

Action of Heat upon Fluorenone-4-carboxylic Acid.—A 100-ml. distilling flask was arranged to be heated by fused potassium nitrate–sodium nitrate mixture contained in a hemispherical iron pan, and provided with a suitable thermometer. By means of an inlet tube reaching nearly to its bottom, a stream of air could be aspirated through the flask. This air was admitted through a Kunz spiral absorption bulb containing 50% potassium hydroxide solution. As the air left the reaction flask it passed through a U-tube containing glass beads and concd. sulfuric acid and thence through a glass wool plug into a second Kunz bulb with 50% potassium hydroxide solution. This bulb was protected from possible adventitious atmospheric carbon dioxide with a soda-lime tube. By heating a weighed quantity of substance in the reaction flask the carbon dioxide evolved was carried along by the air stream to the second Kunz bulb and absorbed. Results on fluorenone-4-carboxylic acid are as follows.

Expt	Acid, g.	Time, min	Temp, °C.	CO_2, g.	% of calcd.
2	2.0246	20	320	0.0130	3.3
3	2.1225	135	330	.0962	23.2
4	1.8855	135	340	.3255	88.2
5	1.5210	120	360	.2625	88.5

The fluorenone-4-carboxylic acid used was prepared by the action[5] of sulfuric acid on diphenic acid.

Action of Heat upon Diphenic Acid.—For Expt. 7 the apparatus described above was employed. For the other runs, in which the fluorenone obtained was measured rather than the accompanying carbon dioxide, a distilling flask of suitable size was heated in the same heating bath and the distillate condensed in a test-tube cooled by ice water. After heating as indicated, the temperature was raised until distillation occurred at

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[4] Fittig and Schmitz, **Ann,** 193, **117–119 (1878).**

[5] Moore and Huntress, THIS JOURNAL, 49, **1329 (1927).**

atmospheric pressure; the use of diminished pressure is possible but unnecessary. The diphenic acid employed was all prepared by the method of Huntress.[6]

Expt.	Add, g.	M. p., acid, °C.	Time, min.	Temp., °C.	CO_2, g.	% CO_2	Fluorenone Wt.	Fluorenone % yield	M. p., u. c. dist. fomd.
7	2.0607	226–228	105	360	0.3728	99.5	...	..	....
9A	2.005	213–215	90	360	....	..	1.22	82	83.5–84.5
9B	10.10	213–215	90	360	....	..	7.52	89	83.5–84.5
12	50.0	213–223	90	360	....	..	29.8	80	70–80
13	50.0	226–228	90	360	....	..	33.7	91	75–82
14	100.0	220–225	30	360	....	..	63.0	85	....

Notes.—1. Run 7 was made to verify for diphenic acid itself the optimum temperature which had been found for fluorenone-4-carboxylic acid.

2. Examination of the product from Expt. 13 showed that the principal impurity was diphenyl. This hydrocarbon is readily removed by the benzene–petroleum ether recrystallization.

3. Various grades of diphenic acid were purposely employed. In Expts. 9A, 9B, 12 and 14 diphenic acid was used which had not been subjected to the usual zinc dust–acetic acid purification. The use of copper diphenate instead of diphenic acid[7] gave only a low yield (36%).

Action of Heat upon Diphenic Anhydride.—During the course of the work one experiment was carried out on diphenic anhydride. When 2.152 g. of this substance was heated for one hundred and twenty minutes at 360° in the apparatus of Expt. 7, there was obtained 0.4061 g. of carbon dioxide corresponding to a 96% yield of fluorenone.

Solubility of Fluorenone and of Diphenyl.—A few solubilities were determined at 23° with results as follows, expressed as grams of substance per gram of solvent.

Solvent	Fluorenone	Diphenyl
Alcohol (95%)	0.075	0.054
Carbon tetrachloride	.19	.43
Ether	.31	.75
Benzene	.68	1.00

Summary

1. Heating diphenic acid at 360° causes rapid and nearly quantitative conversion to fluorenone and carbon dioxide. No previous observation of this fact could be found in the literature. The method is well suited for the preparation of either small or large quantities of fluorenone.

2. Under the same conditions both diphenic and fluorenone-4-carboxylic acids give similar results. Because of this fact no conclusion can at present be drawn regarding the mechanism of the reaction.

3. The preparation of fluorenone by oxidation of fluorene has been critically examined, and an improved procedure worked out which gives 60–70% yields of pure fluorenone, using ordinary apparatus.

CAMBRIDGE, MASSACHUSETTS

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[6] Huntress, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, pp. 30–33.

[7] Cf. Dougherty, THIS JOURNAL, 50, 571–573 (1928).

[COMMUNICATION NO. 467 FROM THE KODAK RESEARCH LABORATORIES]

TREATMENT OF CELLULOSE AND OXIDIZED CELLULOSE WITH ACETIC–SULFURIC ACID MIXTURES

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Introduction

It has previously been recorded in the literature that cellulose could be partially converted to the formic acid ester by the action of anhydrous formic acid.[1] Some years later it was shown by Malm and Clarke[2] that by heating cellulose with glacial acetic acid an acetylcellulose containing approximately one acetyl group for four $C_6H_{10}O_5$ groups could be obtained. This product contained from 6 to 7% of CH_3CO. A recent patent[3] has claimed the preparation of a stable tri-formate of cellulose by the action of anhydrous formic acid and zinc chloride on cellulose.

It has been known since 1879[4] that sulfuric acid is a powerful catalyst in the acetylation of cellulose. Therefore it appeared of interest to investigate the effect of acetic–sulfuric acid mixtures on cellulose. Since none of the previous workers; as far as could be ascertained, had used oxidized cellulose, it seemed that the extension of the investigation to include such products might also be of interest. The oxidation procedures employed were similar to those given in a paper by Murray, Staud and Gray[6] in which definite oxygen equivalents per $C_6H_{10}O_5$ group were used.

As the method of acetyl determination usually employed appeared open to question for the analysis of the acetyl derivatives of oxidized celluloses, several of the preparations were also analyzed by another method in which the oxidation products were less likely to invalidate the results. The comparison of the data obtained by the two methods appears to be of possible interest.

Experimental

The cellulose employed in this investigation was high grade commercial processed cotton linters prepared by treatment of crude linters with alkali under pressure, followed by mild bleaching. The material had the following constants

Cuprammonium viscosity.......................... 9600 centipoises[6]

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[1] E. C. Worden and L. Rutstein, *Kunststoffe*, 2,325 (1912).

[2] C. J. Malm and H. T. Clarke, THIS JOURNAL, 51,274 (1929).

[3] British Patent 260,650, June 30. 1925.

[4] Franchimont, *Compt. rend.*, 89,711–712 (1879).

[5] Murray, Staud and Gray, THIS JOURNAL, 52,1508 (1930).

[6] Determined by the method recommended by the Viscosity Committee of the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem. (Anal. Ed.)*, 1, 49 (1929).

Alpha cellulose content	99 1%[7]
Copper number	0.042[8]
Ash	0.168%
Moisture	3.37%[9]

Oxidations.—(I) One hundred and sixty-two grams of cellulose (1 mole of $C_6H_{10}O_5$), which had been dried at 105° for sixteen hours, was placed in a solution consisting of 31.6 g. of potassium permanganate (Baker's Analyzed C. P.) ($^1/_2$ available oxygen atom per $C_6H_{10}O_5$) in six liters of normal phosphoric acid for six hours at 20–25°. After filtration on a Büchner funnel, the oxidized material was treated with a dilute solution of sodium bisulfite, approximately 1%, and washed with water until the filtrate after standing in contact with the oxidized cellulose for approximately sixteen hours was neutral to brom thymol blue.

(II) The same procedure was repeated using 63.2 g. of potassium permanganate (one available oxygen atom per $C_6H_{10}O_5$).

(III) One hundred and sixty-two grams of cellulose, dried at 105°, was placed in a solution consisting of 39.2 g. of 85% chromic oxide in six liters of water (CrO_3 content, 33.3 g., $^1/_2$ available oxygen atom per $C_6H_{10}O_5$) for twenty-four hours at 20–25°. The oxidized cellulose was then washed with water until the filtrate was neutral to brom thymol blue.

(IV) The same procedure was repeated using 156.8 g. of 85% chromic oxide (CrO_3 content 133.3 g, 2 available oxygen atoms per $C_6H_{10}O_5$).

All of the above oxidations were made in duplicate with an interval of several months between the first and second series.

TABLE I

WEIGHTS OF THE OXIDIZED CELLULOSE RECOVERED BY THE VARIOUS OXIDATIONS

Oxidation procedure		Weight in grams of starting material	Weight in grams of oxidized cellulose recovered	% loss
$KMnO_4$				
$^1/_2$ available oxygen atom per $C_6H_{10}O_5$	I	162	150	7.4
(6 hours, 20-25°)	II	162	147	9.3
1 available oxygen atom per $C_6H_{10}O_5$	I	162	138	14.8
(6 hours, 20-25°)	II	162	137	15.4
CrO_3				
$^1/_2$ available oxygen atom per $C_6H_{10}O_5$	I	162	157	3.1
(24 hours, 20-25°)	II	162	...	..
2 available oxygen atoms per $C_6H_{10}O_5$	I	162	160	1.2
(24 hours, 20-25°)	II	162	...	..

Treatment with Acetic–Sulfuric Acid Mixtures.—Fifty grams of oxidized cellulose from each of the treatments described above and 50 g. of unoxidized cellulose were dried at 55–60° for twenty-four hours and placed in 3-liter balloon flasks, each containing 1500 cc. of glacial acetic acid (99.6–99.8% CH_3COOH) and 15 cc. of concentrated sulfuric acid (specific gravity 1.84). After stoppering, the flasks were maintained at 20–25°

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[7] Determined by Method IV as recommended by the Alpha Cellulose Committee of the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem.* (*Anal.* Ed.), **1,** 52 (1929).

[8] Determined by the method of Staud and Gray, *Ind. Eng.* Chem., 17,741 (1925).

[9] Determined by drying for twelve hours at 105°.

with occasional shaking. Approximately seven gram samples were removed after various intervals of time. The maximum time of treatment was 335 hours.

The samples were washed with water until the wash water in contact with the products remained neutral to brom thymol blue for sixteen hours. In some cases the products were treated with dilute sodium bicarbonate solutions for a few minutes, in the early stages of washing, followed by washing to neutrality with distilled water.

After washing, the samples were dried at 55–60° for twenty-four to forty-eight hours. The products from the first series of oxidations were analyzed for acetyl content by the modified Knoevenagel method given below. Those from the second series were subjected to acetyl determination by two methods: (A) the modified Knoevenagel procedure and (B) a method for determining acetic acid in the presence of other acidic groups. These methods are given in detail below.

Acetyl Content of Cellulose and Oxidized Cellulose Treated with Acetic-Sulfuric Acid Mixtures

(A) Modified Knoevenagel Method.[10]—Approximately one-half gram samples weighed to the nearest centigram are placed in a weighing bottle and dried at 105° for at least four hours. They are then cooled in a desiccator and the bottle and contents weighed to one-tenth milligram. The dried material is transferred to a 250-cc. Erlenmeyer flask and the weight of the sample taken for analysis determined by difference.

Twenty cubic centimeters of 75% by weight aqueous ethanol is added and the flask placed in a $56 \pm 1°$ bath for thirty minutes. Twenty cubic centimeters of $N/2$ sodium hydroxide is added and the flask again placed in the 56° bath for fifteen minutes, after which it is allowed to stand at 20–25° for twenty-four to forty-eight hours. The flasks are kept tightly stoppered during this period and the contents stirred occasionally by gentle shaking. The sides of the flasks are finally washed down with distilled water and the excess alkali is titrated with standard $N/2$ hydrochloric acid. The acetyl percentage is calculated by the formula.

$$\text{Percentage acetyl} = \frac{\text{cc. of } N/2 \text{ NaOH used} \times 0.0215 \times 100}{\text{Weight of sample}}$$

(B) Method for Determining Acetic Acid in the Presence of Other Acidic Groups.[11]—The neutral solutions obtained at the conclusion of analysis by the modified Knoevenagel method are transferred to a one-liter distilling flask and acidified with 25 cc. of 20% tartaric acid. Tartaric acid is used because it is strong enough to free acetic and formic acids from their salts, but not of sufficient strength to liberate hydrochloric and sulfuric acids. The volatile acids, which are freed from their salts in this way, are then steam distilled from the solutions. They are for the most part acetic and formic acids. One liter of distillate is usually required for their complete removal, which is determined by testing the distillate with litmus paper as it drops from the condenser and then distilling 200 to 300 cc. additional.

This distillate is then made alkaline with sodium carbonate and evaporated to dryness on a steam-bath. The alkaline residue is taken up with approximately 25 cc. of distilled water and to it are added 10 cc. of approximately $N/10$ potassium permanganate. The solution is heated on a steam-bath for a few minutes to assure complete oxidation of the formic acid. This solution is next acidified with dilute sulfuric acid

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[10] Knoevenagel, *Cellulosechemie*, 3, 119 (1922).

[11] "The Acid Value of Cellulose Fatty Acid Esters and a Rapid Method for the Analysis of Certain Cellulose Acetates," by T. F. Murray, Jr., C. J. Staud and H. LeB. Gray, to be published presently as Communication No. 461 from the Research Laboratories of the Eastman Kodak Company.

(15% by volume) and the excess potassium permanganate destroyed with *a* slight excess of *N*/10 oxalic acid. This excess of oxalic acid is in turn removed by *N*/10 potassium permanganate until a very faint pink color remains. The solution is then made faintly alkaline with 5% sodium hydroxide for the purpose of converting all acids into the sodium salts. Finally this solution is again acidified with 25 cc. of 20% tartaric acid, when again only those acids weaker than tartaric are freed from their salts. The acids volatile with steam are distilled as before. The distillate should contain only acetic and carbonic acids at this point. This distillate is refluxed for ten to fifteen minutes to remove the dissolved carbon dioxide, cooled to room temperature and the solution titrated with standard *N*/10 alkali using phenolphthalein as indicator. From the amount of alkali used, the amount of acetyl in the sample is calculated.

It is necessary to make a correction for acids in the reagents. This is done by carrying out the determination using water and the reagents only. This correction factor is expressed in centimeters of *N*/10 alkali and is applied before final calculation is made.

Acetyl Content of Products.—The values obtained by analysis of the various oxidized celluloses using the modified Knoevenagel method described above are given for the first series of oxidations in Table II.

TABLE II

RESULTS OR ANALYSES

Treatment, hours	Unoxidized cellulose, % acetyl		Cellulose oxidized with CrO_3 Available oxygen atoms per $C_6H_{10}O_5$				Cellulose oxidized with $KMnO_4$ Available oxygen atoms per $C_6H_{10}O_5$			
			1/2		2		1/2		I	
	I	II	I	II	I	II	I	II	I	II
0	0.0		1.3	1.6	6.4	6.5	4.2	4.1	4.7	4.9
24	0.68	0.64	2.4	2.2	4.5	4.5	2.1	2.2	3.3	3.4
72	1.70	2.00	4.5	4.5	5.0	4.3	2.5	2.4	3.3	3.4
120	2.40	2.80	5.8	5.9	5.5	5.8	2.4	2.5	3.0	3.2
168	4.10	4.90	6.6	6.5	6.0	6.4	2.7	2.6	3.4	3.5
216	5.00	5.10	6.6	6.6	6.2	6.0	2.8	2.9	3.0	3.1
263	5.30	5.40	6.9	6.8	6.5	6.5	2.8	2.7	3.2	2.8
335	6.20	6.20	6.8	6.7	6.5	7.0	3.1	3.1	3.6	3.4

Determinations were made in duplicate and all values are given in Table II. The average values are given graphically in Fig. 1.

The values obtained upon analysis of the second series of oxidations are given in Table III and Fig. 2.

TABLE III

RESULTS OF ANALYSES

Treatment, hours	Unoxidized cellulose, % acetyl		Cellulose oxidized with CrO_3 Available oxygen atoms per $C_6H_{10}O_5$				Cellulose oxidized with $KMnO_4$ Available oxygen atoms per $C_6H_{10}O_5$			
			1/2		2		1/2		I	
	I	II	I	II	I	II	I	II	I	II
0	0.0		2.6	2.8	8.6	8.4	5.6	5.7	6.6	6.4
44	3.8	3.8	6.1	6.1	7.8	...	4.2	3.8	4.5	6.4
95	5.5	5.5	6.7	7.3	8.5	8.2	4.2	4.4	5.1	5.6
162	7.4	7.4	8.8	8.8	8.7	8.4	4.3	4.5	6.1	6.1
210	8.2	8.4	7.8	7.8	8.4	8.5	5.4	4.9	6.3	6.9
258	8.3	7.8	7.9	7.9	8.8	8.9	4.9	4.8	6.4	6.1
330	8.9	8.2	8.0	8.0	9.1	9.3	4.8	4.9	6.2	6.1

Four samples from each of the groups analyzed by the modified Knoevenagel method, given in Table III, *i. e.*, the unoxidized cellulose and products from the second series of oxidation experiments after treatment with the acetic–sulfuric acid mixture, were also analyzed by the second method given above for the determination of acetic acid in the presence of acidic groups, which will hereinafter be called the "Distillation Method." The results are given in Table IV and Fig. 3.

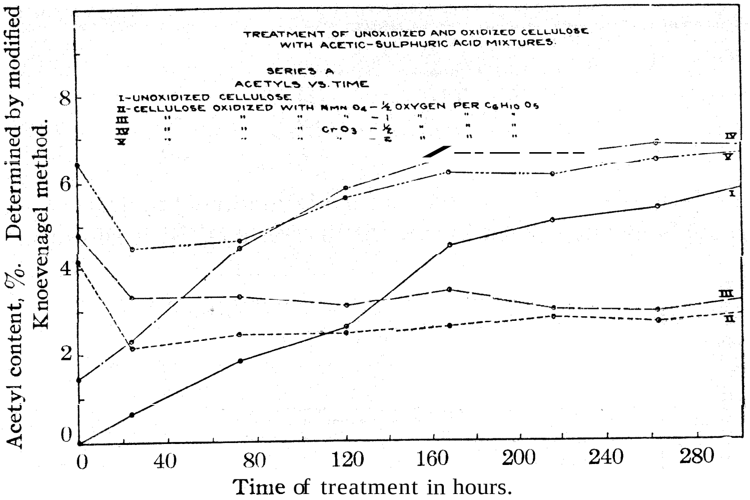

Fig. 1.

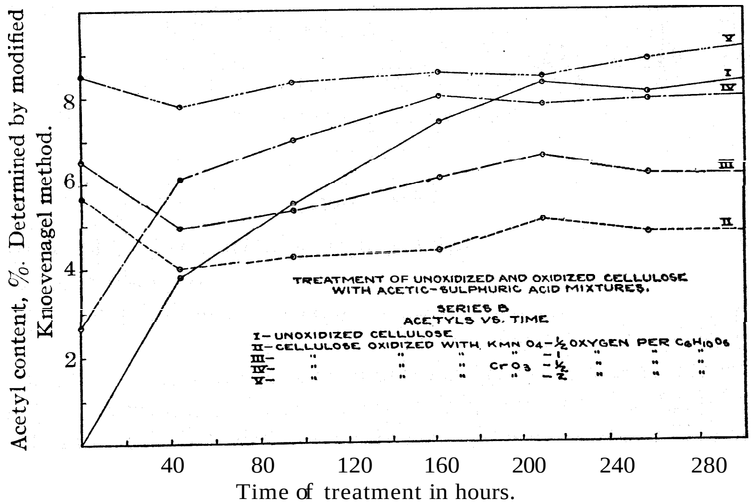

Fig. 2.

TABLE IV

RESULTS OF ANALYSES

Treatment, hours	Unoxidized cellulose, % acetyl	Cellulose oxidized with CrO_3 Available oxygen atoms per $C_6H_{10}O_5$ ½	2	Cellulose oxidized with $KMnO_4$ Available oxygen atoms per $C_6H_{10}O_5$ ½	1
0	0.0	0.22	0.12	0.44	0.23
44	2.7	3.00	.23	0.50	0.28
162	6 2	5.10	.82	0.72	0.90
330	6.4	4.80	.51	1.63	1.35

The relationship of the severity of oxidation and the acetyl content of the products as determined by the distillation method is shown in Fig. 4.

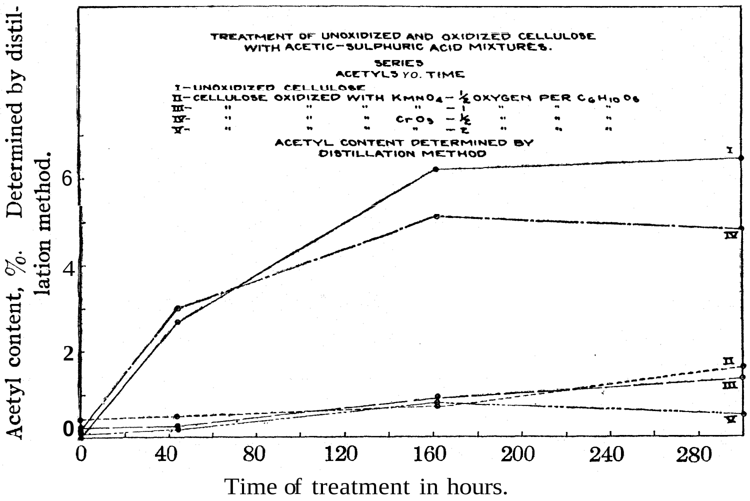

Fig. 3.

Discussion

From an examination of Table I it is seen that the yield of oxidized cellulose is an inverse function of the severity of the oxidizing solutions employed. This confirms the results of Hibbert and Parsons[12] and also that of Murray, Staud and Gray.[5]

When the results of acetyl determinations of the first and second series of unoxidized cellulose and oxidized celluloses, after treatment with acetic-sulfuric acid mixtures, are considered, as given in Tables II and III and in Figs. 1 and 2, at least three points are evident. First, when unoxidized cellulose is used, the acetyl content after **330** and **335** hours approximates that obtained by Malm and Clarke[2] by the action of boiling acetic acid on cellulose. This appears to be another indication that in the reaction between unoxidized cellulose and acetic acid, there is one hydroxyl group

[12] Hibbert and Parsons, *J. Soc. Chem. Ind.*, 44,4731' (1925).

per $C_{24}H_{40}O_{20}$ which behaves in a different manner from the other eleven as indicated by the cellulose formula put forward by Gray.[13]

The second point is that in both series of experiments the acetyl content, as determined by the modified Knoevenagel method, of the materials which had been oxidized using chromium oxide, for 330 and 335 hours, approximates more closely that of the unoxidized cellulose. The third point is that the most vigorously oxidized celluloses show the least acetyl content.

The fact that in many cases the apparent acetyl contents of the starting materials were higher than values subsequently obtained and that these appeared to show correlation with the vigor of the oxidizing solution, led to the trial of the distillation method of determination of acetyl content. It seemed fairly obvious that during the oxidation groups showing acidic reaction had been produced in the cellulose which were of course titrated as acetyl content in the modified Knoevenagel method.

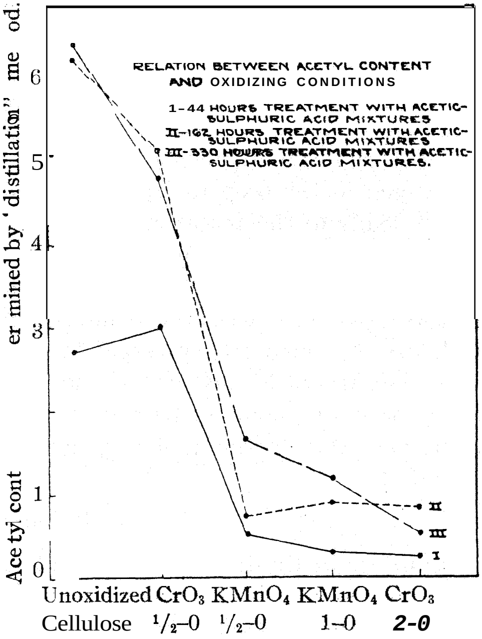

Fig. 4.

It was believed that the presence of combined sulfuric acid might be a factor in the results, but the results given in Table V do not indicate this.

TABLE V

PERCENTAGE OF COMBINED SULFURIC ACID

	Treatment with $CH_3COOH-H_2SO_4$		
	Before	After 44 hours	After 330 hours
Unoxidized cellulose	0.0	0 03	0 33
Cellulose oxidized, 1/2 available oxygen atom per $C_6H_{10}O_5$ using CrO_3	.0	.08	.30
Cellulose oxidized, 2 available oxygen atoms per $C_6H_{10}O_5$ using CrO_3	.0	.07	.50
Cellulose oxidized, 1/2 available oxygen atom per $C_6H_{10}O_5$ using $KMnO_4$	.0	.08	.30
Cellulose oxidized, 1 available oxygen atom per $C_6H_{10}O_5$ using $KMnO_4$	.0	.0	.24

When the distillation method was used in the analysis of the products,

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[13] Gray, *Ind. Eng. Chem.*, 18,811 (1926).

the results given in Table IV and in Fig. **3** illustrate a striking difference from those obtained when the modified Knoevenagel method was used. Although the untreated materials did not give zero results, indicating the probable presence of other volatile materials of acid character not oxidized by potassium permanganate, the values are very much nearer zero and there is a much greater divergence between the acetyl content of the unoxidized and oxidized celluloses.

It is observed in this instance that the values for the acetyl content of the unoxidized cellulose after treatment with acetic–sulfuric acid mixture again approximate that of $C_{24}H_{39}O_{19}(O{-}CO{-}CH_3)$. It is also seen that the esterification is in an inverse ratio to the severity of the oxidizing conditions employed in the preparation of the oxidized cellulose, as shown in Fig. 4, which leads to the tentative conclusion that the hydroxyl group which is most readily acetylated is also probably the most easily oxidized.

Finally, the data obtained by the modified Knoevenagel method offer possible evidence that the acidic groups produced by the oxidation of cellulose are partially converted to non-acidic form by the action of the acetic–sulfuric acid mixture as indicated by the decreased values obtained after forty-four hours of treatment as compared with the apparent acetyl content of the starting materials as shown in Tables II and III and Figs. 1 and 2.

Summary

Cellulose in the form of cotton linters has been oxidized using chromic oxide in amounts of one-half and two available oxygen atoms per $C_6H_{10}O_5$ group and by potassium permanganate at concentrations of one-half and one available oxygen atom per $C_6H_{10}O_5$ group in N phosphoric acid.

The unoxidized and oxidized celluloses have been treated with acetic–sulfuric acid mixtures with the removal of samples at intervals during approximately **330** hours.

The products from the treatment of unoxidized and oxidized celluloses after treatment with acetic–sulfuric acid mixtures have been analyzed by two methods.

The results are given.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. VII. FRACTIONAL PRECIPITATION OF NATURAL RUBBER

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL

RECEIVED MAY 2, 1931 PUBLISHED JULY 8, 1931

Crude rubber is an indeterminate mixture of several substances. The constituents of the mixture can be classified as "resins," soluble in acetone, rubber hydrocarbon $(C_5H_8)n$, soluble in benzene and insoluble "proteins."

The so-called "resins" are conveniently removed by a Soxhlet extraction with acetone. This treatment leaves behind a mixture of the rubber hydrocarbons and the "proteins." The latter can be separated by a variety of methods, which are well summarized by Fisher.[1] However, none is entirely satisfactory, because the methods based on a physical property effect only an imperfect separation, while chemical methods injure one or both constituents.

This paper presents a method of separation based on the progressive precipitation of natural rubber from a mixture of alcohol and benzene by slow cooling. Within certain limits, a system containing definite amounts of natural rubber, benzene and alcohol is homogeneous above a definite temperature, its critical temperature of solution. This critical point is best determined by allowing a hot mixture of rubber, alcohol and benzene to cool and reading the temperature at which a sudden increase of turbidity occurs. The determination can be duplicated within 0.3°.

When a mixture of rubber, alcohol and benzene is heated to a temperature higher than its critical point, until it has become completely clear, and is then allowed to cool to a temperature about 1° below its critical point, a certain amount of gel collects at the bottom of the container, while the supernatant liquid becomes transparent. The gel is a mixture of rubber and nearly all of the "protein." The supernatant liquid contains rubber practically free of "protein"; it can be decanted and yields its rubber content upon cooling or by alcohol addition. If a very pure hydrocarbon is desired, the procedure is repeated.

To systematize the preparation of nitrogen-free rubber, the diagrams given in Figs. 1, 2 and 3 have been experimentally determined. The procedure used was the customary one for the determination of critical temperatures of solution. Figure 1 refers to crude crepe rubber, alcohol and benzene; Fig. 2 refers to pure rubber hydrocarbon, alcohol and benzene; and Fig. 3 refers to synthetic rubber (sodium rubber), alcohol and benzene. The diagrams show that the isotherms have generally the same trend; they are located farther to the right in Fig. 3 than in Fig. 2, and in Fig. 2 than in Fig. 1.

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[1] H. L. Fisher, *Chem. Reviews,* **7,** 51 (1930); *J. Chem. Education,* **8**, 7 (1931).

The use of the diagrams is almost self-evident. A system containing 2.0% of natural rubber, 23.1% of alcohol and 74.9% of benzene is found to have a critical temperature of 43.0". Such a system is represented by the circle *A* on Fig. 1. When this system is kept at 43.0°, it separates into two phases. The gel phase precipitates; it is a mixture of rubber hydrocarbon, "protein" and solvent, with a ratio benzene–alcohol larger than that of the system taken as a whole. The supernatant liquid contains rubber practically free of nitrogenous matter, dissolved in benzene–alcohol, and in this liquid the ratio benzene–alcohol is smaller than in the system taken as a whole. The composition of the supernatant liquid is represented by the circle B, on Fig. 2; it corresponds to 0.55% of nitrogen-free rubber, 30.7% of alcohol and 68.75% of benzene. When such a system is cooled to 41°, it becomes heterogeneous and when it is cooled to 35°, it retains less than 0.1% of dissolved rubber.

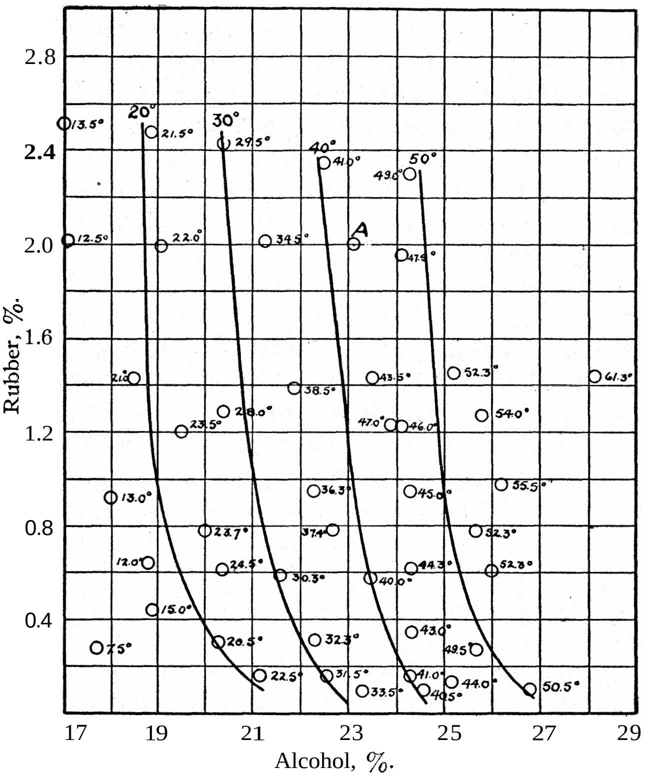

Fig. 1.

Experimental Procedure

Two hundred and fifty grams of crepe rubber with a nitrogen content of 0.25% was dissolved in 8083 g of benzene, heated to about 50". A hot mixture of 4500 cc. of absolute alcohol and 1400 cc. of benzene was added slowly, with constant stirring, until complete solution was obtained. The critical temperature, determined on a 50-cc. sample, was 43.0°. The mixture was then held at 42.0" in a thermostat, for one hour. At the end of this period, the mixture was no longer homogeneous, but consisted of a completely settled gel phase and a clear supernatant liquid. This liquid was decanted, then cooled in an ice-bath, and yielded 52.9 g. of rubber hydrocarbon, hereafter designated as A_1. After removal of the A_1 rubber, the liquid was warmed and poured back on the gel phase. By warming and stirring, the gel phase was caused to dissolve, and a clear solution was then obtained. A sample of this solution exhibited a critical point of **43.5".** Consequently, the solution was placed in a thermostat regulated at 42.5° for one hour, and the above procedure was repeated. This time 30.5 g. of rubber hydrocarbon was obtained, called A_2 hereafter. Two repetitions of these operations yielded fractions A_3 and A_4.

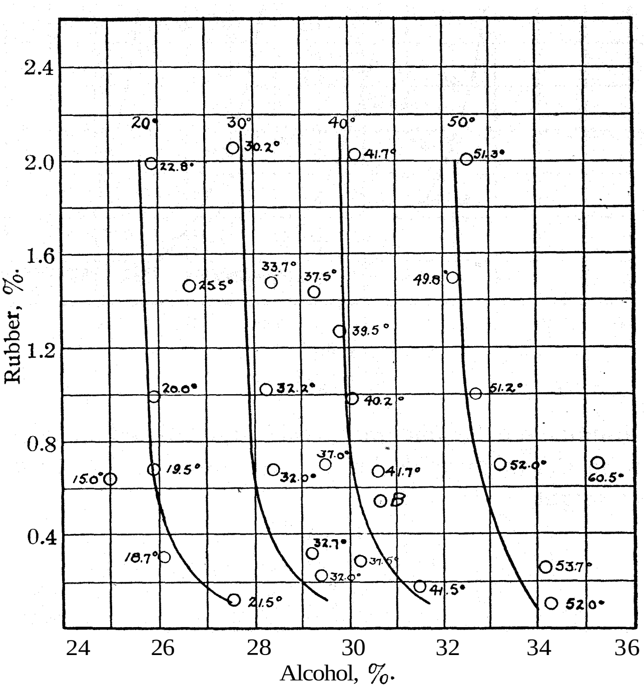

Fig. 2.

After the fraction A_4 had been collected, it was found that the gel phase would no longer dissolve completely in the alcohol–benzene mixture, even when the solvent was brought to its boiling point. Consequently, the insoluble matter was separated from the solvent; the solvent, upon cooling, yielded a fraction called A_5. Finally, the insoluble matter was extracted in a Soxhlet extractor with benzene. The material obtained from the benzene was called A_6, while the insoluble matter was called B. The various fractions were then analyzed for nitrogen. They were decomposed according to the usual Kjeldahl procedure.2 After the addition of alkali, three 50 cc. portions were

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[2] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1927, Vol. II, p. 1593.

distilled, nesslerized, and compared with a set of standard tubes. Blanks were run on all reagents; ammonia-free water was used throughout. Fraction B was decomposed by the usual Kjeldahl method, but the distillate was received in standardized hydrochloric acid, whose excess was titrated with standard sodium hydroxide.

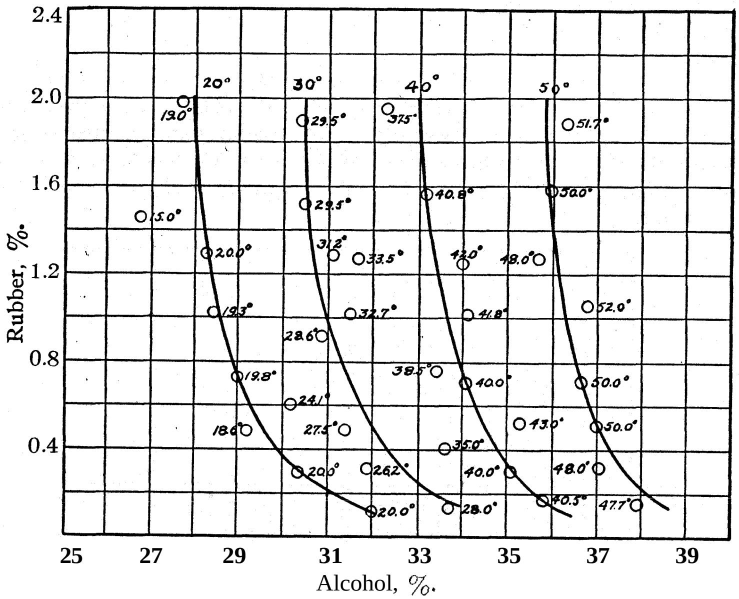

Fig. 3.

Table I summarizes the amounts of each fraction obtained, their critical temperature in the mixture alcohol–benzene described, and their nitrogen contents, by weight.

TABLE I

FIRST FRACTIONATION

	A_1	A_2	A_3	A_4	A_5	A_6	B
Grams	52.9	30.5	26.6	23.6	24.8	38.9	11.6
Crit. temp.	43.0	43.5	44.0	44.7	45.5	....	...
Nitrogen, %	0.026	0.033	0.044	0.125	0.142	0.160	4.21

After the first fractionation was completed, fractions A_1, A_2 and A_3 were combined, dissolved in *a* mixture of alcohol–benzene, and the whole procedure was repeated. Five successive fractions were thus obtained, as during the first fractionation, and they were analyzed for nitrogen. The results are reported in Table II.

TABLE II

SECOND FRACTIONATION

	A_2–1	A_2–2	A_2–3	A_2–4	A_2–5
Grams	28.1	17.1	13.8	16.0	6.4
Nitrogen, %	0.000	0.021	0.028	0.048	0.100

Fractions A_2–2, A_2–3 and A_2–4 were combined, dissolved in alcohol–benzene, and refractioned as previously. The results were as shown in Table III.

TABLE III

THIRD FRACTIONATION[3]

	A_3–1[a]	A_3–2	A_3–3
Grams	20 8	6 1	7.8
Nitrogen, %	0 000	0 011	0.015

[a] The carbon and hydrogen contents of Fraction A_3–1 were determined by micro-combustion. Calcd.: C, 88.17; H, 11.83. Found: C, 88 28, 88.32; H, 11.74, 11.74. This indicates the complete absence of oxygen.

The rubber hydrocarbon obtained by cooling the supernatant liquid has, so far, been referred to as "nitrogen-free rubber." When freshly prepared, this material bears a strong resemblance to the so-called "α-rubber" of Pummerer[4] and it probably contains little if any "β-rubber." During the course of the fractionation, the "0-rubber" seems to concentrate in the fractions rich in protein.

Summary

Temperature–concentration diagrams are given of the systems natural rubber–alcohol–benzene, pure rubber–alcohol–benzene and synthetic rubber–alcohol–benzene A method based on these diagrams is given for the separation of nitrogen-free rubber hydrocarbon by fractional precipitation of natural rubber from a mixture of alcohol and benzene.

COLUMBUS, OHIO

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[3] A point of interest in the behavior of the rubber hydrocarbon was discovered in the course of this fractionation. For example when As–2 was dissolved in benzene and precipitated with acetone, only 14.1 g. was recovered. The other 3 g. remained in the turbid solution, irrespective of the amount of acetone added. The addition of water, however, caused precipitation. Likewise, the addition of a small amount of acetic acid would cause precipitation, seemingly at a different P_H. The residual three grams recovered by the addition of water was nitrogen-free.

[4] H. L. Fisher, *Chem. Reviews*, **7**, 65 (1930).

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

CRYSTALLINE SOLVATES OF ROTENONE

BY HOWARD A. JONES

RECEIVED MAY 2, 1931 PUBLISHED JULY 8, 1931

Rotenone ($C_{23}H_{22}O_6$, m. p. 163°) as ordinarily crystallized from alcohol or ether separates as well-formed, thin plates of rather characteristic hexagonal outline. These crystals may be heated at 105° under atmospheric, or even under reduced, pressure for an extended period of time without loss in weight, indicating that they contain no solvent of crystallization.

Tattersfield and Roach[1] have reported that rotenone separates from certain solvents with solvent of crystallization. Thus they obtained from benzene needle-like crystals which contained 23 and 16% of benzene in two determinations. These investigators also obtained from alcohol needle-like crystals which contained about **3%** of alcohol of crystallization. In a previous paper[2] the present author reported that rotenone separates from some other solutions as crystalline solvates.[3] Thus it was found that the long, needle-like crystals obtained from carbon tetrachloride lost weight on heating, evidently owing to the expulsion of solvent of crystallization.

In order to determine the composition of the compounds formed, two rather simple methods were adopted. In the first of these the crystals were obtained by cooling warm solutions containing rotenone in excess of that soluble at room temperature. The separated crystalline material was filtered and placed in a desiccator containing a 50–50 mixture of the solvent and petroleum oil[4] until the material came to constant weight. A definite amount of this was then weighed and allowed to stand in air for some time to determine its stability, after which it was heated in an electric oven at 105° to constant weight. The total loss in weight was considered to be the amount of solvent of crystallization.

In the other method a weighed quantity of rotenone was dissolved in the solvent, the excess solvent evaporated by placing the dish in a draft of air at room temperature, and the solid material allowed to stand in the solvent–petroleum oil desiccator until it had come to constant weight. The increase in weight was considered to be the solvent added to the rotenone in the solvate compound. Blanks were run on the solvents alone to determine the residue on evaporation, and a suitable correction was made. The material was then allowed to stand in the air to determine roughly its

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[1] Tattersfield and Roach, *Ann. Appl.* **Biol.,** *10,* 1 (1923).

[2] Jones and Smith, THIS JOURNAL, 52,2554 (1930).

[3] The term "solvate" as used in this paper is intended to apply only to solid materials containing solvent of crystallization.

[4] Such mixtures were used arbitrarily in an effort to insure the evaporation of the mother liquor without decomposition of the compound. In the case of the acetic acid compound, 50-50 glycerin and acetic acid was used.

rate of loss of solvent, and finally heated to constant weight at 105°. In the case of solvates this loss in weight should equal the gain in weight on evaporation and should again be the amount of solvent of crystallization.

In the paper[2] previously referred to it was reported that rotenone crystallized from acetic acid, benzene, carbon tetrachloride, chlorobenzene, chloroform, *sym.*-β-dichloroethyl ether, ethylene dichloricle and sometimes from toluene and trichloroethylene in the form of needles, and it was thought that all these might be solvates. In the present determinations *sym.*-β-dichloroethyl ether, toluene and trichloroethylene were not tested because they will be little used as solvents for rotenone. On the other hand, acetone, ethyl acetate and ethyl alcohol were used to prove that these solvents do not form crystalline solvates of rotenone.

The high solvent power of chloroform for rotenone made it impossible to use the procedures outlined, because concentrated, sirupy solutions were formed from which it was difficult to obtain crystalline material. Accordingly a modification of the first method was adopted. A solution of rotenone in chloroform was prepared at a concentration considerably below the saturation value, this solution was warmed, and four to five times its volume of warm petroleum ether added slowly. On cooling, long, needle-like crystals separated. This crystalline material was then filtered and treated as outlined in the first procedure. It was established that this solvate did not contain petroleum ether.

The results obtained are given in Table I. As will be noted acetone, chlorobenzene, ethyl acetate, ethyl alcohol and ethylene dichloride, under the conditions of the experiment, did not form solid solvates. Since Tattersfield's results with alcohol would require a compound with the unusually high proportion of about four molecules of rotenone to one of alcohol, it is probable that his result was incorrect and was due to retained mother liquor. Acetic acid forms a crystalline compound containing two molecules of rotenone to one of acetic acid. These crystals lost only 0.2% of their weight on standing in the air for forty-eight hours, showing efflorescence to be extremely slow. Benzene, carbon tetrachloride and chloroform form crystalline compounds containing one molecule of rotenone to one of solvent. The benzene result agrees with one of the analyses by Tattersfield. These benzene crystals effloresced appreciably in air, losing 1.2% of their original weight on standing for forty-eight hours in the air at room temperature. The chloroform crystals lost about 1.5% in the same time. The crystals containing carbon tetrachloride, however, were fairly stable in air, losing only 0.5% in the same time. On warming these crystalline solvates the odor of the solvent was readily detected.

Attempts were made to determine the melting points of these materials. All lose their solvent of crystallization gradually at a rate dependent on the rate of heating, and then melt at temperatures ranging between 171 and

TABLE I

CRYSTALLINE SOLVATES OF ROTENONE

Solvent	Crystallization method		Evaporation method		Formula of compound and theoretical percentige, solvent
	Cryst. matl, g. After heating, g.	Percentage solvent of compound (from loss in wt.)	Rotenone, g. Evapd. matl., g. After heating, g.	Percentage solvent of compound (from increase in wt.)	
Acetic acid	0.419		1.000		$2C_{23}H_{22}O_6$·-
	.389	7.2	1.076	7.1	CH_3COOH
					7.1
Acetone	1.120		1.000		
	1.120	None	1.000	None	....
			0.997		
Benzene	1.220		1.000		$C_{23}H_{22}O_6 \cdot C_6H_6$
	1.021	16.3	1.195	16.3	16.5
			1.001		
Carbon tetrachloride	0.825		0.500		$C_{23}H_{22}O_6 \cdot CCl_4$
	.598	27.5	.694	28.0	28.1
			.501		
Chlorobenzene	0.285		1.000		
	.282	None	1.003	None	....
			1.002		
Chloroform	0.268				$C_{23}H_{22}O_6 \cdot CHCl_3$
	.208	22.5	...	..	23.2
Ethyl acetate	1.125		1.000		
	1.124	None	1.004	None	....
			1.002		
Ethyl alcohol	0.411		0.500		
	.411	None	.503	None	....
			.500		
Ethylene dichloride	1.462		1.000		
	1.461	None	1.011[a]	None	....
			1.006		

[a] The rotenone underwent some oxidation in this case.

179°, which is above the melting point of ordinary rotenone. On cooling and remelting all give about the same melting points. These temperatures are in the region of the melting point given by Butenandt[6] for a polymorphic form of rotenone (m. p. 176°) which he obtained by grinding ordinary rotenone in a mortar.

All of these solvates separate in the form of rod-like crystals except the acetic acid compound, which is lath-like in appearance. The crystals all have high birefringence, parallel extinction and negative elongation. Crystals of rotenone obtained from ethyl acetate, although not a solvate, are lozenge-shaped instead of hexagonal in outline. We have found this of value as a diagnostic feature in the microscopic examination of crystalline material for rotenone.

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[6] Butenandt and Hildebrandt, Ann., 477, 245 (1930).

The formation of the solvates may also be of value as diagnostic features of rotenone and may be of some application in analytical procedures. Thus in the extraction of derris root with carbon tetrachloride, the rotenone–solvent compound crystallizes from the evaporated extract and may be separated, dried and weighed in the air without heating in the oven, the weight being calculated to that of rotenone.

Summary

Under ordinary conditions rotenone forms with benzene, carbon tetrachloride and chloroform crystalline solvates containing one molecule of rotenone to one of solvent, and with acetic acid a solvate containing two molecules of rotenone to one of solvent.

No crystalline solvates were formed with acetone, chlorobenzene, ethyl acetate, ethyl alcohol and ethylene dichloride.

WASHINGTON, D. C.

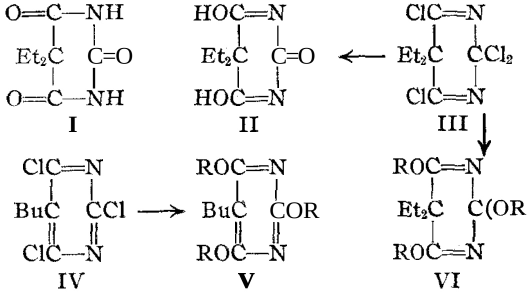
[CONTRIBUTION NO. 446 FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND COMPANY]

OXYGEN ETHERS OF BARBITAL

BY ARTHUR W. DOX

RECEIVED MAY 4, 1931 PUBLISHED JULY 8, 1931

The formula commonly assigned to barbital (5,5-diethylbarbituric acid) represents the keto–lactam structure (I). On theoretical grounds this structure should be more stable than the isomeric enol–lactim (II). At least one of the lactam groupings has the properties of an imide, since a monosodium salt can be prepared which reacts with alkyl halides to form N-alkylated barbitals. If the sodium salt exists as the tautomeric enol, it should yield an oxygen ether, but no such oxygen ethers have thus been obtained. After alkylation of one lactam the resulting 1,5,5-trialkylbarbituric acid again behaves as an imide, the remaining lactam forming a sodium salt which reacts as before. It is thus possible to prepare a 1,3,5,5-tetraalkylbarbituric acid.[1]



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[1] Dox and Jones, THIS JOURNAL, 51, 316 (1929).

From analogy to similar structures, *e. g.*, isatin, carbostyril, etc., the tautomeric enol–lactim (II) should be the less stable form. Nevertheless, its oxygen ethers, once formed, should be relatively stable, though possibly subject to molecular rearrangement under drastic treatment.

In a previous paper[2] the hydrolysis of 2,2,4,6-tetrachloro-5,5-diethyldihydropyrimidine (III) was discussed. Replacement of the four chlorines by hydroxyl, followed by loss of water at C-2, should yield the tautomeric barbital (II). Aside from a quantitative liberation of hydrochloric acid, the only product obtained was diethylmalononitrile, the logical decomposition product of the unstable tautomer. Whether this tautomer exists momentarily as an intermediate product cannot as yet be stated with certainty. In view of the results obtained in the analogous alcoholysis of this tetrachloro derivative, the tentative explanation which assumes the momentary existence of an unstable tautomer acquires greater validity.

The substitution of alkoxyl for chlorine in a chlorinated derivative of an alkylbarbituric acid is recorded in one instance. V. Merkatz[3] treated 2,4,6-trichloro-5-ethylpyrimidine with sodium methoxide and obtained 2,4,6-trimethoxy-5-ethylpyrimidine. No evidence, beyond the method of preparation, was offered in support of the oxygen ether structure of the product. The possibility of rearrangement to an isomeric N-alkyl structure was not mentioned. In the case of tautomeric barbital, which represents a dihydropyrimidine and has two double bonds instead of three, the possibility of rearrangement is a more serious consideration.

Experimental

The reaction described by v. Merkatz, in which the three chlorines of 2,4,6-trichloro-5-ethylpyrimidine were replaced by methoxyl, was first tried with the homologous 2,4,6-trichloro-5-*sec.*-butylpyrimidine (IV),[2] using several alkoxides. The chlorinated pyrimidine was treated with the equivalent of sodium dissolved in the appropriate absolute alcohol. The reaction began almost immediately, as shown by the evolution of heat and the precipitation of sodium chloride. The mixture was heated in a steam-bath for two to four hours, then treated with water and the separated oily product distilled at atmosphere pressure.

2,4,6-TRIALKOXY-5-*sec.*-BUTYLPYRIMIDINES (V)

			Nitrogen, %	
Alkoxyl	B. p., °C.	Formula	Calcd.	Found
Methoxyl	245–250	$C_{11}H_{18}O_3N_2$	12.39	12.35 12.34
Ethoxyl	260-264	$C_{14}H_{24}O_3N_2$	10.44	10.29 10.28
Propoxyl	285-290	$C_{17}H_{30}O_3N_2$	9.03	9.27 9.22
Butoxyl	310-315	$C_{20}H_{36}O_3N_2$	7.95	8.09

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[2] Dox, This Journal, 53, 1559 (1931).

[3] V. Merkatz, *Ber.*, 52, 876 (1919).

Proof of structure was not attempted, since the proof given for the tetraalkoxy derivative below should be equally applicable here.

The 2,2,4,6-tetrachloro-5,5-diethyldihydropyrimidine (III), obtained by treatment of barbital with phosphorus pentachloride, reacted in the same manner with sodium ethoxide and sodium butoxide. The oily products were separated as above, but distilled at 3 mm. instead of atmospheric pressure.

2,2,4,6-TETRAALKOXY-5,5-DIETHYLDIHYDROPYRIMIDINES (VI)

Alkoxyl	B. p., °C. (3 mm.)	Formula	Calcd., % C	H	N	Found, % C	H	N
Ethoxyl	122–123	$C_{16}H_{30}O_4N_2$	61.15	9.55	*8.92*	60.12	9.49	8.88
Butoxyl	180–183	$C_{24}H_{46}O_4N_2$	67.60	10.80	*6.57*	67.36	10.56	6.71

Both are high-boiling liquids, the tetrabutoxy derivative being considerably more viscous than its lower homolog.

Proof of structure was obtained by examining the products of hydrolysis. A homogeneous solution of 1.3885 g. of the tetraethoxy derivative in 10 cc. of concentrated hydrochloric acid was heated in a sealed tube for five hours at 140–150". Considerable pressure was released on opening the tube and the contents, consisting of an aqueous solution and a supernatant oil, were separated in a small funnel. The oil was washed with water and dried with calcium chloride. It was acid to litmus, boiled at 192–193°, and its titration value represented a molecular weight of 114. These properties identify the substance as diethylacetic acid, boiling point 195°, molecular weight 116. It is obviously a secondary product resulting from loss of carbon dioxide from diethylmalonic acid, the direct product of hydrolysis.

Evaporation of the aqueous layer of the reaction mixture left a white crystalline residue. After washing this with absolute alcohol, the yield was 0.4472 g. A portion was analyzed and found to contain 66.22% Cl; calculated for NH_4Cl, 66.36% Cl. The ammonium chloride actually recovered and analyzed accounts for 94.5% of the nitrogen present in the original material. If, however, the substance had been the isomeric N-alkyl derivative, hydrolysis by hydrochloric acid would have yielded ethylamine hydrochloride instead of ammonium chloride. The alcoholic washings from the ammonium chloride gave no picrolonic acid reaction for ethylamine. From another preparation which had been distilled at 260–265° under atmospheric pressure, a very small amount of ethylamine was obtained on hydrolysis, barely enough for analysis of the chloroplatinate and melting point of the picrolonate. The amount was estimated at less than 2% of the total nitrogen. The recovery of ammonium chloride, as before, was almost quantitative.

It is thus apparent that the substance is actually an oxygen ether with alkyl linked to oxygen and not to nitrogen. The isomeric N-alkyl derivative if present occurs in mere traces. The tetraethoxy and tetrabutoxy derivatives obtained as above are of especial interest as representing the first known derivatives of the hypothetical tautomeric barbital. They possess in addition to ether linkages in positions 4 and 6, an acetal structure in the 2-position. Hence they may be regarded as acetals of the ethers of enolic barbital. The isomeric 1,3,5,5-tetraethylbarbituric acid, but without the acetal grouping in position 2, has been prepared by Fischer and Dilthey[4] from ethyl diethylmalonate and *sym.*-diethylurea. This also was a high-boiling liquid.

Summary

2,2,4,6-Tetrachloro-5,5-diethyldihydropyrimidine, a product obtained by chlorination of barbital with phosphorus pentachloride, reacts with sodium alkoxides to form the corresponding 2,2,4,6-tetraalkoxy-5,5-diethyldihydropyrimidines. Hydrolysis by concentrated hydrochloric acid converts the tetraalkoxy derivative into diethylacetic acid and ammonium chloride, the latter in almost quantitative yield, showing that the alkyl is actually linked to oxygen. These tetraalkoxy derivatives represent acetals of the ethers of a hypothetical enolic barbital.

A series of 2,4,6-trialkoxy derivatives was also prepared from 2,4,6-trichloro-5-*sec.*-butylpyrimidine.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE SWAN-MYERS DIVISION OF ABBOTT LABORATORIES]

STUDIES ON POLLEN AND POLLEN EXTRACTS. VII. A GLUCOSIDE FROM CERTAIN GRASS POLLENS

BY MARJORIE B. MOORE AND EDMOND E. MOORE

RECEIVED MAY 4, 1931 PUBLISHED JULY 8, 1931

The existence of glucosides in pollen has been previously recognized. Heyl[1] found the coloring substances of ragweed pollen to be entirely glucosidic, and was able to isolate and identify glucosides of quercitin and isorhamnetin in the alcoholic extract. More recently, Fukuda[2] has isolated a glucoside of isorhamnetin from an alcoholic extract of the pollen of *Typha angustata Bory et Chaub.*

A new glucoside has been isolated in this Laboratory from two grass pollens. The first preparation of this compound was made from the pollen of orchard grass (*Dactylis glomerata L.*) and for this reason we are proposing the name "dactylin." An identical compound was found to separate from an extract of timothy pollen (*Phleum pratense* L.).

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[4] Fischer and Dilthey, Ann., 335,349 (1904).

[1] F. W. Heyl, THIS JOURNAL, 41, 1285–1289 (1919).

[2] Masao Fukuda, *Chem. Abstracts,* 22, 1993 (1928), from Bull. Soc. *Chem. Japan,* 3, 53–56 (1928).

Experimental

Isolation and Purification.—A distilled water extract of either grass pollen (previously ether extracted) was found to deposit a pale yellow crystalline substance after standing for a few hours. After twenty-four hours at 2–5° a good yield of the crystals was obtained. A second smaller crop was recovered after longer standing.

The crystals were separated from the water extract by centrifugation. They were then purified by two recrystallizations from boiling water, washed with alcohol and ether and dried. The melting point, never sharp, is not appreciably changed by the second recrystallization. As the yield of crude crystals is less than 0.5% of the weight of pollen used, the quantity of purified material available for a study of the properties of dactylin was quite small.

Properties.—Dactylin separates as pale yellow tasteless needles, which may be dried at 100°. Decomposition begins slightly below the melting point and the material fuses to a darkened mass before it becomes truly liquid. This behavior is shared by many of its derivatives. The "melting points" as recorded represent the temperatures at which the crystals fuse to form a viscid mass. On this basis the melting point of dactylin from either source or mixed is 183–185° (corr.).

This glucoside is very sparingly soluble in alcohol, glycerol, or cold water, readily soluble in boiling water and practically insoluble in ether, chloroform, acetone, carbon disulfide, benzene, or glacial acetic acid. It is freely soluble in pyridine, with which it forms a compound, m. p. 261–263° dec. (corr.). In cold water which contains sufficient alkali to raise the P_H to about 3.4 or greater, dactylin dissolves, giving an intense yellow solution.

A water solution of the glucoside gives a strongly positive Molisch test, and does not reduce Fehling's solution. With Millon's reagent it gives a red solution, soon changing to brown. If a trace of ferric chloride is added to the dactylin solution, a permanent dull purplish-green color is produced. No precipitate or characteristic color appears in the solution upon addition of barium chloride, silver nitrate, mercuric chloride, calcium chloride, or lead acetate. In cold concentrated sulfuric acid, the glucoside gives a yellow solution, which develops a greenish fluorescence upon standing.

A suspension of dactylin in water is not hydrolyzed by an active emulsin preparation within a week at 37°.

Hydrolysis readily occurs when the glucoside is heated with 5% sulfuric acid in a boiling water-bath. At first a clear solution is formed, but after a few minutes a yellow crystalline precipitate separates. There remains a colorless solution which reduces Fehling's reagent.

The yellow precipitate formed by acid hydrolysis, when washed with water until free from sulfates, then with alcohol and ether and dried at 100°, melts with decomposition at 298–300° (corr.). This melting point was checked with the preparation from each pollen and with a mixture. The crystals appear microscopically as small feathery collections of fine needles. The saturated solution of this material in alcohol, in which it is slightly soluble, gives no characteristic reaction with water solutions of calcium chloride, barium chloride, silver nitrate or mercuric chloride. Lead acetate increases the yellow color of the solution. With ferric chloride it gives a permanent brownish-purple color. When the compound is added to magnesium and glacial acetic acid, a brick-red color appears after the mixture is allowed to stand for a minute. Addition of hydrochloric acid changes the color to a cherry-red.

The soluble hydrolysis product gives no test for pentoses with phloroglucinol. It forms an osazone having the microscopic appearance of dextrosazone, and melting at 204–205° (corr.). This was checked by preparations from both sources.

In two hydrolyses, using crystals from the separate sources, the insoluble material was found to amount to 40.16 and 40.25% of the original glucoside.

Dactylin was found to contain only carbon, hydrogen and oxygen. Samples for analysis were dried at 100°.

Anal. Calcd. for $C_{23}H_{28}O_{15}$: C, 50.74; H, 5.15; for $C_{26}H_{32}O_{17}$: C, 50.65; H, 5.19; for $C_{29}H_{36}O_{19}$: C, 50.58; H, 5.23. Found: (source–orchard grass pollen) C, 50.59; H, 5.25. (Source—timothy pollen) C, 50.56, 50.64; H, 5.19, 5.06.

Which of the above formulas is preferable may be inferred from a consideration of the percentage of insoluble hydrolysis product formed. Assuming the reaction: $C_{23}H_{28}O_{15} + 2H_2O \longrightarrow 2C_6H_{12}O_6 + C_{11}H_8O_5$, the theoretical percentage of this product would be 40.4% (found, 40.2%). If this percentage is calculated, using either of the other above formulas, the values do not agree with the experimental within the limits of probable error. For this reason we believe the formula $C_{23}H_{28}O_{15}$ is justified.

Discussion

The method of isolation of dactylin raises the question as to whether it is originally present as such in the pollen or is formed in its water extract by the action of enzymes upon some parent substance. The latter theory is supported by the fact that the crystals will spontaneously precipitate from a water extract of pollen at the same temperature as that used for extraction. Moreover, in the presence of 50% glycerol (by volume), the precipitation of dactylin does not occur, although the compound after isolation is very difficultly soluble in glycerol.

The reaction with magnesium and acids makes it appear that this glucoside is closely related to those of the hydroxy flavones.[3]

The fact that it is not hydrolyzed by emulsin indicates that dactylin is not a β-glucoside. The sugar present is probably a hexose, two molecules of monosaccharide being present for each molecule of the insoluble hydrolysis product.

Further work is planned to determine the molecular formula and structure of this compound, when a sufficient supply of grass pollen becomes available.

Summary

A glucoside "dactylin" has been isolated from water extracts of orchard grass and timothy pollens, and its properties studied. Analytical results indicate $C_{23}H_{28}O_{15}$ as the empirical formula.

NORTH CHICAGO, ILLINOIS

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[3] Keita Shibata, Yuji Shibata and Itizo Kaswagi, THIS JOURNAL, 41, 208–220 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

RESEARCHES ON ALDEHYDES. IV. THE CATALYTIC REDUCTION OF SIMPLE AND OF SUBSTITUTED CINNAMIC ALDEHYDES

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Introduction

In previous papers we have reported on the synthesis of simple and of substituted 2-alkylcinnamic aldehydes,[2] and on the reduction of some of these to the corresponding unsaturated alcohols by the use of aluminum ethylate or of magnesium chloroethylate.[3]

The present contribution records the catalytic reduction of these cinnamic aldehydes to the corresponding saturated aldehydes, saturated alcohols and aryl paraffins.

Depending upon the amount of hydrogen taken up per mole of initial material, and excluding bimolecular reactions, the various products theoretically obtainable by reduction of a 2-alkylcinnamic aldehyde may be represented thus

$$\mathrm{ArCH{=}CRCHO} + \mathrm{H_2} \longrightarrow \left\{\begin{matrix}\mathrm{ArCH{=}CRCH_2OH}\\ \mathrm{ArCH_2CRHCHO}\end{matrix}\right\} + \mathrm{H_2} \longrightarrow$$

$$\left\{\begin{matrix}\mathrm{ArCH{=}CRCH_3}\\ \mathrm{ArCH_2CRHCH_2OH}\end{matrix}\right\} + \mathrm{H_2} \longrightarrow \mathrm{ArCH_2CRHCH_3}$$

In our experiments we followed the process of Skita,[4] using colloidal palladium as the catalyst in most cases, since he found that with cinnamic aldehyde itself this process caused neither hydrogenation of the benzene nucleus nor formation of bimolecular compounds, under conditions similar to ours. With one mole of hydrogen per mole of cinnamic aldehyde, he reported that his product was nearly pure hydrocinnamic aldehyde.

Straus and Grindel[5] repeated the experiment and stated that their products were the saturated alcohol, the propane and a little unsaturated alcohol, but no saturated aldehyde (except in one case), although pressure and proportion of hydrogen and of catalyst were varied considerably. Since they found that neither the saturated aldehyde nor the saturated alcohol separately could be reduced under these conditions, they suggested that the cinnamyl alcohol and phenylpropene were formed first and were

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[1] Fritzsche Fellow for 1928–1929 at Columbia University. This investigation could not have been undertaken without the generous assistance of Mr. F. E. Watermeyer, President of Fritzsche Brothers, Inc., of New York, the donor of the Fellowship [M. T. B.].

[2] Bogert and Powell, *Am. Perfumer Ess. Oil Rev.*, 25, 617 (1930).

[3] Bogert and Powell, THIS JOURNAL, 53, 1605 (1931).

[4] Skita, Ber., 48, 1685 (1915).

[5] Straus and Grindel, *Ann.*, 439, 276 (1924).

then reduced to the saturated alcohol and phenylpropane, respectively, the velocity of these latter changes being greater than that of the reduction of the initial unsaturated aldehyde. This was their explanation of why little or none of these hypothetical intermediate products was detected.

Such a postulation, however, does not explain the formation of saturated aldehyde noted by Skita and by ourselves. It is true that the unsaturated alcohols are easily reduced under the conditions of the Skita process, while the saturated aldehydes are not, but the saturated aldehyde itself must be formed from its unsaturated progenitor either by direct saturation of the olefin bond, or by a 1,4-addition with subsequent rearrangement

$$\text{ArCH}{=}\text{CRCHO} + \text{H}_2 = \text{ArCH}_2\text{CR}{=}\text{CHOH} \longrightarrow \text{ArCH}_2\text{CRHCHO}$$

It is suggested, therefore, that we may be dealing with several types of reactions taking place concurrently, the saturated aldehyde being formed as just indicated and the saturated alcohol and phenylpropane as postulated by Straus and Grindel, although it should be pointed out that because the saturated aldehyde and saturated alcohol cannot be readily reduced separately and individually by the Skita method, it does not follow necessarily that they may not undergo such a direct reduction under the catalytic effect of the other substances present in the mixture while the unsaturated aldehyde is being reduced.

Adams and Tuley[6] have described a selective reduction of cinnamic aldehyde either to the unsaturated or the saturated alcohol, by suitable additions of small amounts of iron or zinc salts to their platinum-oxide platinum black catalyst, these additions promoting reduction of the aldehyde group and inhibiting the saturation of the olefin bond. The conditions for such selective reduction seem to be highly specific and likely to require prolonged experimentation in each case to learn the correct mixture for the purpose.

With the unsaturated aldehydes we were studying, the Skita process of reduction gave more satisfactory results than we were able to secure with the Adams methods.

Our first run was always made on a 1.5 mole reduction basis, *i. e.*, until 1.5 moles of hydrogen per mole of initial unsaturated aldehyde had been absorbed. The results obtained in that run determined what changes, if any, were desirable in subsequent runs. The saturated aldehydes and saturated alcohols were the principal products with a one or two mole hydrogenation, the propanes being formed in small amounts only. The limit of hydrogenation, with repeated use of catalyst, was not far from two moles of hydrogen, and the amount of hydrogen absorbed in proportion to catalyst varied according to the unsaturated aldehyde used. The yield of saturated aldehyde was favored by restricting the quantity of hydrogen absorbed, while that of the propane was improved by increasing

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[6] Adams and Tuley, THIS JOURNAL, 47, 3061 (1925).

the gas pressure. In one experiment, only the saturated alcohol and aryl paraffin were found. In all other cases, both these and the saturated aldehyde were produced. No unsaturated alcohols or aryl olefins were detected in any of the runs.

The palladous chloride used for the preparation of the catalyst contained traces of platinum, rhodium and hydrochloric acid. The catalyst was not poisoned by the addition of traces of iron, cobalt or nickel salts.

Skita reported that the reduction of cinnamic aldehyde by colloidal palladium yielded mainly hydrocinnamic aldehyde and that the further reduction of the latter was accomplished better with platinum than with palladium. We have found the same to be true in the case of the substituted hydrocinnamic aldehydes prepared by us, namely, that they are either not at all, or certainly not easily, reduced by the usual Skita process with colloidal palladium.

In addition to the products already mentioned, the catalytic reduction of these unsaturated aldehydes always gave higher boiling products, which remained in the distilling flasks after the removal of propanes, saturated aldehydes and saturated alcohols, in the order named, but which have not yet been identified.

Commercial hydrogen from cylinders was used in all of the reductions. The unsaturated aldehyde was subjected to the action of the gas in an Adams hydrogenator. Practically all of the distillations were conducted under diminished pressure and in an atmosphere of nitrogen, to guard against oxidation.

While this investigation was in progress, a French patent[7] appeared, claiming improvement in color and in odor of perfumes by subjection to reduction by hydrogen in the presence of a nickel catalyst, by aluminum amalgam, zinc dust, etc., and citing ionones, geraniol and others as examples of perfumes improved by such reduction, but it does not specifically cover any of the field reported in the following pages.

The saturated aldehydes were colorless, mobile liquids which boiled lower than the corresponding saturated alcohols or unsaturated aldehydes. They all possessed agreeable odors, which varied with the nature of the side chains.

In general, their reactions were normal. The ability of the 2-amyl derivatives to form bisulfite compounds seems doubtful. The other saturated aldehydes prepared all gave bisulfite compounds, although in some instances they formed very slowly.

When this research was begun, the only aldehyde of this type in the literature was the 2-methyldihydrocinnamic aldehyde of Miller and Rohde.[8]

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[7] I. G. Farbenind. A.-G., French Patent 643,352 (Nov. 4, 1927); *Chem. Abstracts*, **23**, 1475 (1929).

[8] Miller and Rohde, *Ber.*, 23, 1080 (1890).

The saturated alcohols were colorless, more or less viscous liquids and, with the exception of the hpdrocinnamic series, practically odorless. They were recovered from the middle fractions of the reduced unsaturated aldehydes, after oximation to remove all aldehydes. In the case of some of the higher homologs, their isolation as acetate or as dinitrobenzoate proved more satisfactory than as the free alcohol.

The aryl paraffins were found in the first runnings of the distillate from the mixture obtained by reduction of the unsaturated aldehyde. Aldehydic impurities were removed by oximation when necessary. The purified propanes were all colorless, mobile liquids. They were all fragrant, the aroma of some of them being quite potent. The scent of 2-benzyl-*n*-butane may be likened to that of safrole containing a little citral. Dihydrosafrole has been described as having only a weak safrole odor, whereas in our judgment it possesses fully as strong if not a stronger odor than safrole itself. The 2-substituted dihydrosafroles all exhaled a strong safrole aroma but rather sweeter than safrole, and the scent of the substituted dihydroanetholes was strongly reminiscent of anethole. The odor of 2-ethyl-3-p-anisylpropane was of anethole type, but also somewhat stronger and sweeter.

Experimental Part

Reduction of Piperonylidene Acetaldehyde, $(CH_2O_2)[3,4]C_6H_3CH{=}CHCHO$

Dihydrosafrole, $(CH_2O_2)[3,4]C_6H_3CH_2CH_2CH_3$.—Piperonylideneacetaldehyde (3,4-methylenedioxycinnamic aldehyde) was reduced by the method of Skita.[4]

To a solution of 12 g. of the unsaturated aldehyde in 125 cc. of 95% alcohol and 40 cc. of water, there were added 20 cc. of a 2% aqueous solution of gum arabic and 10 cc. of a 1% aqueous palladous chloride solution, and the mixture was immediately treated with hydrogen at 3 atmospheres' pressure in the Adams hydrogenator. After forty-five minutes, the absorption of hydrogen ceased abruptly. It was found that two moles of hydrogen had been absorbed and the pressure had fallen to two atmospheres.

The solution was filtered from the catalyst, the filtrate diluted largely with water, extracted with ether and the ether extract treated with 4–6 volumes of saturated sodium bisulfite solution for a day with frequent shaking, to remove aldehydes. This ether solution usually contained 15–25% of the reduction products, and these were the conditions employed in the case of other reductions as well for the separation of the aldehyde bisulfites, the only important variation being in the length of time required for such compounds to separate.

The bisulfite compound precipitated was removed, washed thoroughly with ether and the washings added to the filtrate. The ether layer in this filtrate was separated, washed with a sodium carbonate solution, then with water, dried, the ether distilled off and the residue fractionated under diminished pressure in an atmosphere of nitrogen. The first fraction was dihydrosafrole, without admixture with any safrole or isosafrole, which on rectification boiled at 226–228° (uncorr.). The odor of this dihydro derivative, as mentioned in the introductory portion of this paper, was fully as powerful as that of safrole itself. It was unchanged by digestion with strong potassium hydroxide solution; yield, about 10%.

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[9] Ciamician and Silber, *Ber.*, 23, 1162 (1890).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.13; H, 7.37; for $C_{10}H_{10}O_2$ (safrole or isosafrole); C, 74.04; H, 6.22. Found: C, 73.41; H, 7.55.

The higher boiling fraction, after removal of the dihydrosafrole, contained the saturated alcohol.

Attempts to carry out this same reduction with the Adams and Tuley[6] platinum-oxide platinum black catalyst were less satisfactory, for it was found necessary to re-activate the catalyst thrice before the two mole hydrogenation could be completed. As far as our examination went, the reduction products seemed to be the same as with palladium.

In the palladium reductions, variations in the pressure (1.3, 2, 2.5 or 3 atmospheres) of the hydrogen, did not alter the fact that exactly two moles of hydrogen was absorbed in every case. It affected only the rate of this absorption, which naturally increased with the pressure.

2-Piperonylethanol, $(CH_2O_2)[3,4]C_6H_3CH_2CH_2CH_2OH$, as mentioned above, was found in the second fraction from the distillation of the reduction products of the 3,4-methylenedioxycinnamic aldehyde. It was a colorless, odorless, viscous liquid, b. p. 149–150° (uncorr.) at 6 mm.; n_D^{21} 1.54427; yield, about 70%.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.64; H, 6.72. Found: C, 66.63; H, 6.69.

Acetate.—From the alcohol digested two hours with fused sodium acetate and excess of acetic anhydride; colorless liquid, of faint but agreeable odor, b. p. 145° (uncorr.) at 4 mm.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.83; H, 6.35. Found: C, 64.92; H, 6.58.

Reduction of 2-Piperonylidene-propionaldehyde, $(CH_2O_2)[3,4]C_6H_3CH{=}C(CH_3)CHO$

2-Piperonylpropane, $(CH_2O_2)[3,4]C_6H_3CH_2CH(CH_3)_2$.—A mixture of 10 g. of the unsaturated aldehyde, 150 cc. of 95% alcohol, 5 cc. of the catalyst solution, 20 cc. of gum arabic solution and 30 cc. of water, was treated with hydrogen at atmospheric pressure until 1.25 moles of hydrogen had been absorbed per mole of aldehyde. Several runs were made with these proportions and the accumulated reduction mixtures then worked up as described for the reduction of the piperonylidene acetaldehyde. The bisulfite compound separated was decomposed by agitation with sodium carbonate solution and ether, until the solid had all disappeared. The ether layer was removed, washed with water, dried and the solvent evaporated. The residue was almost pure initial unsaturated aldehyde (oxime, m. p., 124–126°, uncorr.).

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.44; H, 5.30. Found: C, 69.38; H, 5.44.

After the removal of the aldehyde bisulfite from the original reduction mixture, the ether extracts, as before, were washed with sodium carbonate solution, then with water, dried and distilled. After removal of the ether, two fractions were collected, one of boiling point around 120" at 4 mm., and the other at about 150° at 4 mm.

The first fraction on redistillation yielded a colorless mobile oil, b. p. 238–240° (uncorr.) at 760 mm., n_D^{23} 1.51841, of safrole odor, and proved to be the expected arylpropane.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.85. Found: C, 73.99; H, 7.82.

From a similar reduction, with acetic acid as solvent in place of alcohol, the bisulfite separation yielded a mixture of aldehydes, b. p. 140–158° (uncorr.) at 4.5 mm., of an odor quite different from that of the initial unsaturated aldehyde, and which presumably contained some of the saturated aldehyde. The amount of material available, however, was insufficient to enable us to isolate the latter pure.

A preliminary experiment, using 5 g. of the unsaturated aldehyde in place of 10, and the other ingredients of the mixture as already stated, with hydrogen at ordinary pressure, showed that after two moles of hydrogen had been absorbed, the absorption ceased abruptly. As it was believed that this might be carrying the reduction too far, in view of the results obtained by a two-mole reduction of piperonylidene-acetaldehyde, we investigated the piperonylidene-propionaldehyde chiefly from the standpoint of a 1.25-mole reduction as outlined above.

2-Piperonylpropanol, $(CH_2O_2)[3,4]C_6H_3CH_2CH(CH_3)CH_2OH$.—The higher boiling fraction (b. p. around 150" at 4 mm.) referred to above, after taking off the arylpropane in the first runnings, was dissolved in aqueous alcohol and refluxed for one and one-half hours with hydroxylamine, to remove any aldehydes present. The product of this oximation was diluted with water, extracted with ether, the ether extracts washed with dilute hydrochloric acid, to remove any excess of hydroxylamine, then repeatedly with water, with sodium carbonate solution and finally with water again. The ether was removed and the residue, as usual, distilled under diminished pressure in an atmosphere of nitrogen, collecting the fraction of b. p. 147–148° (uncorr.) at 4 mm. The alcohol thus purified formed an odorless, colorless, viscous liquid, $n_D^{22.5}$ 1.54054, which did not absorb bromine in carbon tetrachloride solution.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.27. Found: C, 68.08, 67.97; H, 7.41, 7.40.

Reduction of 2-Piperonylidene-butyraldehyde, $(CH_2O_2)[3,4]C_6H_3CH{=}C(C_2H_5)CHO$

2-Piperonyl-butyraldehyde, $(CH_2O_2)[3,4]C_6H_3CH_2CH(C_2H_5)CHO$.—A mixture of 10.2 g. of the unsaturated aldehyde, 65 cc. of glacial acetic acid, 30 cc. of water, 7 cc. of gum arabic solution and 5 cc. of the catalyst solution absorbed 1.6 moles of hydrogen in two hours at ordinary pressure. A mixture of 10.2 g. of the unsaturated aldehyde, 100 cc. of 95% alcohol, 20 cc. of water, 10 cc. of gum arabic solution and 5 cc. of the catalyst solution, absorbed 1.8 moles of hydrogen in one and one-half hours at ordinary pressure. This latter reduction mixture was worked up in the manner already described.

Decomposition of the bisulfite precipitate yielded the pure saturated aldehyde as a colorless liquid, b. p. 136° (uncorr.) at 3 mm., of weak but agreeable odor.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.86; H, 6.85. Found: C, 70.21; H, 6.82.

2-Piperonylbutane, $(CH_2O_2)[3,4]C_6H_3CH_2CH(C_2H_5)CH_3$.—After removal of the aldehyde bisulfite, the ether extracts were distilled and, following the evaporation of the ether, a fraction of b. p. up to 130" at 3 mm. was collected and then a second one, b. p. about 150° at 2 mm. The lower fraction carried the arylbutane, the upper one the saturated alcohol.

The piperonylbutane on rectification boiled at 255–260° (uncorr.) at 760 mm., mainly at 257°, and its odor was very faint. It was a colorless mobile oil.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.95; H, 8.39. Found: C, 74.73; H, 8.28.

2-Piperonylbutanol, $(CH_2O_2)[3,4]C_6H_3CH_2CH(C_2H_5)CH_2OH$.—From the fraction above the piperonylbutane, the butanol was isolated in the same way as noted for the analogous piperonylpropanol, removing aldehydic contaminants by oximation. After repeated distillation, it was obtained as a colorless, odorless, viscous liquid, b. p. 148–150° (uncorr.) at 2 mm., n_D^{22} 1.53853.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.19; H, 7.75. Found: C, 68.89; H, 7.57.

Reduction of 2-Ethylcinnamic Aldehyde, $C_6H_5CH{=}C(C_2H_5)CHO$

2-Ethylhydrocinnamic Aldehyde (β-Benzyl-*n*-butyraldehyde), $C_6H_5CH_2CH(C_2H_5)CHO$.—The mixture used for reduction was composed of 23 g. of the unsaturated aldehyde, 110 cc. of 95% alcohol, 30 cc. of water, 10 cc. of gum arabic solution and 10 cc. of the palladous chloride solution. At ordinary temperature and pressure, this absorbed less than one mole of hydrogen per mole of aldehyde in forty-five minutes. After the addition of 10 cc. more of the catalyst solution, the absorption rose to 1.25 moles of hydrogen and was increasing so slowly that it was interrupted and the reduction products examined as described under the reduction of piperonylidene-acetaldehyde.

Hydrolysis of the bisulfite compound yielded the pure saturated aldehyde as a colorless liquid, b. p. 115–116" (uncorr.) at 12.5 mm., $n_D^{22.5}$ 1.50839, which formed a mirror with ammoniacal silver solutions. Its odor was agreeable, but not very strong.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.42; H, 8.70. Found: C, 81.32; H, 8.67.

It was not reduced by the Skita process under the condition., which caused reduction of the unsaturated aldehyde, but was reduced by hydrogen under pressure in the presence of the platinum-oxideplatinum black catalyst.

2-Benzyl-n-butane, $C_6H_5CH_2CH(C_2H_5)CH_3$.—After the separation of the above saturated aldehyde, the solvent was removed from the ether extracts and the residue fractionated under diminished pressure in an atmosphere of nitrogen. The first fraction contained the hydrocarbon, the second the saturated alcohol. Both were freed from aldehyde impurities by oximation.

The benzylbutane present in the first fraction (b. p. 98–100° at 30 mm.), was isolated as a liquid, b. p. 190° (uncorr.) at 710 mm., of a weak safrole-type of odor. It has been reported before by Dumesnil,[10] who gave its b. p. as 102° at 15 mm., and by Glattfeld and Cameron,[11] who prepared it by five different methods and found an approximate boiling point of 192° at 710- 720 mm.

2-Benzyl-n-butanol, $C_6H_5CH_2CH(C_2H_5)CH_2OH$.—This saturated alcohol, as separated from the higher boiling fraction of the above reduction mixture, was a colorless, viscous liquid, with a faint sweetish odor, b. p. 105–107° (uncorr.) at 4 mm., or about 256–257° (corr.) at 755 mm.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.43; H, 9.83. Found: C, 80.19; H, 9.63.

It has been prepared previously by other methods, by Guerbet,[12] who recorded its b. p. as 258–261° (corr.) and its odor as lilac-like, and by Von Braun, Rohmer and co-workers,[13] who found a boiling point of 134–135° at 13 mm., and described its fragrance as rose-like.

Reduction of 2-n-Amylcinnamic Aldehyde, $C_6H_5CH{=}C(C_5H_{11})CHO$

2-Amyl-γ-phenylpropane, $C_6H_5CH_2CH(C_5H_{11})CH_3$, was isolated by fractional distillation of accumulated reduction products of the amylcinnamic aldehyde, being found in the first runnings. It was a colorless mobile oil, b. p. 128–130° (uncorr.) at 16 mm., of not very pleasant odor.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.34; H, 11.66. Found: C, 86.95; H, 11.92.

The low figure for carbon suggests that the product was not quite pure.

2-Amyl-3-phenylpropanol (2-Amyl-dihydrocinnamic Alcohol), $C_6H_5CH_2CH(C_5H_{11})$-CH_2OH.—Using the same proportions of ingredients as noted above for the reduction of 2-ethylcinnamic aldehyde, a 1.6 mole reduction product (34 g.) was refluxed for forty-five minutes with 100 g. of acetic anhydride and 3 g. of fused sodium acetate. Distillation of the product gave a principal fraction, b. p. 134–135° (uncorr.) at 3.5 mm., which proved to be the acetate of the saturated alcohol.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.36; H, 9.74. Found: C, 77.85; H, 9.82.

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[10] Dumesnil, Ann. *chim.*, [9] 8, 91 (1916).

[11] Glattfeld and Cameron, THIS JOURNAL, 49, 1043 (1927).

[12] Guerbet, Compt. *rend.*, 146, 1406 (1908); Bull. *soc. chim.*, [4] 3, 944 (1908).

[13] Von Braun, Rohmer and co-workers, Ann., **451**, 50 (1926).

This *acetate* was hydrolyzed by refluxing it for an hour with a 5% alcoholic potassium hydroxide solution. The alcohol was a colorless, viscous liquid, b. p. 119–120. (uncorr.) at 2.5 mm., of weak but rather pleasing odor.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.48; H, 10.76. Found: C, 81.68; H, 10.54.

3,5-Dinitrobenzoate.—The saturated alcohol present in a one-mole reduction product of the amylcinnamic aldehyde was converted to its 3,5-dinitrobenzoate, a reddish, viscous liquid, hydrolysis of which yielded the saturated alcohol, in an impure form (C, 82.15; H, 10.56), but which contained no unsaturated alcohol (no bromine absorption).

Reduction of 2-Methyl-o-methoxycinnamic Aldehyde, $o\text{-}CH_3OC_6H_4CH{=}C(CH_3)CHO$

2-Methyl-3-o-anisyl-propionaldehyde, $CH_3OC_6H_4CH_2CH(CH_3)CHO$.—A mixture of 21 g. of the unsaturated alcohol, 150 cc. of 95% alcohol, 30 cc. of water, 10 cc. of gum solution and 12 cc. of catalyst, when subjected to the action of hydrogen at an average pressure of 2.5 atmospheres, absorbed 1.9 moles of hydrogen exothermally in an hour.

The bisulfite compound separated from the reduction mixture gave the pure saturated aldehyde when hydrolyzed, as a colorless liquid, of a weak sweet odor, b. p. 113–114" (uncorr.) at 5.25 mm., which formed a mirror with ammoniacal silver solutions.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.11; H, 7.93. Found: C, 74.11; H, 8.16.

2-Methyl-3-o-anisylpropane, $CH_3OC_6H_4CH_2CH(CH_3)_2$.—Fractionation of the residual ether solution after removal of the above bisulfite compound gave a fraction, b. p. near 90° at 9 mm., which contained the propane. This hydrocarbon was isolated in the pure state by rectification, without requiring oximation, and was a colorless liquid, b. p. 111–112° (corr.) at 31.25 mm., of agreeable aromatic odor.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.81. Found: C, 80.34; H, 9.77.

2-Methyl-3-o-anisylpropanol, $CH_3OC_6H_4CH_2CH(CH_3)CH_2OH$.—The fraction boiling just above that containing the anisylpropane carried the saturated alcohol. Its boiling point was around 130° at 6 mm. It was oximated, to remove a small amount of aldehyde present, and was then purified by distillation. It was a colorless, odorless oil, h. p. 131.5–132.5° (corr.) at 8.75 mm.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.29; H, 8.94. Found: C, 72.95; H, 8.82.

Reduction of 2-Ethyl-o-methoxycinnamic Aldehyde, $o\text{-}CH_3OC_6H_4CH{=}C(C_2H_5)CHO$

2-Ethyl-3-o-anisylpropionaldehyde, $CH_3OC_6H_4CH_2CH(C_2H_5)CHO$.—A mixture of 20 g. of the unsaturated aldehyde, 150 cc. of 95% alcohol, 30 cc. of water, 10 cc. of gum solution and 10 cc. of the catalyst, was reduced with hydrogen at an average pressure of 2.5 atmospheres, and approximately one mole of hydrogen was absorbed.

On working up the reduced mixture, the aldehyde bisulfite separated very slowly. Its hydrolysis yielded the pure saturated aldehyde as a colorless liquid, b. p. 144–145° (uncorr.) at 16 mm., of faint but not unpleasant odor.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.95; H, 8.39. Found: C, 74.70; H, 8.64.

2-Ethyl-3-o-anisylpropane, $CH_3OC_6H_4CH_2CH(C_2H_5)CH_3$.—The ether filtrate from the aldehyde bisulfite separation was distilled and the following fractions collected: (1) near 100° at 9 mm., and (2) near 135° at 6 mm.

Redistillation of Fraction (1) gave the propane as a colorless, mobile oil, b. p. 100.5–102.5" (corr.) at 9 mm., with an odor like that of the lower homolog described above.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.19. Found: C, 80.27; H, 10.37.

2-Ethyl-3-o-anisylpropanol, $CH_3OC_6H_4CH_2CH(C_2H_5)CH_2OH$.—Fraction (2) noted in the last preparation and boiling at about 135" at 6 mm. consisted mainly of unchanged initial unsaturated aldehyde but, after its removal as oxime, a small amount of the saturated alcohol was isolated, as a colorless, odorless liquid, b. p. 132–134" (corr.) at 55 mm.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.17; H, 9.35. Found: C, 74.17; H, 9.43.

Reduction of 2-Ethyl-p-methoxycinnamic Aldehyde, *p*-$CH_3OC_6H_4CH{=}C(C_2H_5)CHO$

2-Ethyl-3-p-anisyl-propionaldehyde, $CH_3OC_6H_4CH_2CH(C_2H_5)CHO$.—The mixture used was 14 g. of the unsaturated aldehyde, 100 cc. of 95% alcohol, 30 cc. of water, 10 cc. of the gum solution and 10 cc. of the catalyst. The hydrogen was applied at an average pressure of two atmospheres. The absorption ensued exothermally and in thirty minutes about two moles of hydrogen was taken up. With a larger proportion of catalyst, somewhat more hydrogen was absorbed. The reduction product was worked up as in the other cases.

Hydrolysis of the bisulfite precipitate gave the saturated aldehyde practically pure, as a colorless liquid, b. p. 116–117" (uncorr.) at 3 mm., $n_{\mathrm{D}}^{23\ 5}$ 1.51673, which formed a mirror with ammoniacal silver solutions. Its odor resembled that of the 2-ethylhydrocinnamic aldehyde.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.95; H, 8.39. Found: C, 74.61; H, 8.55.

2-Ethyl-3-*p*-anisylpropane (**β-Ethyldihydroanethole**), $CH_3OC_6H_4CH_2CH(C_2H_5)$-$CH_3$.—As usual, after separation of the above aldehyde bisulfite, the ether extracts were distilled and after removal of the ether two fractions were collected, the first one containing the hydrocarbon and the second the saturated alcohol. Both fractions were oximated, to remove any aldehyde still present.

The first fraction was collected at 105–110° at 10 mm., and yielded the pure hydrocarbon as a colorless mobile liquid, b. p. 135–136° (uncorr.) at 29 mm., of anethole odor.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.19. Found: C, 80.15; H, 9.92.

2-Ethyl-3-p-anisylpropanol, $CH_3OC_6H_4CH_2CH(C_2H_5)CH_2OH$.—The higher boiling fraction referred to above was collected at about 140° at 3 mm., and from it was recovered the saturated alcohol, as a colorless, odorless oil, b. p. 129–130" (uncorr.) at 2.5 mm., n_{D}^{22} 1.52398.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.17; H, 9.35. Found: C, 74.42; H, 9.64.

In the above reduction, 36 g. of crude reduction product (from several runs) yielded 4 g. of the saturated aldehyde, 4 g. of the hydrocarbon and 10 g. of the saturated alcohol.

Summary

1. The following have been reduced catalytically: piperonylideneacetaldehyde, its 2-methyl- and 2-ethyl-derivatives; 2-ethyl- and 2-amylcinnamic aldehydes; 2-methyl- and 2-ethyl-o-methoxycinnamic aldehydes and 2-ethyl-*p*-methoxycinnamic aldehyde.

2. The reduction products isolated were the corresponding saturated aldehyde, saturated alcohol and arylparaffin. No unsaturated alcohols or arylolefins were detected.

3. Most of the products described are new. Their physical and chemical properties are recorded, as well as their odors.

New York, N. Y.

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

EXPRESSED BRAZIL NUT OIL

BY H. A. SCHUETTE AND W. W. F. ENZ

RECEIVED MAY 6, 1931 PUBLISHED JULY 8, 1931

The seeds of the Brazil nut tree, Bertholletea *excelsa,* yield an oil whose individuality depends upon the mode of recovery. For example, a "virgin" oil of a color lying between water-white and pale yellow is obtainable by expression, whereas an inferior and materially darker product results when the residual pulp is exhausted with a suitable solvent. Qualitatively there appear to be few, if any, significant differences in the chemical composition of the constituent glycerides of these oils. That they are quantitative was, in a sense, indicated in an earlier communication[1] by the statement that the virgin oil readily solidifies (5–lo°) whereas the residual oil does not show a similar behavior.

The evident desirability of verifying this statement has prompted us to repeat quantitatively an analysis once reported qualitatively.[1] Pertinent data are recorded in this communication.

I. Preparation of Materials and Methods of Analysis

The nuts from which this oil was expressed[2] were purchased in the open market during the Christmas holiday season, when the stocks were fresh, confirmatory evidence for which was found in the very low acidity (0.006% as oleic) of the oil. A division of the fatty acids into two groups was effected by application of the lead salt-ether method[3'] with the necessary correction for the small amount of unsaturated acids contaminating the saturated when this procedure is used.[3b] The former (71.74%) were separated and identified by means of their bromine addition products,[4] while the latter (20.28%) were isolated as methyl esters.[5]

II. Analysis of Oil

(a) Titer Test.—The solidifying point of the insoluble fatty acids (titer test) is one of the few remaining constants of virgin Brazil nut oil which have not been heretofore reported. It was determined by the usual procedure[6]—the fatty acids were prepared by the glycerol–potassium hydroxide method of saponification—and found to be 33.3". This value agrees with that reported' for the residual oil.

(b) Unsaturated Acids.—That linolenic acid is not a constituent of this group was apparent from the fact that no hexabromide separated from the ether solution of the

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[1] Schuette, Thomas and Duthey, THIS JOURNAL, 52, 4114 (1930).

[2] Acknowledgment is made of the assistance given us by Miss Mabel Duthey, who expressed the oil used in this investigation. Filtration was the only operation required for its purification.

[3] (a) Gusserow, ***Arch. Apoth.-Vereins nord Teutschland,*** 27, 153 (1828); Varrentrapp, ***Ann.,*** 25, 197 (1840); (b) Jamieson, ***J. Assoc. Official Agri. Chem.,*** 11, 303 (1928).

[4] Eibener and Muggenthaler, ***Farben-Z.,*** 18, 131 (1912).

[5] Baughman and Jamieson, THIS JOURNAL, 42, 157 (1920).

[6] Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., **1925,** 2d ed., p. 286.

brominated product at −10°. Linoleic and oleic acids, however, are present in appreciable amounts. The presence of the former was shown in the formation of its tetrabromide (m. p. 114°), whereas the latter was indicated by its dibromo derivative (Br, 39.85%). Using this value and the theoretical iodine numbers of oleic and linoleic acids, the percentage composition of the whole was then calculated[5] with the results shown in Table I.

TABLE I

COMPOSITION OF THE UNSATURATED ACID FRACTION

Acid	In oil, %	Glycerides in oil, %	Total,[a] %
Oleic	36 67	41 61	42.79
Linoleic	22.72	25.80	26.54

[a] This column includes the unsaturated acids present with the saturated.

(c) Saturated Acids.—The methyl esters of the saturated acids were separated into five fractions (Table II) whose boiling range lay between 147 and 163° (3 mm.). The mean molecular weights of the respective fractions as calculated from saponification and iodine numbers—the latter serving as a basis for correcting each for the presence of unsaturated acids—indicated the presence of acids in the C_{14} to C_{18} group. These data lead to the following statement of the percentage composition of the saturated acid fraction.

TABLE II

RESULTS OF ANALYSIS OF METHYL ESTERS OF THE SATURATED ACIDS

Fraction	Wt., g.	Iodine no.	Sapon. no.	Mean mol. wt.	Unsatd. acids, wt.	Myristic acid, g.	Palmitic acid, g.	Stearic acid, g.
1	10.23	7 3	2098	267.5	073	153	7.48	..
2	17.62	5.5	2028	2766	094	..	12.74	3.09
3	31.00	6 6	200 0	280.5	1 99	..	18.44	9.12
4	9 71	7 5	197.8	283.6	0 71	..	4.71	3.84
5	3.62	7.6	195.3	287.2	0 27	..	1.33	1.86
Res.	4.94	12 9	...	...	..	..	..	..
Total	..	...	...	...	..	1.53	44.70	17.91

TABLE III

COMPOSITION OF THE SATURATED ACID FRACTION

Acid	In oil, %	Glycerides in oil, %
Myristic	0.47	0.48
Palmitic	11.97	13.74
Stearic	4.80	5.45
Undetermined	1.61	..

Summary

The approximate percentage composition of a sample of virgin Brazil nut oil has been found to be myristin, 0.48; palmitin, 13.74; stearin, 5.45; olein, 42.79; linolein, 26.54. Its solidifying point is higher than that of the oil recoverable from the residual pulp, a difference which is apparently largely due to a lower olein content. The linolein and palmitin contents of both grades of oil are of the same order of magnitude. Myristin, on the other hand, is present in the virgin oil to the extent of one-fourth as much

as in the product of lower quality. The former contains approximately twice as much stearin as the latter.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF AROMATIC KETONES AND BENZILS BY TRIPHENYLMETHYLMAGNESIUM BROMIDE

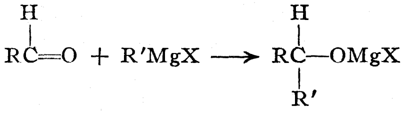
BY W. E. BACHMANN

RECEIVED MAY 11, 1931 PUBLISHED JULY 8, 1931

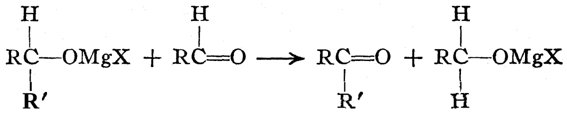
It is clear that the reduction which so frequently occurs in the Grignard reaction may be occasioned in several ways.[1] It has long been known that aliphatic Grignard reagents can exercise a reducing action toward certain compounds; as a rule an unsaturated hydrocarbon is formed in addition to the reduction product.

The work of Gomberg and Bachmann[2] on the reducing action of a mixture of magnesium and magnesium iodide has made it obvious that the Grignard reagent must be filtered from unused magnesium if reduction by this system is to be avoided. A number of instances have been reported in which reduction occurred when unused magnesium was allowed to remain in the Grignard reagent.[3]

Marshall[4] discovered that a mutual oxidation and reduction reaction may occur between excess of an aldehyde and the normal addition compound which is formed by the action of a Grignard reagent on the aldehyde. The reaction which occurs may be formulated as follows



$$\mathrm{R\overset{H}{C}{=}O + R'MgX \longrightarrow R\overset{H}{\underset{R'}{C}}{-}OMgX} \qquad (1)$$



$$\mathrm{R\overset{H}{\underset{R'}{C}}{-}OMgX + R\overset{H}{C}{=}O \longrightarrow R\underset{R'}{C}{=}O + R\overset{H}{\underset{H}{C}}{-}OMgX} \qquad (2)$$

The reaction involves a transfer of H and MgX from a molecule of the secondary alcohol to a molecule of aldehyde; the products are a ketone and a primary alcohol. The importance of this mode of reduction has been overlooked to a great extent; its applicability has been indicated by

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[1] *See* Noller, THIS JOURNAL, 53, 635 (1931).

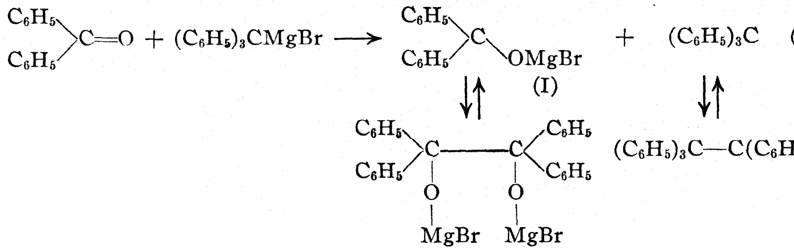
[2] Gomberg and Bachmann, *ibid.*, 49, 236 (1927); 49, 2584 (1927); 50, 2762 (1928); 52, 4967 (1930).

[3] See for example Boyd and Hatt, *J. Chem. Soc.*, 898 (1927); Hatt, *ibid.*, 1623 (1929); Barnett, Cook and Nixon, *ibid.*, 505 (1927); Lagrave, Ann. *chim.*, [10] *8*, 363 (1927).

[4] Marshall. J. *Chem. Soc.*, 105, 527 (1914); 107, 509 (1915); 127, 2184 (1925).

Meisenheimer[5] and more recently by the work of Gomberg and Bachmann[6] and of Shankland and Gomberg.[7] It should be pointed out that this reaction may take place even when the aldehyde is not used in excess; in fact, it may occur when the Grignard reagent preponderates. Thus, if the Grignard reagent is added slowly to the aldehyde, there may be time enough for the oxidation–reduction reaction[8] to take place before all of the aldehyde has reacted with the Grignard reagent. The latter, then, reacts not only with the aldehyde but also with the ketone that is formed in the secondary reaction. We have carried out such a reaction between one mole of benzaldehyde and two moles of phenylmagnesium iodide and obtained 25% of benzyl alcohol and 16% of triphenylcarbinol in addition to benzhydrol.

A singular type of reduction has been found to take place between triphenylmethylmagnesium bromide and certain aromatic ketones. Instead of a normal addition reaction taking place, this Grignard reagent reduces the ketones to pinacols. The reaction proceeds through the intermediate formation of free radicals. The reactions which take place with benzophenone[9] may be formulated as follows



$$(C_6H_5)_2C{=}O + (C_6H_5)_3CMgBr \longrightarrow (C_6H_5)_2C{-}OMgBr\ (I) + (C_6H_5)_3C \qquad (3)$$

Two free radicals, bromomagnesium ketyl[10] (I) and triphenylmethyl, are formed primarily; their presence is indicated by the color of the solution, the triphenylmethyl contributing an orange-yellow and the ketyl a red color (with phenylbenzophenone and especially with diphenylbenzophenone this latter color is an intense blue). These radicals associate to their corresponding dimolecular forms rather than unite with one another to form pentaphenylethanol. On hydrolysis a 93% yield of benzopinacol[11]

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[5] Meisenheimer, *Ann.*, 446, 76 (1926).

[6] Gomberg and Bachmann, THIS JOURNAL, 52, 4967 (1930).

[7] Shankland and Gomberg, *ibid.*, 52, 4973 (1930).

[8] See Ref. 7 for the speed of this type of reaction.

[9] This reaction was first carried out with Professor M. Gomberg in connection with our study of the action of Mg + $MgBr_2$ on triphenylmethyl.

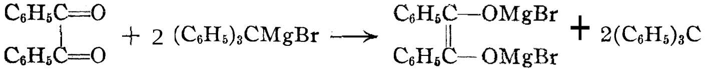
[10] This ketyl radical is identical with that formed by the action of MgBr on benzophenone [Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927)].

[11] Schmidlin, *Ber.*, 39, 4198 (1906), was the first to obtain benzopinacol from the interaction of triphenylmethylmagnesium chloride and benzophenone; however, he attributed the reduction to the magnesium which was present in the mixture. Gilman

and a practically quantitative yield of triphenylmethyl are obtained. Not only benzophenone but also *p*-chloro-, *p*-phenyl- and *p,p'*-diphenylbenzophenone in addition to fluorenone and xanthone have been found to be reduced to pinacols by triphenylmethylmagnesium bromide.

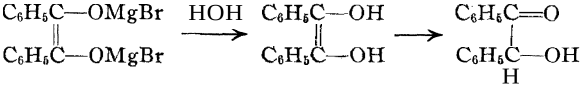
This type of reduction takes place to a slight extent in the reaction between phenylmagnesium bromide and benzophenone. If a filtered solution of the Grignard reagent is added to a solution of benzophenone in a nitrogen atmosphere, the red color of the bromomagnesium ketyl becomes visible. If diphenylbenzophenone is employed, the characteristic deep blue color of the corresponding ketyl appears. Indeed, the colors which have been observed by others[12] in the course of the Grignard reaction are attributed to the formation of ketyl radicals, albeit in minute amounts. Whether other types of reduction or whether even the normal addition reaction of the Grignard reagent takes place through the intermediate formation of radicals[13] is left undecided.

It has further been found that benzil is reduced by triphenylmethylmagnesium bromide. Two molecules of the Grignard reagent react with one molecule of the benzil and there is formed the bromomagnesium salt of stilbene-diol[14] (II) and triphenylmethyl.



$$\begin{array}{l} C_6H_5C{=}O \\ \quad | \\ C_6H_5C{=}O \end{array} + 2\,(C_6H_5)_3CMgBr \longrightarrow \begin{array}{l} C_6H_5C{-}OMgBr \\ \quad \| \\ C_6H_5C{-}OMgBr \end{array} + 2(C_6H_5)_3C \qquad (4)$$

Hydrolysis of the reaction mixture gives benzoin in addition to triphenylmethyl



$$\begin{array}{l} C_6H_5C{-}OMgBr \\ \quad \| \\ C_6H_5C{-}OMgBr \end{array} \xrightarrow{HOH} \begin{array}{l} C_6H_5C{-}OH \\ \quad \| \\ C_6H_5C{-}OH \end{array} \longrightarrow \begin{array}{l} C_6H_5C{=}O \\ \quad | \\ C_6H_5C{-}OH \\ \quad H \end{array} \qquad (5)$$

The presence of the bromomagnesium salt of stilbene-diol prior to hydrolysis was indicated by the color of the mixture during the reaction and was proved by the formation of stilbene-diol dibenzoate,[14] $C_6H_5C(OOCC_6H_5){=}(C_6H_5COO)CC_6H_5$, when the reaction mixture before hydrolysis was

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and Fothergill, THIS JOURNAL, 51, 3149 (1929), likewise, reported the formation of some pinacol (22–31% yields). Compare also the reaction of thio-ketones with the Grignard reagent [Schonberg and Schütz, *Ber.*, 60, 2351 (1927)].

[12] Of these, Davies, Dixon and Jones, *J. Chem. Soc.*, 1916 (1930), report not only that the red color of the ketyl is produced on the addition of benzophenone to amyl Grignard reagents but also that small yields (4–9%) of benzopinacol were isolated. As Noller, Ref. 1, points out, however, these investigators siphoned or decanted but did not filter their solutions from excess of magnesium. Noller subsequently was unable to find any benzopinacol among the products of the action of isobutylmagnesium bromide on benzophenone.

[13] Späth, *Monatsh.*, 34, 1967 (1913); Schlubach and Goes, *Ber.*, 55, 2897 (1922); Blicke and Powers, THIS JOURNAL, 51, 3378 (1929).

[14] Gomberg and Bachmann, *ibid.*, 49, 2584 (1927); Gomberg and Van Natta, *ibid.*, 51, 2238 (1929).

treated with benzoyl chloride. Dimethylbenzil and dichlorobenzil react with triphenylmethylmagnesium bromide in the same manner as benzil. The reaction of this Grignard reagent with benzil is analogous to the reaction that occurs between iodomagnesium hydrazobenzene, $C_6H_5N(MgI)—(IMg)NC_6H_5$, and benzil in which azobenzene[15] and the iodomagnesium salt of stilbene-diol are produced.

Experimental

All operations, including the preparation of the Grignard reagent and its reactions with ketones and benzils, were carried out in an atmosphere of nitrogen.

Triphenylmethylmagnesium Bromide + Benzophenone.—The Grignard reagent was prepared from 16.2 g. of triphenylmethyl bromide in a mixture of 30 cc. of ether and 60 cc. of benzene according to the directions of Gomberg and Bachmann.[16] The filtered solution of triphenylmethylmagnesium bromide was treated with 9.1 g. of benzophenone. The solution immediately became deep red in color. After three hours of refluxing, the solution was hydrolyzed with ice and dilute acetic acid. Air was passed into the orange-yellow solution until oxidation of triphenylmethyl was complete; by using a sintered-glass distributor, this result was attained in less than an hour. The triphenylmethyl peroxide which had precipitated was filtered off and washed with benzene and with acetone: wt., 10.3 g.; m. p. 186°.

The ether–benzene filtrate was allowed to evaporate to dryness. The solid residue was digested with warm petroleum ether (40–60°) in order to remove unreacted benzophenone; only traces of this compound were found in the filtrate. The crude pinacol was then dissolved in 140 cc. of cold acetone; this treatment left 0.5 g. of peroxide undissolved. Evaporation of the acetone solution gave a solid which after treatment with alcohol consisted of practically pure benzopinacol: wt., 8.5 g.; m. p. 186–188°.

In another experiment, the crude pinacol which was obtained on evaporation of the acetone solution was rearranged to β-benzopinacolin by heating it for a few minutes with 40 cc. of glacial acetic acid which contained a few crystals of iodine.[17] In this manner 7.5 g. of pinacolin was obtained. The yield of peroxide was again 10.8 g.

The results obtained from the interaction of triphenylmethylmagnesium bromide and a number of ketones are given in Table I. In each case one mole of Grignard reagent was employed for one mole of ketone.

Triphenylmethylmagnesium Bromide + Benzil.—A solution of 5.2 g. of benzil in 30 cc. of benzene was added to a solution of triphenylmethylmagnesium bromide prepared from 16.2 g. of triphenylmethyl bromide. An opaque dark brown color was formed but this disappeared as the reaction proceeded; at the end of the reaction the solution was transparent orapge in color. These color phenomena are entirely analogous to those observed in the reduction of benzil by the binary system $Mg + MgI_2$. After the solution had been refluxed for two and one-half hours, it was hydrolyzed. Air was passed into the solution in order to oxidize the triphenylrnethyl. The peroxide was filtered off and the filtrate was evaporated to dryness. The solid residue was extracted with ether in a Soxhlet extractor in order to dissolve the benzoin and leave peroxide undissolved. In this manner there was obtained 11.5 g. of triphenylmethyl peroxide and 4.2 g. of benzoin.

Reaction with Benzoyl Chloride.—After refluxing a mixture of 5.2 g. of benzil and the Grignard reagent from 16.2 g. of triphenylmethyl bromide for two hours, the solution

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[15] Bachmann, THIS JOURNAL, 53,1524 (1931).

[16] Gomberg and Bachmann, *ibid.*, 52,2455 (1930).

[17] Gomberg and Bachmann, *ibid.*, 49,246 (1927).

TABLE I

REDUCTION OF KETONES BY TRIPHENYLMETHYLMAGNESIUM BROMIDE

Ketone	Ketone, g.	Yields of products			
		Pinacol		Peroxide	
		G.	%	G.	%
Benzophenone	9.1	8.5	93	10.8	83[a]
4-Chlorobenzophenone	5.41	4.2	78	5.2	80
4-Phenylbenzophenone[b]	6.5	5.6	86	4.5	70
4,4'-Diphenylbenzophenone[c]	8.35	8.0	98	5.0	77
Fluorenone[d]	4.5	3.6	80	4.8	74
Xanthone[e]	4.9	4.1	84	5.0	77

[a] Since solutions of pure triphenylmethyl give only 80–85% yields of triphenylmethyl peroxide, this yield represents practically a quantitative formation of triphenylmethyl.

[b] The color of the reaction mixture was green (from the blue of the ketyl and the orange-yellow of triphenylmethyl). Since the pinacol is little soluble, hydrolysis was carried out in a nitrogen atmosphere and the pinacol which precipitated was filtered off; the triphenylmethyl in the filtrate was then oxidized to peroxide. A portion of the pinacol was rearranged to pinacolin by heating it with acetic acid and iodine; there was obtained the pinacolin, benzoyl-4,4'-diphenyl-triphenylmethane, of m. p. 198°. For descriptions of these and related compounds see Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927).

[c] The mixture was refluxed for one hour. The solution was intense greenish-blue and then intense green in color. The same procedure was employed here as is given under phenylbenzophenone.

[d] Part of the pinacol (1.7 g.) precipitated on hydrolysis of the reaction mixture. For purposes of identification a portion of the pinacol was warmed with 70% sulfuric acid; it gave the expected 9-diphenylenephenanthrone of m. p. 255°.

[e] Most of the xanthopinacol (3.2 g.) precipitated on hydrolysis. A sample when warmed with 70% sulfuric acid gave dixanthylene; m. p. 312°.

was cooled and treated with a solution of 7 cc. of benzoyl chloride in 30 cc. of benzene. After being kept warm for two hours, the mixture was allowed to stand at room temperature for twelve hours. Hydrolysis of the mixture, followed by oxidation of the triphenylmethyl, gave 6.0 g. of stilbenediol dibenzoate of m. p. 158° and 10.5 g. of triphenylmethyl peroxide.

In Table II are listed the results obtained from the interaction of two moles of triphenylmethylmagnesium bromide and one mole of the benzil.

Phenylmagnesium Iodide (2 Moles) + Benzaldehyde (1 Mole).—A filtered solution of phenylmagnesium iodide which had been prepared from 42 g. of iodobenzene in 75 cc. of ether was added drop by drop in the course of an hour to a warm solution of 10.6 g. of freshly distilled benzaldehyde in 30 cc. of benzene. After the addition, the mixture was warmed for one hour and was then allowed to stand overnight. The mixture was hydrolyzed, washed and dried. The solvents were removed by distillation and the mixture was then distilled on a steam-bath under a pressure of 1 mm. The benzyl alcohol which distilled was freed from biphenyl by extraction with water. From the aqueous extract was obtained 2.7 g. (25%) of benzyl alcohol (identified as the phenyl urethan, m. p. 76°, and as the *p*-nitrobenzoic acid ester, m. p. 84-85°).

The residue in the distilling flask was warmed with 40 cc. of ligroin (60-80°); this dissolved the benzohydrol and left 3.5 g. of triphenylcarbinol in the form of large crystals. From the ligroin filtrate there were obtained 8 g. of benzhydrol and an additional 1.0 g. of triphenylcarbinol.

TABLE II

REDUCTION OF BENZILS BY TRIPHENYLMETHYLMAGNESIUM BROMIDE

Benzil	Benzil g.	Yields of products Benzoin G.	 %	 Peroxide G.	 %
Benzil	5.2	4.2	80	11.5	88
Benzil	5.2	6.0[a]		10.5	80
4,4′-Dichlorobenzil	3.5	3.4	95	5.3	81
4,4′-Dichlorobenzil	3.5	4.0[b]		3.6	56
4,4′-Dimethylbenzil	3.0	2.3[c]		2.9	44

[a] Stilbene-diol dibenzoate.

[b] Dichloro-stilbene-diol dibenzoate [Gomberg and Van Natta, THIS JOURNAL, 51, 2238 (1929)] produced by treating the reaction mixture with 4 cc. of benzoyl chloride.

[c] Dimethyl-stilbene-diol dibenzoate. After recrystallization from alcohol it melted at 137–138° and was identical with the dibenzoate prepared from the benzil through the MgI reaction.

Summary

A number of aromatic ketones have been reduced to pinacols by means of the Grignard reagent, triphenylmethylmagnesium bromide. The reduction proceeds through the intermediate formation of radicals according to the following formulation: $RRC{=}O + (C_6H_5)_3CMgBr \longrightarrow RRC{-}OMgBr + (C_6H_5)_3C$. The ketyl radicals then associate to the pinacolate: $2RRC{-}OMgBr \longrightarrow RRC(OMgBr)(OMgBr)CRR$.

Benzils are reduced by triphenylmethylmagnesium bromide to the bromomagnesium salt of stilbene-diols: $RCOCOR + 2(C_6H_5)_3CMgBr \longrightarrow RC(OMgBr){=}(OMgBr)CR + 2(C_6H_5)_3C$.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

SOME NEW LOCAL ANESTHETICS CONTAINING THE MORPHOLINE RING[1]

BY JOHN H. GARDNER[2] AND EDWARD O. HAENNI

RECEIVED MAY 11, 1931 PUBLISHED JULY 8, 1931

In view of the very pronounced local anesthetic activity of the aromatic esters of the dialkylamino alcohols, such as procaine and butyn, it has seemed of interest to study the preparation and physiological properties of an analogous series in which the dialkylamino group is replaced by a morpholine ring. It is not to be expected that the morpholine ring as such should have any particular effect but it is possible that the ether linkage in the ring might serve to increase the solubility of the morpholine derivatives in lipoids and so increase the anesthetic powers.

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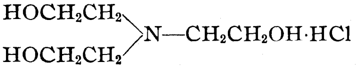
[1] Presented before the Organic Division of the American Chemical Society at Indianapolis, Indiana, April, 1931.

[2] This research has been assisted by a grant to the senior author from the Science Research Fund of Washington University.

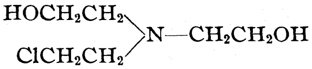
The starting point in this investigation was the preparation of β-4-morpholine-ethanol from triethanolamine. This had been accomplished by Knorr,[3] who dehydrated triethanolamine by heating with sulfuric acid, but did not give a full description of the product. A repetition of Knorr's method led to unsatisfactory results. It was found much more satisfactory to start with triethanolamine hydrochloride. This was obtained from the commercial product by saturating an alcoholic solution with hydrogen chloride gas, the hydrochlorides of the mono- and diethanolamines being soluble in alcohol.[4]

Boehmer and Hancock[6] dehydrated di-β-hydroxyethylaniline to 4-phenylmorpholine by heating under reduced pressure. Triethanolamine was not dehydrated under these conditions, but the hydrochloride (I) gave a product which, after heating with alcoholic potassium hydroxide, yielded the morpholine-ethanol. It seems probable that an intermediate chlorohydrin (II) is first formed and that this, on treatment with potassium hydroxide, is converted into morpholine-ethanol (III). This mechanism is supported by the fact that the crude dehydration product forms morpholine-ethanol only slowly on treatment with cold alkali. A similar mechanism was suggested by Knorr for the preparation of morpholine by heating diethanolamine with hydrochloric acid and subsequent treatment with alkali. He also isolated in an impure condition such an intermediate product obtained by heating di-β-hydroxyethylaniline with hydrochloric acid.[6]



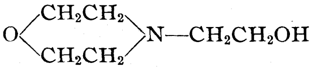
$$\begin{matrix} HOCH_2CH_2 \\ HOCH_2CH_2 \end{matrix} > N-CH_2CH_2OH \cdot HCl$$

I



$$\begin{matrix} HOCH_2CH_2 \\ ClCH_2CH_2 \end{matrix} > N-CH_2CH_2OH$$

II



$$O < \begin{matrix} CH_2CH_2 \\ CH_2CH_2 \end{matrix} > N-CH_2CH_2OH$$

III

From β-4-morpholine-ethanol, the hydrochlorides of the benzoate and p-aminobenzoate were prepared. Morpholine-ethanol, on treatment with benzoyl chloride and sodium hydroxide, yielded the benzoate from which β-4-morpholine-ethyl benzoate hydrochloride was obtained by precipitation with hydrogen chloride gas in benzene solution. β-4-Morpholine-ethyl p-nitrobenzoate hydrochloride was prepared by the interaction of morpholine-ethanol and *p*-nitrobenzoyl chloride in benzene solution. On reduction with hydrogen using Adams' platinum–platinum oxide catalyst, this yielded β-4-morpholine-ethyl p-aminobenzoate hydrochloride.

For the preparation of y-4-morpholinepropanol, trimethylene chloro-

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[3] Knorr, *Ann.*, 301, 9 (1898).

[4] Wurtz, *ibid.*, 121, 227 (1862); Knorr, ***Ber.***, 30, 919 (1897).

[5] Boehmer and Hancock, cited by Adkins and Simington, THIS JOURNAL, 47, 1688 (1925).

[6] Knorr, ***Ber.***, 22, 2084 (1889).

hydrin was condensed with potassium phthalimide and the product hydrolyzed to y-aminopropanol. The general procedure is that described by Putochin[7] with the substitution of trimethylene chlorohydrin for the trimethylene bromide which he used, avoiding complications due to the formation of the diphthalirnido compound. y-Hydroxypropyl phthalimide has been previously prepared by Gabriel.[8]

y-Aminopropanol was converted into y-4-morpholinepropanol by condensation with β,β'-dichloroethyl ether in the presence of anhydrous potassium carbonate. Some other morpholine derivatives have been prepared in a similar manner by Cretcher and his associates,[9] using an excess of the amine in place of the potassium carbonate, but the method has never been described for the preparation of morpholine alcohols. A similar procedure was used in a preliminary experiment for the preparation of morpholine-ethanol from ethanolamine.

γ-4-Morpholinepropanol was converted into the benzoate and *p*-aminobenzoate hydrochlorides in the same manner as the corresponding compounds were prepared from morpholine-ethanol.

Experimental

Triethanolamine Hydrochloride.—Four hundred grams of commercial triethanolamine[10] was dissolved in an equal volume of alcohol, the solution cooled in an ice-bath, and dry hydrogen chloride passed in until precipitation was complete. The precipitate was filtered off, washed with cold alcohol and recrystallized from 70% alcohol; yield, 338 g. of colorless rhombohedra1 crystals, m. p. 176.5–177°.[11] Knorr gives 177°.[4b]

β-4-Morpholine-ethanol.—Five hundred sixty-one grams of triethanolarnine hydrochloride in a 3-liter flask provided with a reflux condenser was heated in an oil-bath at 200–205° under a pressure of 40 mm. for fourteen hours, keeping the water in the condenser jacket at 50–60° to facilitate the removal of water. The resulting brown mass was repeatedly extracted with hot alcohol until only a slight residue of tarry matter remained. The alcoholic extract was cooled and filtered from 65 g. of triethanolamine hydrochloride which crystallized out. The filtrate, about 1500 cc., was boiled under reflux with 175 g. of potassium hydroxide, the resulting solution being strongly alkaline. The morpholine-ethanol solution was filtered from the precipitated potassium chloride and the alcohol removed by distillation. The residue was distilled under 25 mm. pressure, yielding 158 g. (46%) of crude morpholine-ethanol, b. p. 116–123°. Upon redistillation, β-4-morpholine-ethanol was obtained as a colorless oil with a piperidine-like odor, b. p. 118–120° under 24 mm.; d_{25}^{25} 1.0712; d_4^{25} 1.0681; n_D^{25} 1.4770; M_D calcd.: 34.71. Found: 35.46. ***Anal.*** Subs., 0.3776, 0.4023: 31.14, 31.26 cc. of 0.1116 N HCl; 5.49, 3.95 cc. of 0.1235 N NaOH. Calcd. for $C_6H_{13}O_2N$: N, 10.68. Found: N, 10.37, 10.44. Neutral equivalent. Subs., 0.1990, 0.2733: 16.94, 19.69 cc. of 0.1070

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[7] Putochin, Ber., 59, 628 (1926).

[8] Gabriel and Lauer, *ibid.*, 23, 88 (1890); Gabriel, *ibid.*, **38,** 633 (1905).

[9] Cretcher and Pittenger, THIS JOURNAL, 47, 164 (1925); Cretcher, Koch and Pittenger, *ibid.*, 47, 1174 (1925).

[10] We are indebted to the Carbide and Carbon Chemicals Corporation for the triethanolamine used in this investigation.

[11] All melting points in this paper are corrected.

N HCl; 3.09, 0.18 cc. of 0.0956 N NaOH. Calcd. for $C_6H_{13}O_2N$: neut. equiv., 131.1. Found: 131.2, 130.8.

β-4-Morpholine-ethyl Benzoate Hydrochloride.—To a mixture of 8 g. of benzoyl chloride and 7.2 g. of morpholine-ethanol, there was added a 10% solution of sodium hydroxide until the mixture was alkaline. A vigorous reaction occurred and a heavy brown oil separated. The mixture was warmed until the odor of benzoyl chloride was no longer noticeable. The oil was dissolved in benzene and the solution dried over anhydrous sodium sulfate. The benzene solution was saturated with dry hydrogen chloride with the formation of a voluminous white precipitate which was filtered off, washed several times with benzene and dried in the air; yield, 10.7 g. (72%); m. p. 204.6–205.8°.

Anal. Subs., 0.5930, 0.5406: 24.58, 24.81 cc. of 0.1070 *N* HCl; 4.77, 7.31 cc. of 0.0956 N NaOH. Subs., 0.5253, 0.5994: 24.67, 25.09 cc. of 0.1026 N $AgNO_3$; 5.00, 3.09 cc. of 0.1159 N KSCN. Calcd. for $C_{13}H_{18}O_3NCl$: N, 5.15; Cl, 13.05. Found: N, 5.13, 5.06; Cl, 13.17, 13.11. Neutral equivalent. Subs., 0.6792, 0.6526: 26.38, 25.26 cc. of 0.0956 N NaOH. Calcd. for $C_{13}H_{18}O_3NCl$: neut. equiv., 271.6. Found: 269.3, 270.2.

β-4-Morpholine-ethyl *p*-Nitrobenzoate Hydrochloride.—To a solution of 32 g. of *p*-nitrobenzoyl chloride in 250 cc. of benzene there was slowly added a solution of 22 g. of morpholine-ethanol in 50 cc. of the same solvent. The mixture was warmed on the steam-bath for an hour, forming a yellow pasty mass. The solid product was filtered off and washed with benzene. After recrystallization from alcohol, the yield was 26 g. (49%) of short yellow needles, m. p. 214.6–215.4'.

Anal. Subs., 0.5560, 0.6024: 39.91, 39.84 cc. of 0.1070 N HCl; 8.68, 5.19 cc. of 0.0956 N NaOH. Subs., 0.6010, 0.6195: 30.30, 30.39 cc. of 0.1026 N $AgNO_3$; 10.42, 9.94 cc. of 0.1159 N KSCN. Calcd. for $C_{13}H_{17}O_5N_2Cl$: N, 8.85; Cl, 11.20. Found: N, 8.66. 8.75; Cl, 11.21, 11.25. Neutral equivalent. Subs., 0.5122, 0.5256: 16.87, 17.30 cc. of 0.0956 *N* NaOH. Calcd. for $C_{13}H_{17}O_5N_2Cl$: neut. equiv., 316.6. Found: 317.5, 317.7.

P-4-Morpholine-ethyl *p*-Aminobenzoate Hydrochloride.—A solution of 5 g. of the nitrobenzoic ester hydrochloride in 200 cc. of boiling alcohol was shaken for twenty minutes with hydrogen under two to three atmospheres' pressure in the presence of 0.20 g. of Adams' platinum–platinum oxide catalyst.[12] The theoretical amount of hydrogen was absorbed in about seven minutes. The solution was filtered from the catalyst and evaporated under reduced pressure to 40 cc. Upon cooling light yellow crystals deposited. A further quantity was obtained on concentrating the solution to 10 cc. and cooling; yield, 3.3 g. (73%), m. p. 225.8–226.2°.

Anal. Subs., 0.4016, 0.3724: 31.12, 31.19 cc. of 0.1116 N HCl; 6.17, 7.85 cc. of 0.1235 N NaOH. Subs., 0.4604, 0.4885: 30.28, 30.31 cc. of 0.0986 *N* $AgNO_3$; 14.43, 13.44 cc. of 0.0977 N NH_4SCN. Calcd. for $C_{13}H_{19}O_3N_2Cl$: N, 9.77; Cl, 12.37. Found: N, 9.45, 9.44; Cl 12.14, 12.17. Neutral equivalent. Subs., 0.4604, 0.4885: 12.74, 13.49 cc. of 0.1235 N NaOH. Calcd. for $C_{13}H_{19}O_3N_2Cl$: neut. equiv., 286.6. Found: 292.6, 293.2.

γ-Aminopropanol.—A mixture of 50 g. of trimethylene chlorohydrin and 88 g. of potassium phthalimide in a three-necked 500-cc. flask provided with a reflux condenser and an efficient mechanical stirrer was heated, with stirring, in an oil-bath to 155°. At this temperature a vigorous reaction took place and the bath was removed until the reaction subsided. The bath was again placed under the flask and the mixture was heated

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[12] Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

to 180–190° for two and one-half hours. The resulting pasty mass was extracted several times with hot water. The extract was filtered and cooled. The heavy brown oil which precipitated was separated. After standing for two days it solidified to a yellowish sticky mass. A portion dried on a porous plate softened at 68° and melted at 74°. Gabriel[ab] gives m. p. 75° for γ-hydroxypropyl phthalimide.

The crude product was boiled for a half hour under reflux with a solution of 100 *g.* of potassium hydroxide in 450 cc. of water. The resulting solution was distilled using a short Hempel tube until 200 cc. of distillate had been collected. This fraction was practically free of γ-aminopropanol and was discarded. The Hempel tube was then removed and the remaining liquid distilled without a column. In order to drive over the last of the aminopropanol, two portions of 50 cc. of water were added to the residue and distilled. The combined distillates were freed from water by redistillation using the Hempel tube and the residue was finally purified by distillation from a Claisen flask; yield 15 g. (42%), b. p. 185–190°. Putochin gives 185–186°.[7]

γ-4-Morpholinepropanol.—A mixture of 22.5 g. of γ-aminopropanol, 45 g. of β,β'-dichlorodiethyl ether and 45 g. of powdered anhydrous potassium carbonate in a two-necked 200-cc. flask provided with a reflux condenser and an efficient mechanical stirrer was heated with vigorous stirring in an oil-bath. When the temperature reached 120" a vigorous reaction set in with a rapid evolution of carbon dioxide. The oil-bath was removed until the reaction moderated. After about half an hour, the bath was replaced and the mixture was heated for two and one-half hours at 170°. After cooling, the mixture was extracted four times with 50-cc. portions of hot benzene, the combined extracts dehydrated over anhydrous potassium carbonate and the benzene distilled off. The residue was distilled under 24-mm. pressure, the γ-4-morpholinepropanol being collected at 134–136°. The yield was slightly increased by redistilling the lower and higher fractions; yield, 29 g. (67%); d^{25}_{25} 1.0452; d^{25}_{4} 1.0422; n^{25}_{D} 1.4752; M_D calcd.: 39.33. Found: 39.21.

Anal. Subs., 0.3618, 0.3922: 30.18, 29.81 *cc.* of 0 1116 N HCl; 8.18, 5.52 cc. of 0.1235 N NaOH. Calcd. for $C_7H_{15}O_2N$: N, 9.65. Found: 9.55, 9.45. Neutral equivalent. Subs., 0.5309, 0.5178: 32.21, 31.48 cc. of 0.1116 N HCl. Calcd. for $C_7H_{15}O_2N$: neut. equiv., 145.1. Found: 147.7, 147.4.

γ-4-Morpholinepropyl Benzoate Hydrochloride.—The procedure was the same as that used in the preparation of p-4-morpholine-ethyl benzoate hydrochloride: yield from S *g.* of γ-4-morpholinepropanol and 9 *g.* of benzoyl chloride, 8 *g.* (51%), m. p. 190.1–190.5".

Anal. Subs., 0.5220, 0.4937: 29.98, 30.10 cc. of 0.1116 N HCl; 12.53, 13.39 cc. of 0.1235 *N* NaOH. Subs., 0.4229, 0.5186: 30.06, 30.48 cc. of 0.0986 *N* $AgNO_3$; 12.63, 12.37 cc. of 0.0977 *N* NH_4SCN. Calcd. for $C_{14}H_{20}O_3NCl$: N, 4.90; Cl, 12.42. Found: N, 4.83, 4.84; Cl, 12.29, 12.28. Neutral equivalent. Subs., 0.5207, 0.5314: 14.80, 15.10 cc. of 0.1235 N NaOH. Calcd. for $C_{14}H_{20}O_3NCl$: neut. equiv.. 285.6. Found: 284.9, 285.0.

γ-4-Morpholinepropyl p-Nitrobenzoate Hydrochloride.—The procedure was the same as that used in the preparation of the lower homolog except that a mechanical stirrer was used and the time of heating was increased to two hours; yield from 10 g. of γ-4-morpholinepropanol and 17 g. of *p*-nitrobenzoyl chloride, 20 g. (89%), after recrystallization from alcohol, m. p. 232.8–233.2°.

Anal. Subs., 0.6190, 0.5307: 38.01, 30.15 cc. of 0.1116 N HCl; 5.45, 2.13 cc. of 0.1235 *N* NaOH. Subs., 0.5046, 0.5006: 30.11, 30.03 cc. of 0.0986 *N* $AgNO_3$; 14.98, 15.03 cc. of 0.0977 *N* NH_4SCN. Calcd. for $C_{14}H_{19}O_5N_2Cl$: N, 8.47; Cl, 10.72. Found: N, 8.08, 8.18; Cl, 10.58, 10.58. Neutral equivalent. Subs., 0.5006, 0.5355: 12.25, 13.08 cc. of 0.1235 N NaOH. Calcd. for $C_{14}H_{19}O_5N_2Cl$: neut. equiv., 330 6. Found: 330.9, 331.2.

γ-4-Morpholinepropyl *p*-Aminobenzoate Hydrochloride.—The reduction was carried out in the same manner as was described for the lower homolog. From 7.5 g. of the p-nitrobenzoate hydrochloride there was obtained 4.8 g. (70%) of γ-4-morpholinepropyl p-aminobenzoate hydrochloride, m. p. 193.3–193.7'.

Anal. Subs., 0.3303, 0.3342: 29.92, 30.43 cc. of 0.1116 N HCl; 10.04, 9.88 cc. of 0.1235 *N* NaOH. Subs., 0.3727, 0.5436: 25.21, 30.30 cc. of 0.0986 *N* $AgNO_3$; 12.91, 12.38 cc. of 0.0977 N NH_4SCN. Calcd. for $C_{14}H_{21}O_3N_2Cl$: N, 9.31; Cl, 11.79. Found: N, 8.90, 9.12; Cl, 11.66, 11.60. Neutral equivalent. Subs., 0.4977, 0.5436: 13.05, 14.25 cc. of 0.1235 N NaOH. Calcd. for $C_{14}H_{21}O_3N_2Cl$: neut. equiv., 300.6. Found: 308.8, 308.9.

Pharmacological Report.—Some preliminary pharmacological tests on these compounds were made by Dr. H. S. Gasser of the Washington University School of Medicine. While the data available will not justify any quantitative summary, some qualitative conclusions can be drawn. Studying the effect in nerve block, all compounds showed at most slight action when made up to one per cent. in Ringer's solution. When adjusted to *P*H 7.4, however, all were effective. In each case it was found that the p-aminobenzoate was more effective than the corresponding benzoate, and each of the propanol derivatives more effective than the corresponding ethanol derivative. γ-4-Morpholinepropyl p-aminobenzoate hydrochloride was more effective than cocaine.

On the rabbit's cornea, none of the compounds was effective when applied in one per cent. solution, but when adjusted to *P*H 8, the propanol derivatives produced almost immediate anesthesia. In 0.2% solution at PH 8, γ-4-morpholinepropyl p-aminobenzoate hydrochloride produced anesthesia in almost as short a time as cocaine, but in 0.05% solution, PH 8, while cocaine produced anesthesia in two minutes, the new compound was without effect.

The toxicity of only two of the new compounds has been tested. β-4-Morpholine-ethyl benzoate hydrochloride gave a minimum lethal dose in rabbits of approximately 120 mg. per kg. body weight, and γ-4-morpholinepropyl p-aminobenzoate hydrochloride, 60 mg., as compared to 15 mg. for cocaine.

Relative Acidities.—Since it is well known that the effectiveness of a local anesthetic varies with the hydrogen-ion concentration of the solution in which it is applied,[13] determinations were made of the hydrogen-ion concentrations of 0.5% solutions of each of these compounds. Since precipitates were formed on adding alkali to solutions of the *p*-aminobenzoate hydrochlorides, the PH values at precipitation were determined in these cases. For comparison, similar determinations were made on solutions of procaine and diethylaminoethyl benzoate hydrochloride.

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[13] Trevan and Boock, **Brit.** J. *Exp. Path..* 8, 307 (1927)

The latter compound was prepared for us by Mr. L. A. Burrows of this Laboratory. The results are shown in Table I.

TABLE I

RELATIVE ACIDITIES

Morpholine-( )-hydrochloride	PH	0.5% solution PH at precipitation
Ethyl benzoate	4.0	8.0 no precipitation
Ethyl *p*-aminobenzoate	4.2	6.7
Propyl benzoate	4.3	8.0 no precipitation
Propyl *p*-aminobenzoate	4.4	6.9
Procaine	5.2	8.0 no precipitation
Diethylaminoethyl benzoate hydrochloride	4.8	7.9

Summary

1. A series of local anesthetics of the alkamine ester type in which the dialkylamino group has been replaced by a morpholine ring has been prepared and described.

2. Some preliminary pharmacological tests on these compounds have been made.

3. These compounds have been found to possess considerable local anesthetic activity and low toxicity.

This investigation is to be continued.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 72]

CONDENSATIONS BY SODIUM INSTEAD OF BY THE GRIGNARD REACTION. II.[1] REACTION WITH BENZONITRILE. PREPARATION OF DIPHENYLKETAZINE

BY AVERY A. MORTON AND JOSEPH R. STEVENS

RECEIVED MAY 15, 1931 PUBLISHED JULY 8, 1931

When benzonitrile is added to a mixture of chlorobenzene and sodium in ether the solution becomes intensely red. We ascribe the occurrence of this color to the presence of sodium diphenyl methylene imine, which is formed according to equation (1) below. This appears reasonable since the reactions of the solution with water, oxygen and iodine lead to the formation of benzophenone, benzophenone oxime and diphenylketazine, respectively (equation 2), in all of which the red color is destroyed.

$$C_6H_5CN + C_6H_5X + 2Na \longrightarrow (C_6H_5)_2C{=}NNa + NaX \qquad (1)$$

$$2(C_6H_5)_2C{=}NNa + \left\{\begin{array}{l} 4H_2O \longrightarrow 2(C_6H_5)_2C{=}O + 2NH_3 + 2NaOH \\ O_2 \longrightarrow 2(C_6H_5)_2C{=}NONa \\ I_2 \longrightarrow [(C_6H_5)_2C{=}N]_2 + 2NaI \end{array}\right. \qquad (2)$$

The action of iodine on the corresponding magnesium compound, diphenyl methylene imino magnesium bromide, obtained by the addition

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[1] First paper of this series, THIS JOURNAL, 53, 2244 (1931).

of benzonitrile to phenylmagnesium bromide has never been observed. It therefore followed naturally to try such a reaction, equation (3), with

$$2(C_6H_5)_2C{=}N{-}MgBr + I_2 \longrightarrow (C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2 + 2MgIBr \quad (3)$$

the result that the diphenylketazine was prepared in good yield. This is a decided improvement over the older method of Curtius and Rauterberg.[2] The corresponding reaction of the magnesium compound with oxygen did not cause the formation of any oxime.

We are unable to say that sodium is better than magnesium with benzonitrile probably because of the strong tendency of the latter to polymerize under the influence of sodium.[3] We overcame this in part by the use of a stirrer and the gradual addition of the benzonitrile to the reaction mixture. However, the work has led to a better method of preparing diphenylketazine and to the preparation of the oxime by the reaction of oxygen with a nitrogen–sodium linkage.

Further studies are being made on the decomposition of the sodium imine compound and the corresponding magnesium compound as well as other condensations by sodium instead of by the Grignard reaction.[4]

Experiments

Benzonitrile and Chlorobenzene.—The experiment was performed in an atmosphere of dry nitrogen: 4.6 g. of sodium sand was put into a three-necked flask with 200 cc. of anhydrous ether; 11.2 g. of chlorobenzene was added and the flask heated on a hot-plate while the mixture was stirred. As soon as the reaction began, 10.3 g. of benzonitrile in 30 cc. of ether was added slowly through a dropping funnel over a period of one and a half hours. The solution became of a very deep red color, probably owing to the formation of the sodium imine compound. At the first part of the reaction enough heat was evolved to maintain refluxing, but after all of the nitrile had been added the mixture was again heated on the hot-plate for two hours. The sodium imine compound was not isolated from this mixture but was treated directly with other substances.[5]

Reaction with Air.—When air was blown through the cold imine solution, with stirring, the red color disappeared. The mixture was then treated with water, the ether evaporated and the water solution filtered. When neutralized with dilute hydrochloric acid, 6 g. of benzophenone oxime, as shown by a mixed melting point, was precipitated; yield, 30.5%.

Reaction with Iodine.—Iodine added to the solution of the sodium imine prepared as described above decolorized the solution, the completion of the reaction being almost

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[2] Curtius and Rauterberg. *J. prakt. Chem.*, [2] 44, 198 (1891).

[3] Hofmann, *Ber.*, 1, 194 (1868); Lottermoser. *J. prakt. Chem.*, [2] 54,132 (1896).

[4] In our study of the reaction of carbon dioxide with organic chlorides, chlorobenzene was heated under 30 pounds' pressure of carbon dioxide in the presence of sodium. The exothermic nature of the reaction once started was so great that it became uncontrollable and blew the container with explosive violence. This word of caution is given in advance of the article describing all of these experiments in order to emphasize again the care that must be exercised when working with sodium.

[5] Preliminary experiments on the decomposition of the sodium imine compound with water showed a mixture of benzophenone and the corresponding orime, the latter being due to the presence of air.

equivalent to an end-point in a titration. Much heat was evolved and a yellow solid was precipitated. The mixture was decomposed with water in the cold and filtered without evaporating the ether. The solid residue was extracted with carbon bisulfide and the latter was evaporated to dryness, yielding a yellow solid. Upon washing with hot acetone, 3 g. of a bright yellow crystalline solid (m. p. 160–162°) was obtained; yield, 16.7%. Diphenylketazine is recorded as melting at 162 and 164°.[2,6]

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.67; H, 5.60. Found: C, 86.68, 86.47; H, 5.78, 6.81.

Preparation of the Sodium Imine Compound from Sodium and Diphenyl Methylene Imine.—Diphenyl methylene imine[7] (approximately 0.05 g.) dissolved in anhydrous ether was sealed up in a small tube with a sliver of sodium. A deep red color, similar to that obtained in the reactions given above, developed. When iodine was added, a yellow precipitate formed but the material could not be purified sufficiently in the micro tube to determine whether it was the ketazine. However, when the sodium imine compound so prepared was kept in an open tube in a desiccator for two days so that air could come in contact with it (ether added to compensate for evaporation loss) benzophenone oxime was formed in quantities sufficiently large for easy identification, m. p. 141°.

Preparation of the Ketazine from the Magnesium Compound.—To a warm ether solution of phenylmagnesium bromide, made from 20 g. of bromobenzene and 3.1 g. of magnesium in 200 cc. of ether, was added 10 g. of benzonitrile. After five minutes the stirring was stopped and the ether solution was allowed to cool. The magnesium compound crystallized out in needles from a common center. The crystals were then broken up and 16 g. of iodine added to the mixture with heating and stirring. The stirring was continued for two hours and the mass allowed to stand for a day. It was again stirred for ten hours, the ether evaporated, the mass heated to 100° and stirred for two hours. It was then decomposed with dilute acid, the precipitate filtered, dried and extracted with hot benzene. The benzene was evaporated to 100 cc., an equal volume of petroleum ether added and the resulting precipitate washed with more petroleum ether. The solid had a melting point of 164° and showed no depression when mixed with the product obtained from the reaction of iodine with the sodium imine compound; yield, 10 g. (57.4%). Instead of using iodine the decomposition of the magnesium compound was carried out by the addition of bromine to the solution under a gentle refluxing. A large amount of heat was evolved but no hydrobromic acid was observed. When decomposed with cold dilute hydrochloric acid and purified as described above, 2 g. (7.6%) of ketazine, m. p. 162°, identical with that formed by the addition of iodine was obtained.

Attempted Reaction of the Magnesium Compound with Oxygen.—Oxygen was blown through a solution of the magnesium compound, prepared as above described, for ten hours, benzene being added to compensate for the loss of ether. No benzophenone oxime could be isolated. The experiment was repeated using dry lead dioxide instead of oxygen but again no oxime was found.

Conclusion

Benzonitrile reacts with phenyl halides in the presence of sodium forming, probably, sodium diphenyl methylene imine.

The mixture so obtained reacts with water, air and iodine forming benzophenone, benzophenone oxime and diphenyl ketazine.

[6] Purgotti and Viganò, *Gazz. chim. ital.*, **31**, II, 550 (1901).

[7] Prepared according to the directions of Lachman, "Organic Syntheses," 10, 28 (1930).

The ketazine may also be prepared by means of the reaction of the corresponding magnesium compound with iodine.

The formation of the ketazine is a new and better method of preparing these compounds.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE REACTIVITY OF THE METHYLATED SUGARS. IV. THE ACTION OF DILUTE ALKALI ON TRIMETHYLXYLOSE[1]

BY CHARLES EZRA GROSS WITH W. LEE LEWIS

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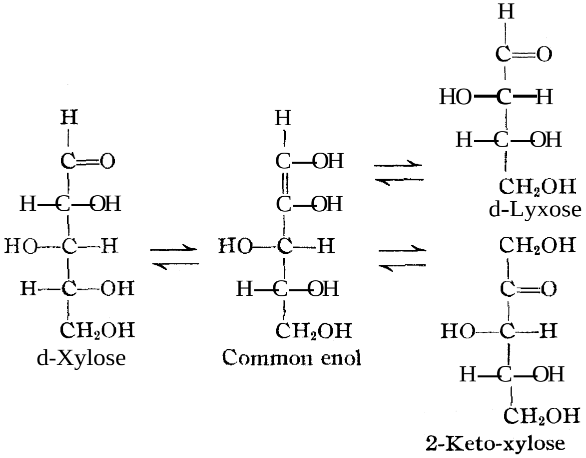
The theory of intermediate enol formation[2] which has proved so valuable in elucidating sugar reactions has nevertheless rested more upon plausibility than proof. The methylated sugars lend themselves to testing more directly the mechanism of these reactions by limiting in a predictable manner enol formation.[3] This follows from the lesser lability of the methyl group as compared with the replaced hydrogen of the sugar hydroxyl. Thus the theory of selective hydration and dehydration in enol formation



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[1] Abstracted from a dissertation submitted to the Graduate School of Northwestern University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

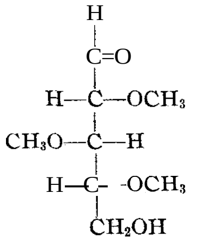
[2] Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, **14,** 156 (1895); Fischer, *Ber.*, **28,** 1149 (1895); Wohl and Neuberg, *ibid.*, **38,** 3099 (1900); Nef, *Ann.*, **357,** 214 (1907); **376,** 1 (1910); **403,** 204 (1914); Evans, *Chem. Reviews*, 6, *281* (1929); Shaffer and Friedemann, *J. Biol. Chem.*, **86,** 345 (1930); Evans and Conaway, THIS JOURNAL. 52, 3680 (1930).

[3] (a) Gustus with Lewis, *ibid.*, **49,** 1512 (1927); (b) Wolfrom with Lewis, *ibid*, **50,** **837** (1928); (c) Greene with Lewis, *ibid.*, **50,** **2813** (1928).

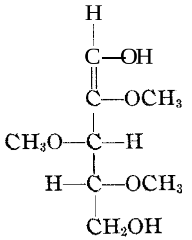
has been shown untenable, and the elimination of ketose formation in the Lobry de Bruyn reaction controlled at will.[3b,c]

The present paper deals with an extension of this method of study to a pentose, 2,3,4-trimethylxylose. For purposes of comparison, xylose was first treated with dilute alkali using the conditions of time, temperature and concentration previously found to give a minimum of saccharinic acid formation.[3b] Under these conditions, the system shown in the formulas just given would be expected. The major products were found to be d-lyxose and d-xylose and a condensation product of four moles of the expected 2-keto-xylose.

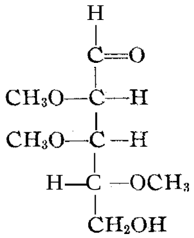
In the case of the trimethylxylose, no ketose formation would be expected due to the blocking effect of the methoxyl group on the second carbon atom. The following system should result from the treatment of 2,3,4-*d*-xylose with dilute alkali



Trimethylxylose

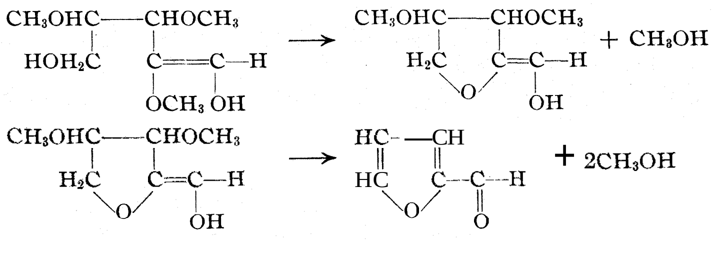


Common monomethyl enol



Trimethyllyxose

When trimethylxylose was treated with dilute alkali under the conditions applied to d-xylose, evidence was obtained of a stable enol. Trimethylxylose and trimethyllyxose were proved to be present. When, however, dilute acid was added to the reaction mixture in order to de-enolize it, the total aldose fell below 100% and furfural appeared. It is suggested that the furfural results from the action of acid upon the monomethyl enediol according to the equations



This conclusion is based upon the fact that a direct relation was established experimentally between the amount of presumptive enol present and of furfural formed. Furthermore, the amount of alcohol found after de-enolization with dilute acid was roughly twice the amount found in the alkaline reaction mixture. This removal of alcohol in two portions of roughly one-third and two-thirds supports the preceding equation. Since no ketose was found present, the methyl alcohol could not have had its source in demethylation incident to ketose formation. It is believed that no furfural results from xylose under these conditions because the intermediate enol is transient. In none of the studies of the action of dilute alkalies upon unmethylated sugars have we ever found evidence of a substance of high iodine absorbing power.[4]

The gum isolated from the de-enolized reaction mixture was shown to consist of about 70% of trimethyllyxose and 26% of trimethylxylose with about 4% of partially demethylated material. The sugars were separated by fractional crystallization of the brucine salts of their acids. These were further converted into the crystalline phenylhydrazides for identification.

Experimental Part

Preparation of **Trimethylxylose.**—Normal 2,3,4-trimethylxylose was prepared by the methylation of four moles (600 g.) of commercial xylose with dimethyl sulfate according to the method of Carruthers and Hirst.[5] The yield of β-methyltrimethylxyloside was 528 g. or 69% of the theoretical collected at 80° and 3 mm. pressure. Four hundred and twenty grams of purified β-methyltrimethylxyloside was hydrolyzed by heating a 7% solution containing 7% of hydrogen chloride at 80° for three hours. The solution was then neutralized, evaporated and the trimethylxylose extracted from the salty residue with chloroform. After the chloroform was removed. the residue was crystallized from ethyl ether. In the above manner, 230 g. of crystalline material was obtained, a yield of 60% of the theoretical. Upon recrystallization from absolute ether and careful drying, there was obtained 190 g. of pure material giving a final $[\alpha]^{20}_{D}$ of +17.8° (a = +1.0° in a 2-dm. tube when c is 2.8116 in water). Carruthers and Hirst[5] record a final [a], of +20° in water and +21° in methyl alcohol. Phelps and Purves[6] found $[\alpha]^{20}_{D}$ +17.7° in aqueous solution, for the final specific rotation of pure trirnethylxylose. Hirst and Carruthers record a melting point of 87–90"; Phelps and Purves record 91–92". In order to check the purity of the product, it was redistilled and collected at 111° and 3 mm. and at 121° and 5 mm. The liquid gave a refractive index of 1.4603 when supercooled to 20". The entire product solidified upon cooling and was again crystallized from absolute ether. After careful drying the substance was analyzed for methoxyl.

Anal. Subs., 0.0335, 0.0911; AgI, 0.3410, 0.3353. Calcd. for $C_5H_7O_2(OCH_3)_3$: OCH_3, 48.4. Found: OCH_3, 48.2, 48.6.

The substance was optically homogeneous in polarized light. It gave a final specific rotation of +17.8° (a = +1.32° in a 2-dm. tube when c is 3.70 in water). In methyl alcohol the final specific rotation was +21.3° (a = +1.11 in a 1-dm. tube when c is 5.214").

The Action of Dilute Alkali on *d*-**Xylose.**—One-half mole (75 g.) of pure d-xylose [specific rotation +19.2° (a = +0.94" in a 1-dm. tube when *c* = 4.895 in water)] was made to 500 cc. with 0.04 N calcium hydroxide solution saturated at 35°. The final concentration of the sugar was molar in 0.035 N calcium hydroxide solution at 32°.

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[4] *Cf.*, however, Montgomery and Hudson, THIS JOURNAL, 52, 2103 (1930).

[5] Carruthers and Hirst, *J. Chem. Soc.*, 121, 2299 (1922).

[6] Phelps and Purves, THIS JOURNAL, 51, 2443–9 (1929).

The iodine oxidation method of Cajori[7] as modified by Wolfrom and Lewis[3b] was found to apply to the determination of xylose if the time of oxidation was thirty-five to forty-five minutes. The change in aldose content is shown in Table I and graphically in Fig. 2. The change in rotation appears in Table I and graphically in Fig. 1. The final rotation was +11.2° at 30° when *c* was molar and the aldose content 77.4%. The hydrogen-ion concentration corresponds to a P_H of 5.85 as determined by the quinhydrone electrode. The initial P_H of the lime water was 12.6, and dropped to 10.6 upon addition of the sugar.

TABLE I

EQUILIBRATION OF d-XYLOSE IN DILUTE ALKALI

Time, hours	$[\alpha]^{30}_D$ [a]	Aldose, %[b]	Aldose, %[c]	Time, hours	$[\alpha]^{30}_D$ [a]	Aldose, %[b]	Aldose, %[c]
0		99.6		96	12.0	81.3	
6	17.8	95.4		120	11.9		
12	16.7	94.4		122		80.6	
24	15.4	91.0	90.7	144	11.40		
36	14.8			167	11.36		
48	14.0	87.8		168.5		78.6	
71	13.2			191	11.2	77.2	76.3
72		84.3		214	11.2	77.5	

[a] C = molar. [b] By iodine titration. [c] The sample is treated with 3 *N* hydrochloric acid for three hours at 20°. It is then neutralized and oxidized in the usual manner, and the excess of iodine titrated with thiosulfate.

The saccharinic acid content was calculated as 3.4% by direct titration after removal of calcium ions. No furfural was present according to the aniline acetate test.

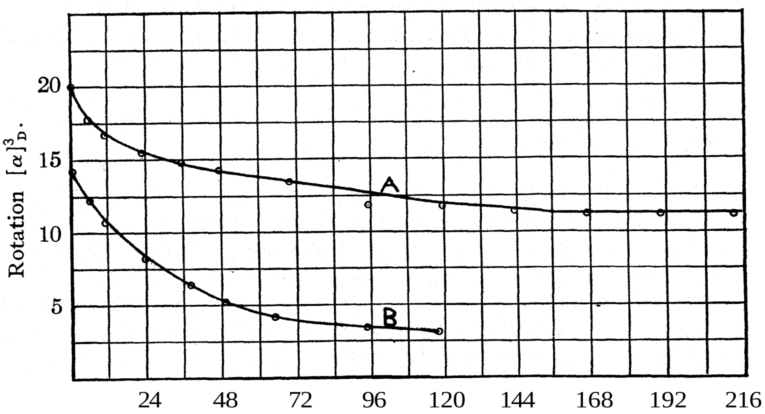

Fig. 1.—Change in rotation of d-xylose and trimethyxlylose in dilute alkali: A, xylose; B, trimethylxylose.

Separation of Aldoses and Ketoses.—By the oxidation of 350 cc. (corresponding to 50.03 g. of xylose) of the final equilibrated solution using Hudson and Isbell's[8] neutral bromine method, the aldoses were converted to aldonic acids and the ketoses presumably unattacked. The final solution (corresponding to 49.0 g. of xylose due to

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[7] Cajori, *J. Biol. Chem.*, 54, 617 (1928).

[8] Hudson and Isbell, THIS JOURNAL, 51, 2225 (1929).

sampling) freed of benzoate, bromide and silver ions, after concentration to 150 cc. was treated with an excess of cadmium carbonate. The excess cadmium carbonate was removed by filtration and the cadmium salts precipitated by the addition of 500 cc. of ethyl and 500 cc. of methyl alcohols with rapid stirring. The cadmium salt dried over sulfuric acid *in vacuo* weighed 58.0 g.

The filtrate from the precipitation of cadmium salt was evaporated to dryness and then taken up in absolute methyl alcohol and added with vigorous stirring to absolute ether. A very fine white precipitate formed which on standing became distinctly granular. The total yield of this ketosic material was 4.82 g.

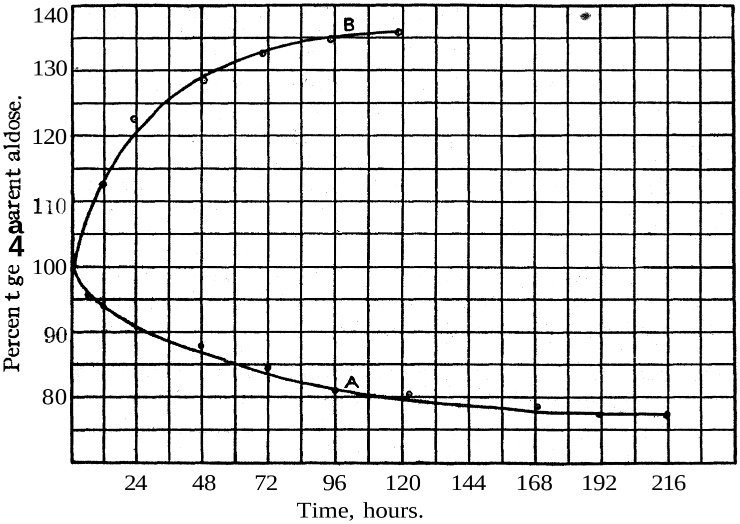

Fig. 2.—Change in apparent aldose content calculated from the iodine titration: A, xylose; B, trimethylxylose.

Separation of the Cadmium Salts.—Fifty-seven grams of cadmium salt was dissolved in water and the amount of cadmium bromide sufficient to convert all cadmium salts to cadmium bromide, cadmium xylonate double salt was added. Sixty-six and one-tenth grams of the double salt was obtained after concentrating and allowing the solution to stand. It gave a specific rotation of +8.4° (α = 0.20° in a 2-dm. tube when *c* is 1.182 in water). It contained 21.23% of bromine. Nef[9] recorded a specific rotation of +7.4°, while Hudson and Isbell[8] found a rotation of +8.8°.

Anal. Subs., 0.0912: AgBr, 0.0455. Calcd. for $CdBr_2 \cdot Cd(C_5H_9O_6)_2 \cdot 2H_2O$: Br, 21.31. Found: Br, 21.23.

To identify the xylonic acid further, 6.0 g. of the double salt was converted to the brucine salt after removal of the cadmium and bromine ions. There was obtained 3.5 g. of once recrystallized brucine xylonate which melted at 172–173° and gave a specific rotation of −19.1° (α = −0.544° in a 1-dm. tube when *c* is 2.842 in water). Nef[10] records a melting point of 172–174° and a specific rotation of −18.7°.

The residual liquor from the precipitation of cadmium bromide cadmium xylonate double salt was freed of cadmium and bromide ions and then converted to the brucine

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[9] Nef, *Ann.*, 403, 263 (1914).

[10] Nef, Ref. 9, p. 234.

salt. This yielded 16.9 g. which was very sparingly soluble in alcohol. From the alcohol-soluble portion **0.5 g.** of brucine xylonate and **0.8** g. of brucine lyxonate were separated by fractional crystallization. The total of **17.7** g. of brucine lyxonate had a specific rotation of −26.4° ($\alpha = -0.92°$ in 1-dm. tube when c is **3.483** in water). Ten grams was then converted to the phenylhydrazide, which gave **4.0** g. of anhydrous phenylhydrazide. This melted at 162–164° and gave **a** specific rotation of **−11.0°** ($\alpha = -0.18°$ in a 2-dm. tube when c is **0.818** in water). Wohl and List[11] recorded a melting point of **162–164°** and a specific rotation of **−11.2°** for the anhydrous phenylhydrazide. The brucine xylonate was identified by melting unchanged with known brucine xylonate.

Nature and Constants of the **Ketose.**—The ketose isolated reduced Fehling's solution only upon heating and did not reduce neutral permanganate solution. The ketose expected would be a "gamma" sugar and yet the material isolated exhibited none of the properties of a "gamma" sugar. The isolated solid material would not condense with methyl alcoholic hydrogen chloride even after three hours' refluxing. The final rotation in water was +3.0° ($\alpha = +0.09$ in a 2-dm. tube when c is **1.474** in water). In methyl alcohol the final rotation was +6.4° ($\alpha = +0.133°$ in a 1-dm. tube when c is 2.068 in methyl alcohol). **A** determination of the molecular weight by rise in boiling point of methyl alcohol gave **524** and **540.** If four moles of keto-xylose condensed with the elimination of three moles of water, the resulting compound would have a molecular weight of **546.**

Summary of Products Isolated from Equilibrated Solution of **Xylose.**—From 100 g. of xylose equilibrated there were isolated the following products calculated to equivalent xylose: first, **52.9** g. of xylose as xylonic acid derivatives (this represents the amount of xylose unchanged after equilibration); second, 8.3 g. of xylose as lyxonic acid derivatives; third, 9.8 g. of xylose as the crystalline condensed ketose; fourth, **3.4** g. of xylose as the presumptive saccharinic acid.

Action of Dilute Alkali on **Trimethylxylose.**—It was determined in preliminary experiments that the iodine oxidation method for aldose, as used on xylose, was applicable to trimethylxylose if the time of oxidation was at least ten minutes. The changes in rotation and in aldose content when trimethylxylose was treated with saturated lime water at 35° are recorded in Table II and graphically in Figs. 1 and 2. The solutions gave a final specific rotation of +3.0° and were but very slightly alkaline. No furfural was present in the alkaline equilibrated solution. Calculations based on the known rotations of the two epimers, trimethyllyxose and

TABLE II

EQUILIBRATION OF TRIMETHYLXYLOSE IN DILUTE ALKALI

Time, hours	$[\alpha]^{30}_{D}$ [a]	Apparent aldose, % [b]	Time, hours	$[\alpha]^{30}_{D}$ [a]	Apparent aldose, % [b]
0.5		100.3	33.5	6.5	
1.25	14.6		49.0	5.2	128.5
7.0	12.0		58.0	4.5	
11.75	10.9		71.0		132.9
12.0		112.4	95.0	3.1	134.5
24.0	8.1	122.4	119.0	3.0	135.6

[a] C equals molar. [b] Calculated from the iodine titration.

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[11] Wohl and List, **Ber.,** 30, **3105** (1897).

trimethylxylose, and the final rotation indicated the presence of 37.2% of trimethyllyxose. Direct titration after removal of the calcium ion indicates 2.5% of acidic substances calculated as saccharinic acid.

The high apparent aldose indicates the presence of an "enolic" substance encountered by Wolfrom and Lewis[3b] and Greene and Lewis[3c] in treating methylated sugars with dilute alkali. The latter authors showed that, in the case of tetramethylglucose and tetramethylmannose, no ketose or methyl alcohol was present in the reaction mixture. In the present work no direct evidence has been obtained for the absence of ketose, but the materials isolated were entirely aldonic in character since no reducing sugar was left after neutral bromine oxidation.

When the equilibrated solutions (200 cc.) were distilled at low pressure and in a 35°-bath using all precautions to prevent the loss of vapor from multiple receivers at −20°, a distillate one-third the volume of the equilibrated solution distilled was collected. Upon repeated refractionation at atmospheric pressure, a final distillate was obtained upon which methyl alcohol was determined by means of the specific gravity and refractive index. Two separate equilibrations gave, respectively, 0.359 and 0.342 mole of methyl alcohol per mole of trimethylxylose equilibrated. A trace of furfural was also found in the distillate amounting to 0.0006 and 0.0005 mole per mole of trimethylxylose, respectively.

The Action of Dilute Acid upon the Equilibrated Solutions.—It was found that very low concentrations of acid produced furfural from the equilibrated solutions of trimethylxylose. This is in decided contrast to the behavior of dilute acid upon either equilibrated solutions of xylose or tetramethylglucose. In the case of tetramethylglucose, the effect of acid is primarily that of de-enolization. In the case of trimethylxylose, the action is primarily that of furfural production and, perhaps, of de-enolization as well. The rate of de-enolization is shown in Table III and graphically in Fig. 3.

TABLE III

DE-ENOLIZATION OF EQUILIBRATED TRIMETHYLXYLOSE SOLUTION (0.0667 M) BY DILUTE ACID (0.667 N)

Time, hours	Apparent aldose, %[a]	Time, hours	Apparent aldose, %[a]
0	136.6	6.67	98.6
0.5	109.0	9.5	96.4
1.0	107.8	17.67	93.2
1.33	104.9	28.0	90.7
3.67	101.9	44.0	90.0

[a] By iodine titration.

It was found that the action of the same concentration of acid upon untreated trimethylxylose, the condensed keto-xylose isolated and equilibrated solutions of xylose, produced no furfural. The production of furfural by the action of acid upon equilibrated solutions of trimethylxylose was attributed to the decomposition of the 1,2-monomethylene-diol.[12]

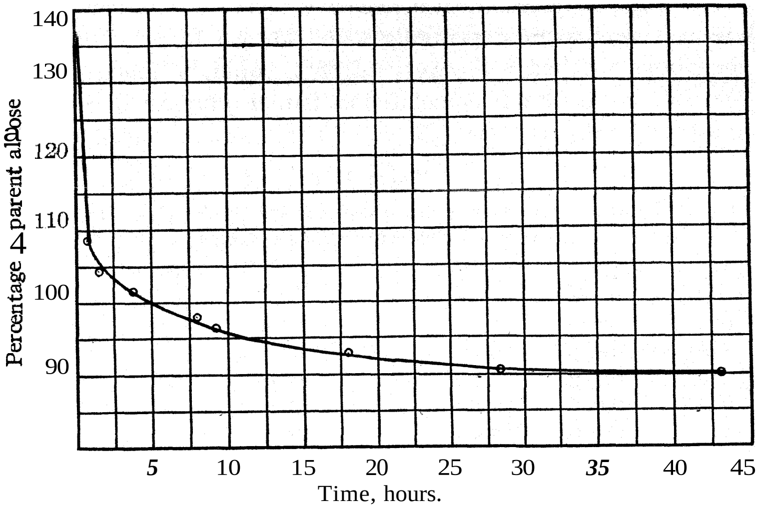

Fig. 3.—Rate of de-enolization of trimethylxylose solutions in dilute acid.

In Table IV and Fig. 4 are shown the relative amounts of furfural produced by the action of the same acid concentrations for the same time upon equilibrated solutions having various apparent aldose values (enol content).

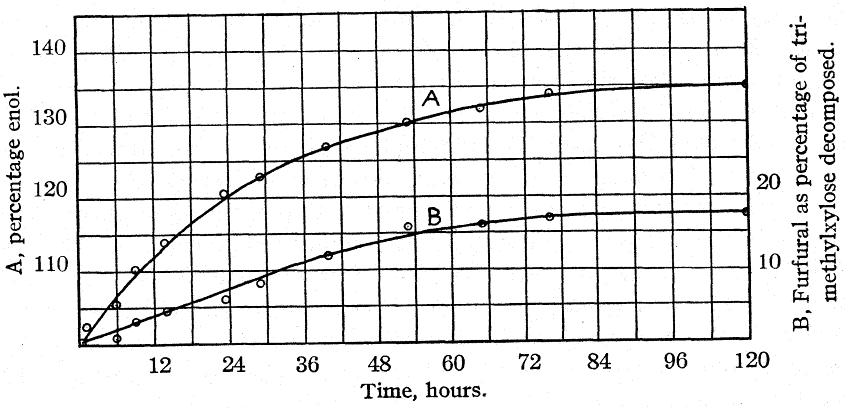

Fig. 4.—Relationship of presumptive enol to furfural formation.

Molar solutions of trimethylxylose made as usual with saturated lime water were heated at 35° until the aldose values were as indicated. They were made 0.0667 M in sugar and 0.667 *N* in hydrochloric acid and heated

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[12] *Cf.*, however, Carruthers and Hirst, Ref. 5, who report furfural formation during the acid hydrolysis of trimethyl-β-methylxyloside.

for twelve hours at 35°. The furfural was then determined colorimetrically[13] on the distillate from the acid solution after neutralization. The distillation was continued until a negative test was obtained on 1 cc. of distillate. It was found repeatedly using known furfural mixtures that with the above method a recovery of 88% could be made consistently. In Table IV the furfural is calculated as trimethylxylose decomposed and corrected for an 88% recovery.

TABLE IV

RELATION OF IODINE TITRATION EXPRESSED AS APPARENT PER CENT. ALDOSE TO FURFURAL PRODUCTION BY ACID

Time, hours	Apparent % of aldose	Furfural as % trimethyl-xylose decomp.	Time, hours	Apparent % of aldose	Furfural as % trimethyl-xylose decomp
0	100.0	..	29.0	123.0	8.17
1.0	102.5	0.25	40.0	127.0	11.82
6.0	105.2	.80	53.0	130.0	15.90
9.5	110.0	3.22	65.0	132.0	15.80
14.0	114.0	4.70	76.5	134.0	16.60
23.5	120.5	6.36	120.0	135.0	17.75

Amount of Methyl Alcohol after De-enolization.—In a manner similar to the determination of methyl alcohol present in the equilibrated solution, the amount of methyl alcohol formed during de-enolization was determined. This amounted to 0.790 mole per mole of trimethylxylose equilibrated. Thus, the total methyl alcohol found after de-enolization was 0.350 and 0.790 or 1.140 moles, an amount corresponding to 38.1% of trimethylxylose decomposed to furfural, assuming that all methyl groups are lost from each molecule of trimethylxylose decomposing. It was shown in preliminary experiments that furfural itself is decomposed by the mild acid used; so the difference of 17.75% of furfural found and the 38.1% indicated by methyl alcohol found may be explained on the basis that some furfural was decomposed by the acid before it was determined.

A significant fact appears to be the relationship of the amounts of methyl alcohol in the alkaline equilibrated solution and that formed by the action of acids upon the equilibrated solution after removal of the free methyl alcohol. The relationship is roughly 1 to 2, suggesting that one mole of methyl alcohol is split off in alkaline solution and two additional moles in the acid solution from each mole of trimethylxylose decomposing. This would be in conformity with the equations given on page 2773.

Preliminary Separation of the Equilibrated Solution.—The presence of trimethyllyxose was indicated by the levo rotation of the sirup isolated after acid treatment of the equilibrated solution. An impure *d*-trimethoxyglutaric dimethyl ester was formed by the method of Hirst and Purves[14]

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[13] Leach, "Food Inspection and Analysis," 3d ed., **1913**, p. 746.

[14] Hirst and Purves, *J. Chem. Soc.*, **123**, 1352 (1923).

from the trimethylpentose gum isolated. A pure *l*-trimethoxyglutaramide was separated after conversion to the amides. A pure *i*-trimethoxyglutaramide could not be obtained.

A bromine oxidation and subsequent formation of brucine salts gave derivatives which could be separated due to differences in their solubilities in acetone.

Quantitative Study of the Equilibration of Trimethylxylose.—Two-tenths of a mole (38.4 g.) of trimethylxylose was made up to a volume of 200 cc. with lime water saturated at 35". The initial aldose content by the iodine oxidation method was 100.5% and after heating at 35° for one hundred and twenty hours, it was 138%. The final specific rotation was +3.0° and the solution was alkaline to phenol red indicator. No furfural was present according to the aniline acetate test.

The above equilibrated solution was de-enolized by heating a solution 0.1 M in trimethylxylose and 1 M in respect to hydrochloric acid for one hour at 35°. The solution was then neutralized with sodium carbonate.

The solution was then concentrated under diminished prescure, precautions being taken as usual to prevent loss of methyl alcohol from the distillate. Upon continued refractionation of the neutral distillate after polymerizing the furfural by the use of sodium hydroxide and determining the content of methyl alcohol by means of the specific gravity and refractive index of the final distillate, it was found that 7.74 g. of methyl alcohol boiling at 65° was recovered from 37.4 g. of trimethylxylose. The methyl 3,5-dinitrobenzoate formed from it melted at 107°[15] and melted unchanged on mixing with the known compound. The total amount of methyl alcohol found (7.74 g. from 37.4 g. of trimethylxylose) corresponds to 1.24 moles per mole of trimethylxylose equilibrated. Calculated *as* trimethylxylose decomposed, it represents a complete decomposition of 41.3%.

After concentration of the de-enolized solution to 100 cc., this volume was extracted with five 200 cc. portions of chloroform. The aqueous portion was then evaporated to dryness and the salt residue crushed and extracted with two 500 cc. portions of boiling chloroform. The combined chloroform extracts were dried and evaporated. The gum was then dried by heating at 80° and 10 mm. for several hours. The gum weighed 20.8 g., which is a recovery of 55.7% of the theoretical of trimethylpentose. This gum gave 100.3% presumptive trimethylpentose by the iodine oxidation method. It gave a specific rotation of −13.2" (c = 5 in water) and contained 44.6% of methoxyl (calcd. 48.4%). The above constants indicate a mixture largely of trimethyllyxose with some trimethylxylose and probably some partially demethylated pentose.

After the above determination had been made, 20.0 g. of gum remained which was oxidized with bromine according to the method of Hudson.[8] After fifty-six hours the

TABLE V

PARTIAL SEPARATION OF BRUCINE SALTS

Fraction	Weight, g.	Rotation, degrees
I	42.0	−18.9
II	5.5	−23.1
III	2.7	−22.7
IV	5.2	−33.0
Total	55.4	

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[15] Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, 1923, p. 151.

solution no longer reduced boiling Fehling's solution. It was then treated in the usual manner for the removal of the objectionable ions and the free acids converted to brucine salts. After removal of the water, the brucine salts were dissolved in a minimum of hot water and fractionated as shown in Table V.

The theoretical yield of brucine salt of trimethylpentonic acid would be **60.6** g. The yield was then **91.4%** of the theoretical. By a tedious process of fractional crystallization from acetone, the above fractions were resolved into the least soluble brucine trimethylxylonate and the more soluble brucine trimethyllyxonate, with a small residue of extremely soluble partially de-methylated pentonic acids.

Table VI

Separation of Brucine Salts

Compound	Weight, g.	Specific rotation, degrees	M. p., °C.	Methoxyl, %
Trimethylxylonate	12.63	-6.6	114–115	26.45
Trimethyllyxonate	33.59	-23.0	99–100	26.68
Partially methylated pentonates	2.0	-30.2	145–150	19.0
	48.22	Calcd. methoxyl,		25.8

The brucine salts separated **(45.22 g.)** amounted to a recovery of **89.0%** of the theoretical **(55.4 g.)**. The amount separated **(48.22** g.) corresponds to a yield of **79 6%** from the **trimethylpentose gum** oxidized **(20.0** g.).

Known brucine trimethylxylonate gave a specific rotation of $-6.2°$ ($\alpha = -0.221$ in **a** 1-dm. tube when c is **3.57** in water) and melted at **114.5–115°**. The methoxyl content was **26.42%.**

Anal. Subs., **0.1107: AgI, 0.2215.** Calcd. for $C_{26}H_{27}N_2O_5(OCH_3)_5$: OCH_3, 25 8. Found: OCH_3, 26.42.

The presumptive brucine trimethylxylonate **(12.63** g.) gave a specific rotation of -6.6" ($\alpha = -0.187$ in a 2-dm. tube when c is **1.42** in water) and melted at 114–115°. It contained **26.45%** methoxyl.

Anal. Subs., **0.1013: AgI, 0.2032.** Calcd. for $C_{26}H_{27}N_2O_5(OCH_3)_5$: OCH_3, 25.8. Found: OCH_3, 26.45.

To identify still further the presumptive brucine trimethylxylonate, **9.0** g. was converted to the phenylhydrazide according to the method of Hirst.[16] The hydrazide once recrystallized from benzene weighed 3.18 **g.,** which is **68.8%** of the calcd. It melted at 134–135° and when again recrystallized melted at 136–137°. The rotation is +31.1° ($\alpha = +0.335$ in a 1-dm. tube when c is **1.079** in methyl alcohol). It contains **30.8%** of methoxyl. **Hirst[16] records** a melting point of **137–138.5".**

Anal. Subs., **0.0908: AgI, 0.2120.** Calcd. for $C_{11}H_{13}N_2O_2(OCH_3)_3$: OCH_3, 31.2. Found: OCH_3, 30.8.

The presumptive brucine trimethyllyxonate **(33.59** g.) melted at 99–100° and gave a specific rotation of $-23.0°$ ($\alpha = -0.554$ in a I-dm. tube when c is **2.41** in water). The methoxyl content was **26.68%.**

Anal. Subs., **0.1066: AgI, 0.2155.** Calcd. for $C_{26}H_{27}N_2O_5(OCH_3)_5$: OCH_3, 25.8. Found: OCH_3, 26.68.

Ten grams of the presumptive brucine trimethyllyxonate was converted to the phenylhydrazide according to the method of Hirst[16] after removal of the brucine. There was obtained 3.82 g. once recrystallized from benzene, which amounts to a yield of 74.6%.

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[16] Hirst. J. *Chem. Soc.*, **3147 (1928).**

It melted at 179–180° and after a second recrystallization melted at 179.5–180°. The specific rotation was −30.1" (α = −0.465" in a 1-dm. tube when c is 1.548 in methyl alcohol). It had a methoxyl content of 30.78%.

Anal. Subs., 0.1144: AgI, 0.2663. Calcd. for $C_{11}H_{13}N_2O_2(OCH_3)_3$: OCH_3, 31.2. Found: OCH_3, 30.78.

The presumptive brucine partially demethylated pentonates (2.0 g.) melted at 145–150° and when mixed with either brucine trimethyllyxonate or xylonate melted over a range 20° lower. The specific rotation was −30.2" (α = −0.37° in a 1-dm. tube when c is 1.231 in water). It contained 19.2 and 18.8% of methoxyl.

Anal. Subs., 0.1047, 0.1295: AgI, 0.1521, 0.1842. Calcd. for $C_{26}H_{28}N_2O_6(OCH_3)_4$: OCH_3, 21.1; for $C_{26}H_{29}N_2O_7(OCH_3)_3$: OCH_3, 16.2. Found: OCH,, 19.2, 18.8.

Therefore the gum consisted of about 70% trimethyllyxose, 26% trimethylxylose and 4% of partially methylated materials. Considering the methyl alcohol isolated as indicating the complete decomposition of trimethylxylose to furfural and methyl alcohol, then 41.3% was decomposed. The gum isolated accounts for 55.7% and therefore a calculated total of 97% of the equilibrated xylose is accounted for as isolated. The furfural found is only a portion of that formed since acid causes its decomposition. The gum isolated was separated into its components in 79.6% yield after conversion to aldonic acid and separation of the brucine salts from acetone. Trimethylxylonic and trimethyllyxonic acids were identified as the known crystalline phenylhydrazides.

Conclusion

From the equilibration of 38.4 g. of trimethylxylose (less 1 g. for samples) there was isolated 20.8 g. of trimethylpentose gum or 55.7%. There was also isolated 7.74 g. of methyl alcohol, which indicates the decomposition of 41.3% of the trimethylxylose used, assuming loss of three moles of methyl alcohol from each mole of trimethylxylose decomposed. The total trimethylxylose accounted for in this manner is, therefore, 97.0%.

The remainder of the trimethylpentose gum (20.0 *g.)* was oxidized to trimethylpentonic acids and converted to brucine salts. A total of 55.4 g. of brucine salt was isolated or a yield of 91.4%. The 55.4 g. of brucine salt was separated by fractional crystallization from acetone into brucine trimethyllyxonate 33.59 g., brucine trimethylxylonate 12.63 g. and brucine mono- and di-methoxypentonic acids 2.00 g. The separation was effected with a recovery of 89.0%. The brucine salts separated amounted to 79.6%.

If the amount of trimethylxylose and trimethyllyxose were relatively the same in the original equilibrated solution as in the gum isolated, then the equilibrated solution would have had 38.8% of trimethyllyxose and data for rotations indicated 37.0%. The composition of the isolated gum was trimethyllyxose, 69.6%, trimethylxylose, 26.2% and partially demethylated pentose, 4.2%.

Summary

1. When xylose was treated with lime water at 35°, there were identified 52.9% of xylose, 8.3% of lyxose, 9.8% of a crystalline condensed ketose and 3.4% of presumptive saccharinic acid, expressed as percentage of pentose.

2. The equilibrated solution gave no evidence of a stable enol and treatment with acid did not produce furfural.

3. When trimethylxylose was treated with dilute alkali under the same conditions, it was transformed in part into the epimeric trimethyllyxose, a high iodine absorbing compound believed to be the monomethylenediol and saccharinic acid, the latter in small amount.

4. Methyl alcohol was found in the alkaline solution of trimethylxylose approximately in the proportion of one mole to each mole of methylated sugar decomposed. On treatment with dilute acids, two further moles of methyl alcohol was liberated per mole of sugar decomposed and furfural was formed. A mechanism is proposed for this reaction.

5. The gum formed consisted of trimethylxylose, trimethyllyxose and partially demethylated products in the proportion of 26 to 70 to 4 parts, respectively. Indirect evidence is advanced for the absence of ketose.

6. The conversion of normal trimethylxylose into normal trimethyllyxose confirms the identity of their ring structures.

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[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS. VI. FURTHER EXAMPLES OF REVERSIBILITY. THE FORMATION OF ADDITION COMPOUNDS

BY JOHANNES S. BUCK AND WALTER S. IDE

RECEIVED MAY 21, 1931 PUBLISHED JULY 8, 1931

In Part V[1] the reversibility of the benzoin condensatio[redacted]as demonstrated by means of the reaction $\mathrm{RCHOHCOR} + \mathrm{R'CHO} \quad \mathrm{RCHOHCOR'}$. This change took place under conditions comparable to those of the usual benzoin reaction. A scheme was formulated for the equilibrium conditions of a benzoin reaction mixture of any type. As noted in part V the scheme implied that a number of other transformations were possible, and most of these implications have now been investigated. Positive results were obtained in two of the possible reactions, namely

$$\mathrm{RCHOHCOR'} + \mathrm{R''CHO} \longrightarrow \mathrm{RCHOHCOR''} \qquad \text{(I)}$$
$$\mathrm{RCHOHCOR} + \mathrm{R'CHOHCOR'} \longrightarrow \mathrm{RCHOHCOR'} \qquad \text{(II)}$$

The results are tabulated. The remaining possibilities

$$\mathrm{RCHOHCOR'} \longrightarrow \mathrm{RCHOHCOR} + \mathrm{R'CHOHCOR'} \qquad \text{(III)}$$
$$\mathrm{RCHOHCOR'} + \mathrm{R''CHOHCOR'''} \longrightarrow \mathrm{R'CHOHCOR''} + \mathrm{RCHOHCOR}^{W} \qquad \text{(IV)}$$
$$\mathrm{RCHOHCOR'} + \mathrm{RCHOHCOR''} \longrightarrow \mathrm{R'CHOHCOR''} + \mathrm{RCHOHCOR} \qquad \text{(V)}$$
$$\mathrm{RCHOHCOR'} + \mathrm{RCHO} \longrightarrow \mathrm{RCHOHCOR} \qquad \text{(VI)}$$

were examined, but only negative results were obtained. The inability to isolate the expected product means either that it was formed in amounts

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[1] Buck and Ide, THIS JOURNAL, 53, 2350 (1931).

too small to isolate by the methods available or that it was less stable under the conditions of the reaction than was the starting material. It must be borne in mind that continual destruction of material takes place in the reaction mixture, and that the reaction therefore cannot be forced beyond a certain point. Also, the fact that many aldehydes do not form simple benzoins greatly limits the choice of starting materials.

The transformation RCHOHCOR' → R'CHOHCOR was not investigated in the present work.

Experimental

The experimental work was carried out in a manner similar to that described in part V,[1] the starting materials being refluxed in aqueous-alcoholic potassium cyanide solution for a given time, determined by trial. The positive results are recorded in Tables I and II. Negative or indecisive results were obtained in all of the following cases.

Reaction (I).—Benzanisoin and o-chlorobenzaldehyde, benzpiperoin and furfural, benzanisoin and furfural, o-chlorobenzveratroin and benzaldehyde, *o*-chlorobenzveratroin and *p*-dimethylaminobenzaldehyde, o-chlorobenzveratroin and anisaldehyde, *o*-chloro-*p'*-dimethylaminobenzoin and piperonal.

Reaction **(II)**.—**Benzoin** and anisoin, piperoin and anisoin, furoin and anisoin, piperoin and furoin.

Reaction **(III)**.—**Benzanisoin,** benzpiperoin, benzfuroin.

Reaction **(IV)**.—**Benzpiperoin** and *o*-chloro-*p'*-dimethylaminobenzoin, benzanisoin and o-chlorobenzpiperoin, o-chlorobenzpiperoin and p-dimethylaminobenzoin.

Reaction **(V)**.—**Benzpiperoin and** o-chlorobenzpiperoin, *p*-**dimethylaminobenz**anisoin and o-chlorobenzanisoin, *p*-dimethylaminobenzanisoin and benzanisoin.

Reaction (VI).—*p*-Dimethylaminobenzanisoin and anisaldehyde.

The above-cited examples do not, of course, exhaust all the possibilities,

Table I

Reaction (I)

Benzoin	Taken, g.	Aldehyde	Taken, g.	Product	Yield, g.	KCN, g.	Alcohol, cc.	Heating, hours
o-Chloranisoin	5.54	Dimethylaminobenz-	5.96	*o*-Chloro-*p'*-dimethylaminobenzoin	3.33	4.0	40	2.5
Benzanisoin	4.84	Dimethylaminobenz-	5.96	Dimethylaminobenzoin	2.04	4.0	40	3.0
Benzpiperoin	5.12	o-Chlorobenz-	5.64	o-Chlorobenzpiperoin	3.13	4.0	40	1.5
Benzpiperoin	5.12	Dimethylaminobemz-	5.96	Dimethylaminobenzoin	1.93	4.0	40	2.0

Table II

Reaction (II)

Benzoin I	Taken, g.	Benzoin II	Taken, g.	Product	Yield, g.	KCN, g.	Alcohol, cc.	Heating, hours
Benzoin	4.24	Piperoin	6.00	Benzpiperoin	0.98	5.0	50	3.2
Benzoin	4.24	Furoin	3.84	Benzfuroin	3.00	3.0	50	1.0

but they represent what, in the authors' opinion, are the ones offering the best prospects of success.

Note on the Formation of Addition Compounds.—There is a remarkable tendency among mixed and simple benzoins to form crystals containing equimolecular amounts of two different benzoins. The following pairs show this property clearly: (a) benzoin and benzpiperoin, (b) benzoin and anisoin, (c) benzoin and piperoin, (d) anisoin and piperoin, (e) piperoin and p-dimethylaminobenzoin. If equimolecular amounts of these are dissolved together in alcohol and allowed to crystallize, well-formed crystals are obtained in almost the theoretical yield. The crystal form differs from that of either of the components, and the solubility is generally somewhat less. The melting points are lower (about what would be expected for a mechanical mixture of the components) and are raised by the addition of either component. Repeated crystallization from alcohol fails to separate the constituent benzoins. It is evident that an additive compound is formed. If this were not so, oils or gums, or at any rate a mixture of crystals, would be obtained. Oils and gums are in fact painfully frequent outside of the above and perhaps a few other cases.

Molecular weight determinations in acetic acid and in benzene (both cryoscopic) gave values approximately the mean of the molecular weights of the component benzoins, indicating that the addition compounds do not persist in solution. No optical phenomena appear to be involved as solutions and liquors, even after several fractionations, show no rotation.

The bearing of the above observations on mixed benzoin work is important. Apart from complicating fractional crystallizations, these additive compounds interfere with certain preparations. Thus, in the preparation of benzpiperoin, if the reaction mixture (containing very little water) is refluxed for twenty to thirty minutes only, the addition compound of benzoin and piperoin is produced. It is evident that, on further heating, the reaction (II) [Table 11] must take place, resulting finally in a mediocre yield of benzpiperoin. It is precisely in cases where such addition compounds have not been observed or cannot have been formed that the best yields of mixed benzoins are obtained, e. g., with p-dimethylaminobenzoin.

The formation of addition compounds between certain benzoins is doubtless analogous to the formation of dimerides in the acyloin series. Dirscherl and Braun,[2] in discussing the dimerides of acetoin, attribute their existence to partial valency linkages. In the benzoin series such partial valency linkages must be very feeble, as no dimerides are known and the addition compounds do not persist in solution.

Summary

The reversibility of the benzoin condensation has been further demonstrated by means of two of the reactions previously mentioned.' The

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[2] Dirscherl and Braun, *Ber.*, 63,416 (1930).

formation of addition compounds between certain benzoins has been observed.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

MOLECULAR REARRANGEMENTS INVOLVING OPTICALLY ACTIVE RADICALS. II. THE HOFMANN REARRANGEMENT OF OPTICALLY ACTIVE ACID AMIDES

BY EVERETT S. WALLIS AND S. C. NAGEL

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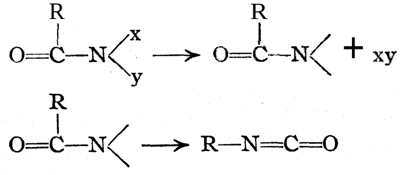
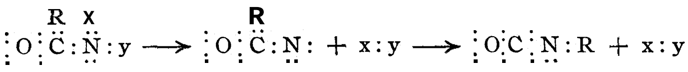
It has long been known that aliphatic and aromatic acid amides are converted into amines by treatment with chlorine or bromine and an alkali. Hofmann discovered this reaction[1] and detected among the products an isocyanate. It has since been shown, however, that the first product formed is a halogen amide. Of the several theories which have been advanced to explain this rearrangement, perhaps the most fruitful has been the interpretation of Stieglitz and his students[2] developed from the suggestion of Tiemann[3] that an acid amide is converted into an amine through the formation of an unstable intermediate univalent nitrogen compound. Their investigations have made it evident that the Lossen, Curtius and Hofmann rearrangements are fundamentally alike and they have proposed that all rearrangements of this character take place as follows



$$O{=}\overset{R}{\overset{|}{C}}{-}N\begin{matrix}x\\y\end{matrix} \longrightarrow O{=}\overset{R}{\overset{|}{C}}{-}N\langle + xy$$

$$O{=}\overset{R}{\overset{|}{C}}{-}N\langle \longrightarrow R{-}N{=}C{=}O$$

In terms of modern valence relationships Jones and Hurd[4] suggested an interpretation of this mechanism based on the Lewis conception of chemical bonds and electrons:



$$\vdots O \vdots \overset{R}{\ddot{C}} : \overset{X}{\ddot{N}} : y \longrightarrow \vdots O \vdots \overset{R}{\ddot{C}} : \ddot{N} : + x : y \longrightarrow \vdots O \dot{:} C \dot{:} \ddot{N} : R + x : y$$

From this interpretation it was assumed that the radical, R, in its wandering from the carbon atom to the nitrogen atom existed momentarily as a free radical, and that the ease of the rearrangement of such types of compounds depended upon the tendency of the radical, R, in the univalent

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[1] Hofmann, *Ber.*, 15, 407 (1882).

[2] Stieglitz, *Am. Chem. J.*, *18*, 751 (1896); *ibid.*, 29, 49 (1903); Stieglitz and Earle, ibid., 30, 399, 412 (1903); Stieglitz and Slossen, *Ber.*, 28, 3265 (1895); *ibid.*, 34, 1613 (1901); Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914).

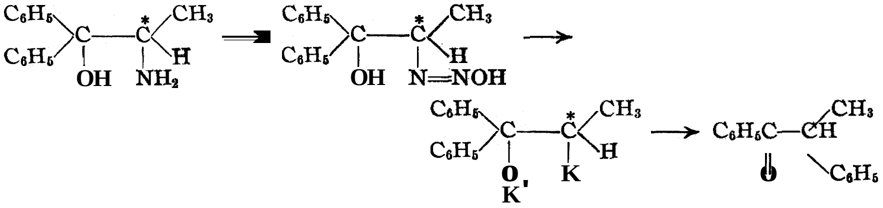
[3] Tiemann, *Ber.*, 24, 4162 *(1891)*.

[4] Jones and Hurd, THIS JOURNAL, 43, 2422 (1921).

nitrogen derivative to exist as a free radical. This hypothesis has since been tested in this Laboratory by Jones and his co-workers[4,5] and many facts have been found which are wholly in agreement.

In carrying out certain of these investigations Jones and Wallis[6] studied the nature of the products formed by the rearrangement of certain optically active acid azides and optically active hydroxamic acids in which the radical, R, is an optically active radical. From the viewpoint of the above hypothesis three possibilities suggested themselves: (1) the radical might racemize during rearrangement and yield inactive products; *(2)* it might retain its activity and its configuration; (3) it might retain its activity but change its configuration, that is, undergo Walden inversion. The first possibility was excluded by their experiments with *d*-benzylmethylacetazide, $(C_7H_7)(CH_3)CHCON_3$. This compound was found to give on rearrangement an optically active isocyanate, which could be converted by aniline into an optically active monosubstituted urea, and by hydrolysis into an optically active amine hydrochloride. These facts suggested two possible interpretations, one based on the theory of partial valence, the other based on the assumption of carbonium ions. A survey of the properties of optically active compounds described in the literature led them to suggest that the second interpretation was perhaps the more probable; that in such rearrangements the radical, R, if existing momentarily as a free radical must do so in such a way as to maintain a configuration required to produce an optically active rearrangement product, that is, it is a positive radical which is of the nature of a carbonium ion, and that in its migration from the carbon atom to the nitrogen atom it leaves behind the electron it shared with the carbon atom.

Since the publication of these experiments McKenzie and his co-workers[7] have carried out investigations on molecular rearrangements of optically active compounds involving migration of groups from one carbon atom to another adjacent carbon atom. It has been shown by them that under certain conditions optically active tertiary amino alcohols and pinacols can undergo rearrangement to give optically active ketones. They have suggested the following mechanism for the change which takes place in the tertiary amino alcohols



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[5] Jones and Root, THIS JOURNAL, 48, 181 (1926).

[6] Jones and Wallis, *ibid.*, 48, 169 (1926).

[7] McKenzie, Rogers and Mills, *J.* Chem. *Soc.*, 129, 779 (1926); Ber., 62B, 272 (1929).

where K and K' are electric charges. It is evident from this that their interpretation involves the same assumption as previously expressed by Jones and Wallis[6] for the rearrangement of optically active acid azides, that is, that in the rearrangement it is possible that the optically active radical may exist for a certain length of time as a carbonium ion, and that the asymmetry is retained due to the fact that an electric charge plays the part of the fourth grouping.

We have continued these investigations on carbon to nitrogen rearrangements involving optically active radicals in order to seek an answer to the second and third possibilities suggested by the above interpretation for the rearrangement of acid azides, hydroxamic acids and halogen amides. Does the radical retain its configuration during the rearrangement, or does it change its configuration and undergo Walden inversion? For this purpose d-benzylmethylacetamide $(C_7H_7)(CH_3)CHCONH_2$, $[\alpha]_D^{20}$ +38.94°, was prepared, and its rearrangement by bromine and an alkali studied. It was thought that some information could be obtained from a comparison of the specific rotation of the amine hydrochloride produced in the Curtius rearrangement of an optically active acid azide with the same amine hydrochloride produced by the Hofmann rearrangement of an optically active acid amide. The conditions of the rearrangement are very different and if partial inversion (racemization) takes place it can be detected, as it is improbable that in two rearrangements carried out under such different conditions the amount of inversion would be the same in the two instances. McKenzie[7] has found that in the rearrangement of optically active tertiary amino alcohols and pinacols the molecule undergoes partial racemization. In the case of the tertiary amino alcohols there is a change in the sign of the rotatory power. Our experiments with d-benzylmethylacetamide show that in the rearrangement and subsequent hydrolysis of the isocyanate the amine hydrochloride which is produced is optically active, $[\alpha]_D^{20}$ +16.8°. It has the same sign for the rotatory power as the acid amide from which it is obtained, and its specific rotation is the same as the specific rotation of the amine hydrochloride produced in the rearrangement of the *d*-benzylmethylacetazide.[6] It seems, therefore, that we can now state with some degree of certainty that in these two rearrangements the amine hydrochloride has either the same configuration as the original acid amide and acid azide, or that during the rearrangement the radical undergoes complete Walden inversion. Partial inversion seems unlikely.

Experimental Results

Preparation of ***d*-Benzylmethylacetamide**, $(C_7H_7)(CH_3)CHCONH_2$.—This compound was prepared from d-benzylmethylacetic acid. The acid used in these experiments was prepared from ethyl acetoacetate according to the method of Conrad[8] with a

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[8] Conrad, *Ann.*, 204, 177 (1880).

few modifications as described by Jones and Wallis.[9] It was resolved into its optically active isomers by the method of Kipping and Hunter.[10] Its rotation, **a,,** at 20° without solvent in a 50-mm. tube was +10.08'. The acid was converted into its chloride by means of thionyl chloride according to the method of Pickard and Yates.[11] The chloride boiled at 120° (15 mm.) and gave a rotation of +12.60° in a 50-mm. tube at 20" without solvent; 15 g. of the chloride was dissolved in 200 cc. of dry ether, and the solution saturated at 0° with dry ammonia gas. A heavy white precipitate of ammonium chloride formed. The mixture was allowed to stand at room temperature for fifteen minutes and then filtered. The ether solution was concentrated to about one-half its volume, and then placed in the ice box overnight. A white crystalline material separated out. This was filtered, washed with petrol ether (30–60°) and dried in a vacuum desiccator. *d*-Benzylmethylacetamide crystallizes from ether in long, beautiful needles. It melts at 104.5°; 0.3916 g. dissolved in ether, and made up to a volume of 50 cc. gave α_D $0.61 ° at 20° in a 2-dm. tube; $[\alpha]^{20}_D$ +38.94°.

Anal. Subs , 0 4270: N, 33.05 cc. (23°, 758 mm.). Calcd.: N, 8.59. Found: N, 8.66.

The filtrates from the fractional crystallization of the quinine salt of benzylmethylacetic acid were worked up and a mixed levo acid was obtained. This acid was converted into the corresponding mixed levo amide by the method described above for the pure dextro modification: 0.3269 g. of this material in 25 cc. of benzene solution gave **a,** −0.83" at 20° in a 2-dm. tube; $[\alpha]^{20}_D$ −31.7".

Rearrangement of ***d*-Benzylmethylacetamide** to d-Benzylmethylmethylamine Hydrochloride, $(C_7H_7)(CH_3)CHNH_3Cl$.—Several experiments were carried out in order to determine the best conditions for the rearrangement. It was found that an excess of bromine greatly diminished the yield of the amine hydrochloride. The following procedure gave the best results: 1.5 g. of sodium hydroxide was dissolved in 12 cc. of water and cooled to 0°; 0.5 cc. of liquid bromine was then added in small portions and the contents stirred until homogeneous. To this solution was added 1.0 g. of *d*-benzylmethylacetamide. After it had dissolved the solution was slowly warmed. When the temperature reached about 70–80° rearrangement took place, the solution became suddenly cloudy, and an oil separated out on top of the liquid. The mixture was heated to the boiling point and distilled. Water was added frequently. The oily distillate was strongly alkaline in its reaction toward litmus and had an amine odor. When acidified with dilute hydrochloric acid a clear water-white solution was obtained. This was evaporated to dryness on the water-bath. The white crystalline salt was extracted twice with ether to remove any unchanged amide that might have passed over, and then thoroughly dried in a vacuum desiccator; 1.0 g. was obtained. A portion of it melted at 145°; 0.7810 g. dissolved in water and made up to 25 cc. gave a, +1.33° at 20°; $[\alpha]^{20}_D$ +21.3°. Experiments showed that the specific rotation of this substance changed with concentration. Therefore for a comparison of the rotatory power with the same amine hydrochloride prepared from the d-acid azide the following solution was prepared, and its rotatory power determined: 0.9584 g. was dissolved in water, and made up to 20 cc. This solution gave **a,** at 20° in a 2-dm. tube +1.61°; $[\alpha]^{20}_D$ +16.8°. This is the same concentration that was used by Jones and Wallis6 in their experiments on *d*-benzylmethylmethylamine hydrochloride prepared from d-benzylmethylacetazide. The value of the specific rotation reported by them was $[\alpha]^{20}_D$ +16.6°. The mixed levo amide on rearrangement gave the corresponding levo amine hydrochloride; 0.3500 g. in 25 cc. of aqueous solution gave **a,** at 20° in a 2-dm. tube −0.28"; $[\alpha]^{20}_D$ −10.0°

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[9] Jones and Wallis, THIS JOURNAL, 48, 174 (1926).

[10] Kipping and Hunter, J. *Chem. Soc.*, ***83,*** 1005 (1903).

[11] Pickard and Yates, Trans. *Chem. Soc.*, ***95,*** 1019 (1909).

Summary

Benzylmethylacetamide has been prepared in a pure dextro and a mixed levo modification.

Evidence is submitted to show that when this compound undergoes the Hofmann rearrangement the amine hydrochloride so obtained is optically active. It is further shown that the rotatory power has the same sign as the amide from which it is produced, and that the value of the specific rotation of the *d*-amine hydrochloride produced from the d-acid amide is the same as the value of the amine hydrochloride obtained by Jones and Wallis from d-benzylmethylacetazide.

A discussion of these results is given with special reference to the Walden inversion.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OR THE RENSSELAER POLYTECHNIC INSTITUTE]

THE PREPARATION OF CYCLOPROPYL CYANIDE AND TRIMETHYLENE CHLOROBROMIDE[1]

BY J. B. CLOKE, R. J. ANDERSON, J. LACHMANN AND G. E. SMITH

RECEIVED JUNE 2, 1931 PUBLISHED JULY 8, 1931

Cyclopropyl Cyanide.—During the last few years workers in this Laboratory have found it necessary to prepare quantities of cyclopropyl cyanide as the starting material in a series of investigations on the stability of certain cyclopropane derivatives. Since the ordinary procedures for the preparation of this rather costly reagent have given unsatisfactory yields, a number of attempts have been made to devise a better process.

Cyclopropyl cyanide was first made by Henry in 1898 by the distillation of y-chlorobutyronitrile with dry potassium hydroxide,

$$ClCH_2CH_2CH_2CN + KOH = \underline{CH_2—CH_2—CH}—CN + KCl + H_2O$$

but its true nature was not recognized until a year later.[2] Although certain workers have claimed that this process gives "satisfactory" results, this has not been the general experience, since losses arise as the result of hydrolysis end polymerization. More recent descriptions of the method have been given by Haller and Benoist, Nicolet and Sattler and by one of us.[3] It is

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[1] The experimental data reported herein have been abstracted from theses on cyclopropane derivatives which have been presented to the Rensselaer Polytechnic Institute by Raymond J. Anderson, John Lachmann and Gustavus E. Smith in partial fulfilment of the requirements for the degree of Chemical Engineer.

[2] M. L. Henry, Bull. *sci. acad. roy. belg.*, [3] **36**, 34 (1898); *ibid.*, [3] 37, 17–22 (1899).

[3] Haller and Benoist, *Ann. chim.*, [9] 17, 28 (1922); Nicolet and Sattler, THIS JOURNAL, 49, 2068 (1927); Cloke, *ibid.*, 51, 1180–1181 (1929).

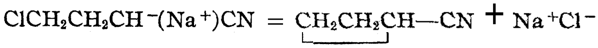
our opinion that the 40–55% yields of Nicolet and Sattler were unusually good for the potassium hydroxide method.

Other attempts to devise better methods for the preparation of cyclopropyl cyanide have been recorded. Bruylants and Stassens[4] carried out the reaction with potassium hydroxide in alcohol, but only γ-ethoxybutyronitrile was obtained and not a trace of cyclopropyl cyanide. In another investigation in which sodium alcoholate was allowed to react with y-chlorobutyronitrile Bruylants[5] obtained a mixture of the cyclopropyl cyanide and γ-ethoxybutyronitrile. By the action of pyridine and quinoline at water-bath temperature on y-chlorobutyronitrile, this investigator obtained only vinylacetonitrile and none of the cyclic compound. The present paper describes the preparation of the cyclopropyl cyanide by the action of sodamide on γ-chlorobutyronitrile in both liquid ammonia and ether solutions.

The formation of cyclopropyl cyanide by the action of sodamide on γ-chlorobutyronitrile may be explained in the same way as the alkylations of such substances as ethyl acetoacetate, diethyl malonate, phenylacetonitrile, etc. Thus, the y-chlorobutyronitrile may be assumed to exist in two tautomeric forms, *viz.*, the nitrile, $ClCH_2CH_2CH_2CN$, and the imide, $ClCH_2CH_2CH{=}C{=}NH$, structures. In the light of the carbide ion theory of Stieglitz, which has been extended by Rising[6] to salts of phenylacetonitrile, the action of sodamide on the y-chlorobutyronitrile may first be assumed to give both the "nitride" ion, $ClCH_2CH_2CH{=}C{=}N^-Na^+$, and the "carbide" ion, $(ClCH_2CH_2CHCN)^-\ Na^+$, which also are tautomeric, as follows

$$\left.\begin{array}{l} Cl{-}CH_2CH_2CH{=}C{=}NH \\ \qquad\downarrow\uparrow \\ Cl{-}CH_2CH_2CH_2{-}CN \end{array}\right\} + Na^+NH_2^- = \left.\begin{array}{l} Cl{-}CH_2CH_2CH{=}C{=}N^- \\ \qquad\downarrow\uparrow \qquad - \\ Cl{-}CH_2CH_2{-}\overset{-}{C}H{-}CN \end{array}\right\} Na^+ + NH_3$$

Finally the latter carbide salt may be supposed to undergo almost instantaneous internal condensation to give the cyclopropyl cyanide and sodium chloride



$$ClCH_2CH_2CH^-(Na^+)CN = \underbrace{CH_2CH_2CH}{-}CN + Na^+Cl^-$$

Dry sodamide was first employed in place of the potassium hydroxide of Henry in order to eliminate the hydrolysis of the nitriles, since it was first supposed that the hydrolyses were chiefly responsible for the losses in the Henry reaction. Next, after the foregoing work had demonstrated that a large amount of polymerization also occurred, the reaction was carried out in liquid ammonia with the expectation that the low temperature would minimize the polymerization. The first results, however, were disappoint-

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[4] Bruylants and Stassens, Bull. *sci. acad. roy.* belg., [5] 7, 702–719 (1921).

[5] Bruylants, *ibid.*, [5] **6**, 479–486 (1920).

[6] Rising and Zee, THIS JOURNAL, 49, 541–545 (1927); 50, 1699–1707 (1928); Rising, Muskat and Lowe, *ibid.*, 51, 262–265 (1929).

ing, since only 40–50% yields of the monomeric cyclic nitrile were obtained, polymerization accounting for most of the loss. Finally, these polymerization losses were largely eliminated: first, by the neutralization of the excess sodamide in the liquid ammonia-ether solution by the use of ammonium chloride; and, second, and more important, by the carrying out of all distillation work under diminished pressure with the aid of a very efficient condensing system. In this way, the later runs, starting with 21 g. of the γ-chlorobutyronitrile and **10** g. of sodamide, have consistently given from 75–90% of the cyclopropyl cyanide. With ether as the solvent and a comparatively long period of stirring and gentle simmering, the same quantities of reagents have given yields which have been about 10–20% lower, due to larger polymerization losses. Similar results have been obtained by E. C. Knowles[7] in the preparation of 1-phenyl-1-cyanocyclopropane from α-phenyl-γ-chlorobutyronitrile.

Trimethylene Chlorobromide.—Trimethylene chlorobromide was required for the preparation of the γ-chlorobutyronitrile, $ClCH_2CH_2CH_2Br + KCN = ClCH_2CH_2CH_2CN + KBr$,[8] which was employed in the synthesis of the cyclopropyl cyanide. The trimethylene chlorobromide has been prepared by the addition of hydrogen bromide to allyl chloride,[9] by the action of mercuric chloride on trimethylene dibromide,[10] and by the addition of sulfuric acid to a mixture of trimethylene chlorohydrin and hydrobromic acid solution.[11] Although the last process is definitely superior to those which precede, it has never given entirely satisfactory results in this Laboratory, since the product contains considerable quantities of trimethylene dibromide. The formation of the latter compound, which has always occurred with us, not only leads to diminished yields of the trimethylene chlorobromide, but it also entails a time-consuming fractionation. This difficulty is eliminated by the method which is described in this paper by means of which 90–94% yields of practically pure chlorobromide have been obtained by the addition of trimethylene chlorohydrin to phosphorus tribromide. The addition of the tribromide to the chlorohydrin has been found by Van Wyck[12] to be much less advantageous. Furthermore, the interaction of phosphorus trichloride and trimethylene bromohydrin gave poor yields, as would be expected.

Experimental Part

Trimethylene Chlorohydrin, $ClCH_2CH_2CH_2OH$.—The trimethylene chlorohydrin which was used for the preparation of the trimethylene chlorobromide was prepared

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[7] Doctorate Dissertation, Rensselaer Polytechnic Institute.

[8] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 52.

[9] Reboul, *Ann. chim. phys.*, [5] 14, 487 (1878); Bruylants, *Bull. sci. acad. roy. belg.*, 12, 1085–1094 (1908).

[10] Friedel and Silva, *Jahresb.*, 498 (1874).

[11] Kamm and Marvel, This Journal, 42, 307 (1920).

[12] Van Wyck, "Thesis," Rensselaer Polytechnic Institute.

according to the directions of Marvel and Calvery.[13] The process of Hultman, Davis and Clarke[14] gives less trouble.

Anal. Calcd. for C_3H_7OCl: Cl, 37.51. Found: Cl, 37.40.

Trimethylene Chlorobromide, $ClCH_2CH_2CH_2Br$.—Two methods were studied for the preparation of the trimethylene chlorobromide. In the first process one mole of trimethylene chlorohydrin was distilled with two moles of 48% hydrobromic acid in a continuous separation apparatus similar to that of Hultman, Davis and Clarke. Three variations of the method gave only 40% yields of the pure chlorobromide.

In the optimum variation of the second process, the phosphorus tribromide method, a two-liter, three-necked, round-bottomed flask was provided with a dropping funnel, a motor stirrer and a small reflux condenser to which was attached a calcium chloride tube. One mole (271 g.) of phosphorus tribromide was then run into the flask, which was immersed to the neck in an ice-bath; the stirrer was started and, as soon as the tribromide was cold, a two-mole quantity (189 g.) of trimethylene chlorohydrin was allowed to drop slowly into the cold tribromide over a period of two hours. The solution was then heated with stirring on a water-bath for about ten hours. At this point the mixture was allowed to cool, when it was poured into a liter of cold water and then washed with several portions of 10% sodium carbonate solution until all acid had been removed. Finally the chlorobromide was dried over calcium chloride and distilled, which gave 296 g. of chlorobromide, b. p. 140–143°. This corresponds to a 94% yield.

In several earlier runs in which 1.75 moles of chlorohydrin and 1 mole of phosphorus tribromide were used, but without the stirring during the heating on the boiling water-bath, 90% yields of the trimethylene chlorobromide were obtained.

γ-**Chlorobutyronitrile.**—The γ-chlorobutyronitrile was made by the action of potassium cyanide on the trimethylene chlorobromide.[8]

Cyclopropyl Cyanide, $\overline{CH_2CH_2C}HCN$.—Three different procedures were employed for the preparation of the cyclopropyl cyanide. Although the first method has been found to be inferior to the other two, it has been included for the sake of completeness.

Procedure 1. The Preparation of Cyclopropyl Cyanide in Liquid Ammonia.—About 250 cc. of liquid ammonia was run out of a cylinder into a 500-cc. Dewar flask. A quantity of sodamide (Kahlbaum's) was then ground up in a mortar under ether in order to exclude direct contact with moist air. At this point the γ-chlorobutyronitrile was added to the ammonia, and this was followed by the moist sodamide, which was added in small portions with a spoon. After standing for five hours, during which the flask was connected with a calcium oxide tower, about 200-300 cc. of anhydrous ether was added to the ammonia solution; next the etherammonia solution was separated from the solid by filtration through a Buchner funnel under a hood and the residue was washed with a little ether. The solution was then distilled on the water-bath with the aid of a Vigreux column until most of the ether had been removed; finally, the residue was transferred to a 50-cc. round-bottomed flask and distilled through a 1 X 60 cm. Vigreux column. The results of the first four of several such runs are given in Table I.

In another run in which the liquid ammonia was allowed to evaporate completely before the ether was added, only polymers of the cyclopropyl cyanide were obtained, several of these were formed.

Procedure 2. Optimum Procedure for the Preparation of the Cyclopropyl Cyanide.—As before, the sodamide (Kahlbaum's) was ground up in a mortar under about 150 cc. of dry ether, but to a greater degree of subdivision. About half of the ether was

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[13] Marvel and Calvery, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 112.

[14] Hultman, Davis and Clarke, THIS JOURNAL, 43, 369 (1921).

TABLE I

RESULTS OF RUNS

Run	γ-Nitrile, g.	$NaNH_2$, g.	Time in hrs of standing	Yield, %
1	50	25	5	44.7
2	50	30	5	51.5
3	25	16	5	43
4	50	30	5	35.4

then carefully decanted from the sodamide into a dry flask, when the sodamide was transferred a little at a time to a solution of 21 g. of γ-chlorobutyronitrile in 250 cc. of liquid ammonia in a Dewar flask, which was well shaken after each addition of the sodamide. Except when it was necessary to add or remove material, the flask was connected to a 152-cm. lime tower. The addition of the sodamide was made by means of a medicine dropper, which readily sucked up the fine sodamide together with the ether. From time to time some of the previously decanted ether was returned to the mortar in order to keep the sodamide completely covered by a layer of ether. After all of the sodamide had been transferred to the ammonia–ether solution, the mixture was shaken more or less steadily during the periods recorded in Table II.

At the cessation of the shaking the excess sodamide was neutralized by the addition of ammonium chloride (usually 2 g.), using solid phenolphthalein as indicator, when the solution was filtered through a Buchner funnel into a suction flask with the usual precautions. The suction flask was then provided with a stopper carrying a bubbling tube, which was connected through a stopcock to a source of dry air, and an exit tube, which was connected to the receiver. The latter was made by the sealing of a 76-cm. length of 8-mm. tubing 7.6 cm. from the bottom of a 2.5 × 25 cm. Pyrex test-tube, followed by the winding of the long tube around the test-tube and the sealing of an adapter to the end. This condenser was cooled in an ice–ammonium chloride mixture, which was contained in a liter vacuum flask. Suction was then carefully applied to the receiver, but with the stopcock practically closed, until the ammonia and some of the ether had been removed. At this point the receiver was connected with a 50-cc. modified Claisen–Vigreux distilling flask, wherein the ether solution of the nitrile was fractionally distilled under diminished pressure. Care was taken to recover any nitrile which was carried over into the receiver with the ether. The yields of cyclopropyl cyanide from the γ-chlorobutyronitrile with the other pertinent facts follow in Table II.

TABLE II

YIELDS OF CYCLOPROPYL CYANIDE

Run	γ-Nitrile, g.	$NaNH_2$, g.	Time of addn., minutes	Reaction time, minutes	Yield, %	Yield (corr.), %
1	21	9	30	30	78.5	
2	21	10	40	20	74.7	81.3
3	21	10	30	60	89.7	
4	45	21.5	55	90	77.5	

The corrected yield in Run 2 takes into account the amount of γ-chlorobutyronitrile which was recovered. The combined runs, which boiled from about 35–38° at 16–19 mm., distilled completely from 133–135° at ordinary pressures.

Procedure 3. The Preparation of Cyclopropyl Cyanide in Ether.—A weight of 10 g. of finely ground sodamide, about 200 cc. of ether and 21 g. of γ-chlorobutyronitrile were transferred to a 500-cc. flask which was provided with a reflux condenser and a stirrer. The temperatures and the durations of the reaction for three experiments will be found in Table III. The distillation process was the same as that described for Procedure 2. For the first two runs, in which chloronitrile was recovered, corrected yields have been given. In this procedure, however, more polymerization occurred than in Procedure 2, but less than in Procedure 1.

TABLE III

DATA FOR EXPERIMENTS

Run	Approx. temp., °C.	Reaction time. hrs.	Yield, %	Yield (corr.), %
1	30	7–8	41	64.7
2	Refluxing	16	69.4	80.2
3	Refluxing	25	74.7	..

Summary

1. Cyclopropyl cyanide may be obtained in 75–90% yields by the action of sodamide on γ-chlorobutyronitrile in a liquid ammonia–ether solution. The reaction in ether solution appears to be less efficient.

2. Trimethylene chlorobromide may be prepared in 90–94% yields by the action of phosphorus tribromide on trimethylene chlorohydrin.

TROY, NEW YORK

NOTES

The Cholesterol Content of Shrimp Waste.—The ethyl ether extraction of the dried shrimp and shrimp waste prepared by Vibrandt and Abernethy[1] produced a viscous oil, dark red by transmitted light and soluble in the common organic solvents. According to elemental analysis the oil contains no sulfur, halogens, nitrogen or heavy metals.

Treatment of the oil with alcohol at 60° precipitated an insoluble brown resinous material and subsequent cooling of the alcoholic solution to 0° effected a fairly rapid separation of monoclinic crystals from the viscous, red oily residue.

Purification of Crystals.—Decolorization of the hot alcoholic solution of the crystals thus obtained with animal charcoal and subsequent crystallizations from hot alcohol produced a material which melted at 146.5°. Measurements under the microscope showed monoclinic plates with angles of 79.5 and 100.5". The average yield of these crystals from three separate crystallizations and purifications is 19.08% on the basis of the original oil. The total quantity of sterols in the shrimp waste was not determined.

Identification.—The purified crystals were then treated with digitonin by the method of Windaus[2] and further identified by the Liebermann[3]

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[1] F. C. Vilbrandt and R. F. Abernethy, "Utilization of Shrimp Waste," United States Fisheries Document No. 1079 (1930).

[2] A. Windaus, *Chem.-Ztg.*, 37,1001 (1913).

[3] Oliver Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, 1924, p. 123.

and the Hagarsalkowski[4] tests for cholesterol, obtaining positive tests. Further identification of the crystals as cholesterol was accomplished by the preparation of the benzoate[5] and acetate[6] derivatives.

The high cholesterol content of the shrimp oil led to feeding tests for antirachitic potency of the oil by the authors and F. P. Brooks,[7] giving encouraging results. Since the extract of shrimp waste amounts to 2.25% of the waste, a production of 80,000 pounds of cholesterol could have been accomplished by the extraction of the waste of the 1927 crop of shrimp.

ROY F. ABERNETHY[8]
FRANK C. VILBRANDT[9]

RECEIVED AUGUST 4, 1930
PUBLISHED JULY 8, 1931

A Simple Method for the Preparation of Glycine.—The preparation of glycine by the classical method,[1] employing the reaction between monochloroacetic acid and ammonia, has proved generally unsatisfactory because of the lengthy procedures involved in the isolation of a product free from ammonia and chloride and because of the low yield of pure glycine resulting. Robertson[2] found after a careful study of the course of the reaction between monochloroacetic acid and ammonia, that the yield of glycine could be greatly increased by the use of a large excess of ammonia and that there occurred a corresponding decrease in the amount of imino-diacetic acid and trimethylene-amine-tricarboxylic acid, the principal impurities resulting from side reactions. Based upon this observation, he proposed a method in which a 60 to 1 molecular ratio of ammonia to monochloroacetic acid was employed. This increased the actual concentration of glycine formed in solution to 86% of the theoretical. While a 50% final yield of pure glycine was obtained, the isolation of the product was accomplished after the laborious and expensive procedure of removing the ammonium chloride by the use of silver oxide.

Since, when a large excess of ammonia was used, the concentration of glycine formed was large in comparison with the amount of side reaction products, the possibility of *direct* precipitation of glycine seemed worthy of investigation. As was suggested by Robertson, 60 moles of

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[4] D. Holde and E. Mueller, "Saponifiable Hydrocarbons, Fats and Waxes," 1922, p. 519.

[5] S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 172.

[6] R. J. Anderson, *J. Biol. Chem.*, **71**, 707 (1926).

[7] F. C. Vilbrandt, R. F. Abernethy and F. P. Brooks, "Preliminary Report on the Antirachitic Properties of Shrimp Oil," THIS JOURNAL, 52, 4940 (1930).

[8] Department of Chemistry, University of North Carolina, Chapel Hill, N. C.

[9] Department of Chemical Engineering, Iowa State College, Ames, Iowa.

[1] Kraut, *Ann.*, 266, 295 (1891).

[2] G. R. Robertson, THIS JOURNAL, 49, 2889 (1927).

ammonia and 1 mole of monochloroacetic acid were allowed to react. The excess ammonia was distilled off and the resulting aqueous solution was concentrated to a small volume. When 95% methyl alcohol was added to this solution, glycine promptly crystallized out and a 72–74% yield of an impure product resulted. By careful recrystallization a 60–64% yield of ammonia and chloride-free glycine was obtained. Our work does not indicate that the use of pyridine with methyl alcohol in the precipitation of glycine is necessary as was reported by Boutwell and Kuick.[3] As a result of our experiments, a simple, rapid and inexpensive method for the preparation of pure glycine is offered.

Experimental

Method of Preparation.—One mole (94.5 g.) of monochloroacetic acid is added gradually with shaking to 4 liters of ammonium hydroxide (sp. gr. 0.90) in a 5-liter round-bottomed flask. When all of the monochloroacetic acid is dissolved and the solution is thoroughly mixed, the flask is stoppered and set aside undisturbed for forty-eight hours at room temperature. The solution, which is colorless or faintly yellow, is then concentrated on a water-bath under reduced pressure to a volume of about 200 cc. The concentrated aqueous solution is then made up to 250 cc. with water and transferred to a 2-liter beaker, and the glycine is crystallized out by gradually adding, with stirring, 1500 cc. (six volumes) of 95% methyl alcohol (the use of absolute methyl alcohol offers no advantage). The mixture is placed in an ice box for four to six hours to allow complete crystallization. The supernatant liquid is then decanted from the crystals onto a Biichner funnel, the remaining crystals are suspended in approximately 500 cc. of 95% methyl alcohol, and are transferred to the filter. The beaker is rinsed twice with 100–120 cc. portions of 95% methyl alcohol, and the rinsings are poured over the crystals in the funnel. Finally, as much of the liquid as possible is pressed out, the crystals are washed with a small amount of ethyl ether, and dried in air. A yield of 54–55 g. of glycine, 72–74% of the theoretical, is obtained.

Since the product contains a trace of ammonia (by Nessler's reagent) and chloride (by silver nitrate), a second crystallization is carefully made by dissolving the crystals in 210–215 cc. of water, with warming, and precipitating with 5 volumes (1250 cc.) of 95% methyl alcohol. After crystallization in an ice box, the glycine is filtered, washed and dried, as previously outlined. A yield of 48–49 g., 64–65% of the theoretical, results. If the product still shows a faint trace of ammonia, a second recrystallization may be made, which will yield 45–48 g. The final product is white and finely crystalline. The recovery of further amounts of glycine from filtrates is not practicable because only a small amount

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[3] P. W. Boutwell and L. F. **Kuick,** THIS JOURNAL, ***52*,4166** (1930).

of the product, heavily contaminated with ammonium chloride, is obtained. The recovery of the excess ammonia and of the methyl alcohol greatly reduces the cost of preparation by this method. The use of permutit in removing the last traces of ammonia was not found to be superior to precipitation with methyl alcohol alone.

Analysis of Product.—Molar solutions of five samples of glycine prepared by the above method showed no trace of ammonia with Nessler's reagent, nor of chloride with silver nitrate. Melting points and mixed melting points (with Eastman's ammonia-free glycine, No. 445) were determined by the capillary tube method. Both gave values of 236–239° (uncorrected), with decomposition and effervescence, after browning at 228°. Analyses for the nitrogen content, determined by the Kjeldahl method, gave values ranging from 18.44 to 18.76% (theoretical 18.67%).

Summary.—1. A simple, inexpensive method for the preparation of glycine from monochloroacetic acid and ammonia is outlined.

2. A 60–64% yield of glycine free from ammonia and chloride is obtained.

Contribution from the
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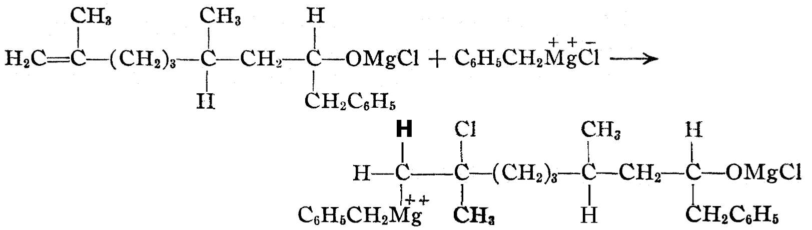
Denver, Colorado

James M. Orten
Robert M. Hill

Received April 21, 1931
Published July 8, 1931

The Purported Addition of Benzylmagnesium Chloride to the Ethylenic **Linkage** in **Citronellal.**—It has been suggested[1] that the recent[2] indirect proof offered for the non-addition of benzylmagnesium chloride to the ethylenic linkage in citronellal is not decisive, and that a new possible mechanism is



$$\mathrm{H_2C{=}\overset{\overset{CH_3}{|}}{C}{-}(CH_2)_3{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{CH_2C_6H_5}{|}}{\overset{\overset{H}{|}}{C}}{-}OMgCl + C_6H_5CH_2\overset{++}{Mg}\overset{-}{Cl} \longrightarrow}$$

$$\mathrm{H{-}\underset{\underset{C_6H_5CH_2\overset{++}{Mg}}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}{-}(CH_2)_3{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{CH_2C_6H_5}{|}}{\overset{\overset{H}{|}}{C}}{-}OMgCl} \qquad \text{(I)}$$

(A)

In this manner, "a complex molecule is obtained which is similar to that suggested by Rupe,[3] except that the second molecule of the Grignard reagent is attached in a slightly different manner."

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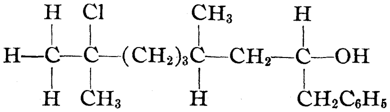
[1] Kharasch, "Annual Survey of American Chemistry," 1930, Vol. V, p. 193.

[2] Gilman and Schulz, This Journal, 52, 3588 (1930).

[3] Rupe, Ann., 402, 161 (1914).

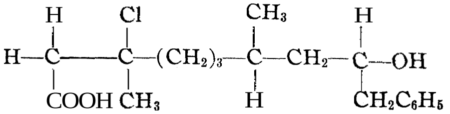
Actually, this mode of addition is quite unlike that proposed by Rupe. On hydrolysis, one would expect Compound (A) to give



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{CH_3}{\overset{Cl}{C}}{-}(CH_2)_3\underset{H}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_2C_6H_5}{\overset{H}{C}}{-}OH}$$

and toluene. However, Rupe's analysis shows his product to contain no chlorine, and to have in place of the chlorine the equivalent of a benzyl group. Furthermore, the same product is obtained with benzylmagnesium bromide. Accordingly, Compound (A) is without any experimental support.

Granting that Compound (A) is correct, it represents an unsymmetrical organomagnesium compound of the general formula R—Mg—R'. Although such compounds have not yet been prepared, it is known that the symmetrical R—Mg—R compounds on carbonation (followed by hydrolysis) yield the corresponding carboxylic acids, RCOOH. We do not know how R—Mg—R' compounds would behave on carbonation, but it appears altogether reasonable to expect them to give the two carboxylic acids, RCOOH and R'COOH, in varying quantities depending on the nature of the R— groups. If this be true then Compound (A) on carbonation should give $C_6H_5CH_2COOH$ and



$$\mathrm{H{-}\underset{COOH}{\overset{H}{C}}{-}\underset{CH_3}{\overset{Cl}{C}}{-}(CH_2)_3{-}\underset{H}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_2C_6H_5}{\overset{H}{C}}{-}OH}$$

Actually, the latter acid is not obtained, because when the reaction mixture of citronellal and an excess of benzylmagnesium chloride is carbonated, only phenylacetic acid is obtained, as evidenced by melting point, mixed melting point and neutralization equivalent.

The possibility that RMgX adds to an ethylenic linkage to give an R—Mg—R' compound which might undergo but partial carbonation to give RCOOH to the exclusion of R'COOH is rendered remote by other reported experimental evidence. First, a different RMgX compound (phenylmagnesium bromide) after reaction with citronellal and then carbonation gave presumably pure benzoic acid.[2] Second, if addition of RMgX to an ethylenic linkage did occur with olefins of a type to give rise to R—Mg—R' compounds in which the R— and the R'— groups were closely related but not identical, then carbonation should give a mixture of acids, but no such mixtures have been obtained.[4]

[4] Giman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928). Earlier pertinent references are contained in this article.

Our unavoidable conclusion is that benzylmagnesium chloride does not add to the ethylenic linkage in citronellal.[5]

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

HENRY GILMAN
W. F. SCHULZ

RECEIVED JUNE 2, 1931
PUBLISHED JULY 8, 1931

COMMUNICATIONS TO THE EDITOR

THE STABILITY OF NITROGEN PENTOXIDE AT 1000 ATMOSPHERES OF OXYGEN IN THE PRESENCE OF NITROGEN TETROXIDE

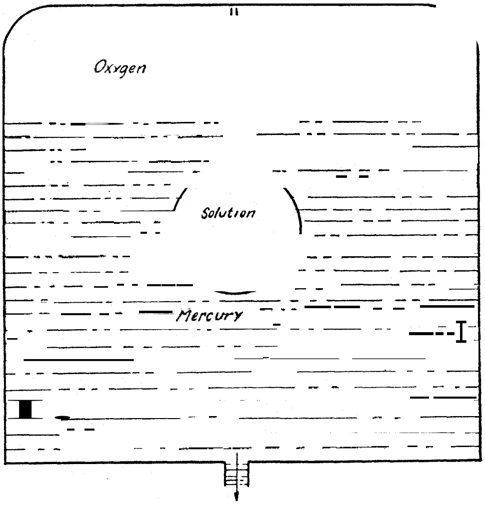
Sir:

The equilibrium

$$N_2O_5 = N_2O_4 + {}^1/{}_2O_2$$

has been investigated at 1000 atmospheres' pressure of oxygen by dissolving nitrogen tetroxide and nitrogen pentoxide in carbon tetrachloride in an apparatus shown schematically in Fig. 1.

It was found that at this pressure of oxygen the reaction goes completely to the right. With the gas evolution apparatus used for analysis it was possible to detect as little as 0.5 cc. of oxygen, which, with the volumes of nitrogen pentoxide solution used, is equivalent to a partial pressure of **0.00155** atmosphere of nitrogen pentoxide at 25°. The partial pressure of nitrogen tetroxide in one of the runs was 0.710 atmosphere, so that the equilibrium constant in atmospheres is greater than 1.48×10^4. The values given for the partial pressures depend on the assumption of a perfect solution of nitrogen tetroxide, nitrogen pentoxide and carbon tetrachloride and upon a solubility determination of nitrogen pentoxide in a solution of nitrogen tetroxide in carbon tetrachloride. This equilibrium constant gives a free energy change less



To pressure pump and gage

Fig. 1.

Professor Rupe is in agreement with this conclusion, and he is now engaged in a further study of the constitution of the product obtained from citronellal and benzylmagnesium chloride.

than —5600 cal. Now, assuming that the entropy of nitrogen tetroxide is equal to or less than that of nitrogen pentoxide, then the total increase in entropy is equal to or less than 24 units, the entropy of $^1/_2O_2$. Using these values in the equation

$$AF^o = \Delta H - T\Delta S^\circ$$

we obtain for ΔH a value equal to or less than 1600 calories.

The value given for ΔH in the "International Critical Tables" is 2690 cal. Either this value is too high or the entropy of nitrogen tetroxide is greater than that of nitrogen pentoxide, which would be surprising.

It was not feasible, with the apparatus used, to go higher than 1000 atmospheres' pressure.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

LOUIS LEWON
HENRY EYRING

RECEIVED JUNE 1, 1931
PUBLISHED JULY 8, 1931

THE PHOTO-REACTION OF HYDROGEN AND IODINE MONOCHLORIDE

Sir:

In a recent communication [THIS JOURNAL, 52, 2793 (1930)] Rollefson and Lindquist criticize our conclusions [Nature, **127,** 93 (1931)] regarding the photo-reaction of hydrogen and iodine monochloride, namely, that excited chlorine atoms may not be necessary for it to take place. They maintain that, as our hydrogen pressure was large compared with the pressure of iodine monochloride, the chlorine atoms (excited *to* the $^2P_1$ state by collisions) would have more chance of reacting with the hydrogen than with the iodine monochloride. Nevertheless, we have been able to bring about the reaction with hydrogen pressures (circa 70 mm.) comparable with the pressure of iodine monochloride.

We used Merck's crystalline iodine monochloride contained in a small glass tube which was subsequently broken in the reaction vessel. Hydrogen passing through a palladium tube was brought to the required pressure in the reaction vessel, which was then sealed up. The pressure was recorded on a glass spiral gage, and no contact with impurities, tap-grease, etc., was permitted [Ashley and West, Nature, **127,** 308 (1931)]. The vessel was then irradiated with a mercury vapor lamp through a filter of quinine sulfate solution, and also through a filter of picric acid and cupric sulfate, transmitting only the 5461, 5764 and 5791 A. lines. The reaction is slow but measurable, and the rate of iodine formation increases when the initial hydrogen pressure is increased. If the chain mechanism suggested is correct, the reaction, even under the most favorable conditions, could only have roughly 1/500,000 the speed of the hydrogen-chlorine reaction. Doubtless the reaction $ICl + Cl = Cl_2 + I$ takes place as Rollefson and Lindquist suggest, but it would be unwise to infer from any of these experiments that the chlorine atom is unexcited.

Rollefson and Lindquist give only a few details of their experimental conditions, gas pressures, etc., but they mention one significant fact, namely, that their chlorine pressure was always large compared with the pressures of hydrogen and iodine monochloride. In these circumstances the iodine compound in the vapor phase may have been mainly iodine trichloride. This substance is of a lighter color than iodine monochloride, and must have an altogether different absorption spectrum. We have found that the vapors of iodine monochloride and chlorine react very readily, and, indeed, Rollefson and Lindquist themselves admit that they froze out iodine trichloride in the solid phase.

We do not wish to make any further statement until we have completed the study of the reaction kinetics.

PHYSICO-CHEMICAL LABORATORY
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T. IREDALE
D. P. MELLOR

RECEIVED JUNE 2, 1931
PUBLISHED JULY 8, 1931

CATALYTIC REDUCTION OF MIXTURES OF PARA-NITRO- AND NITROSO-PHENOLS WITH KETONES

Sir:

It has recently been shown by the writer that *p-sec.*-alkylaminophenols are formed by the catalytic reduction of mixtures of p-nitro- or nitrosophenol and ketones at room temperatures [Major, THIS JOURNAL, 53, 1901 (1931)]. The suggestion was made that the reaction probably involved formation of *p*-hydroxy-phenylhydroxylamine as an active intermediate product of the reduction and that this compound condensed with the ketone and finally that the condensation product was reduced to the alkylaminophenol. Vavon and Krajčinović have reported that they have been able to make the condensation product between benzaldehyde and phenylhydroxylamine, $C_6H_5CH{=}N(O)C_6H_5$, by the catalytic reduction of a mixture of nitrobenzene and benzaldehyde [Vavon and Krajčinović, Compt. rend., 187, 420 (1928)].

However, it was noted that heat was formed during the catalytic reduction of mixtures of p-nitro- and nitrosophenol and acetone. There remained, then, the possibility that the heat of the reaction between p-nitro- or nitrosophenol and hydrogen was sufficient to cause the *p*-aminophenol which formed to condense with the ketone. This condensation product would then be readily reduced to *p-sec.*-alkylaminophenol.

Evidence which apparently favored this point of view was obtained when a solution of 0.1 mole of *p*-aminophenol in acetone was heated to the boiling point and then shaken with hydrogen in the usual way in the presence of a platinum oxide catalyst. Hydrogen was absorbed and 50% of the theoretical yield of p-isopropylaminophenol was recovered from the reaction mixture.

On the other hand, it was found that a mixture of 0.05 mole of p-aminophenol, 3.5 moles of acetone and 0.1 g. of Adams' platinum oxide catalyst did not absorb any more hydrogen than was necessary to reduce the platinum oxide when the temperature of the reaction mixture was kept at 4–5° or at 26–32.5°. The mixture was shaken at 4–5° for one hour and at 26–32.5° for two and three-quarter hours.

It was also found that in one and one-half hours very little *p*-isopropylaminophenol was formed during the reduction of a solution of 0.05 mole of *p*-nitrosophenol in 3.5 moles of acetone in the presence of the platinum oxide catalyst at 4–5°. On the other hand, in one hour at 16–32.5° the catalytic reduction of 0.05 mole of p-nitrosophenol in 3.5 moles of acetone gave a 60% yield of p-isopropylaminophenol.

It seems fairly evident, then, that while catalytic reduction of a mixture of *p*-aminophenol and acetone at elevated temperatures will produce *p*-isopropylaminophenol, this reduction does not occur to any appreciable extent during a few hours at room temperature. However, catalytic reduction of a mixture of p-nitrosophenol and acetone at room temperature does give p-isopropylaminophenol. Accordingly, it seems most likely that *p*-hydroxyphenylhydroxylamine is formed as an intermediate during the reduction and that due to its somewhat greater activity than p-aminophenol it condenses with the ketone and the condensation product is in turn reduced to *p-sec.*-alkylaminophenol.

LABORATORY FOR PURE RESEARCH
MERCK AND CO., INC.
RAHWAY, N. J.
RANDOLPH T. MAJOR

RECEIVED JUNE 11, 1931
PUBLISHED JULY 8, 1931

AN ADSORPTION METHOD FOR THE DETERMINATION OF THE AREA OF A POWDER

Sir:

The writers have devised a simple procedure which seems to give information that is more definite with respect to the area of a fine powder than that given by any earlier method.

The powder, titanic oxide or silicon dioxide, for example, is dried in a high vacuum at as high a temperature as can be used without affecting the area of the crystals. The cool, dry powder is immersed in a solution of oleic acid, butyric acid or some other suitable acid, in very dry benzene, and the suspension is shaken until equilibrium is attained. After the powder has settled, a sample of the supernatant liquid is drawn off. The benzene of this sample and of a sample of the initial solution is evaporated off, if oleic acid is the solute chosen, and the oleic acid left from each solution is dissolved in 95% ethyl alcohol. The alcohol solutions are then titrated with carbonate-free sodium hydroxide dissolved in water. The difference in concentration is considered to give the amount of acid adsorbed by the surface of the powder. Only air that is thoroughly dried by phosphorus pentoxide is allowed to enter the vessel in which the solution is prepared and the flasks in which the adsorption experiments are carried out.

Figure 1 shows how the amount of oleic acid adsorbed by the surface of one gram of powder varies with the concentration of the final or equilibrium solution of oleic acid in benzene. At concentrations above 0.01 to 0.02 mole per kilogram of benzene, the adsorption becomes practically constant, and the oleic acid on the surface of the grains of powder may be said to form a condensed film. There is some evidence which seems to indicate that this film is monomolecular.

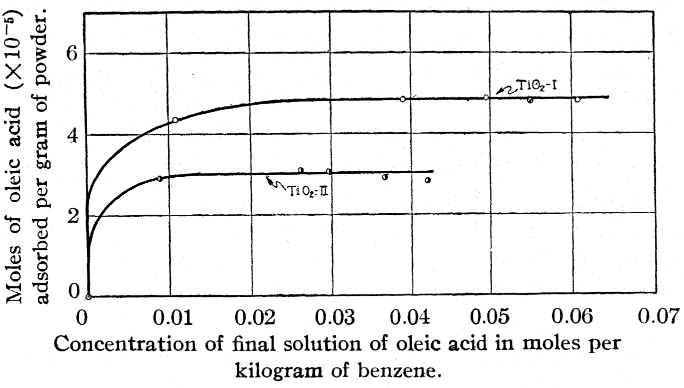

Fig. 1.

It may be assumed that the area occupied per molecule of oleic acid at the interface is 20.0 sq. Å., which is about the mean value for condensed films of the acid on water at a zero film pressure. On this basis, the area for TiO$_2$-I was calculated as 22.9 sq. m. per cc. of titanic oxide (3.89 grams), and for TiO$_2$-II as 14.4 sq. m. per cc. The ratio of these values is 1.59, while the ratio for the energy of immersion [Harkins and Dahlstrom, to be published] in ethyl acetate for the same two powders is 1.53, and the ratio of the weights of propyl alcohol adsorbed [Gans and Brooks, to be published] from the vapor per unit weight of these powders at a constant vapor pressure equal to one-half the saturation pressure at room temperature is 1.53.

The area of the powder TiO$_2$-II as determined for us by a microscopic method [Dunn, *Ind. Eng. Chem., Anal. Ed.*, *2*, 59 *(1930)*], applicable to crystalline powders, is 13.8 sq. m. per cc. of powder, on the assumption of a spherical shape for each particle. This is in good agreement with the value 14.4 obtained by the adsorption method. However, the closeness of the agreement is to some extent accidental, since the adsorption method includes the area of the colloidal part of the powder, which is not included by the microscopic method. Further comparisons with various other methods will be made later.

GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

WILLIAM D. HARKINS
DAVID M. GANS

RECEIVED JUNE 12, 1931
PUBLISHED JULY 8, 1931

CRYSTALLIZATION OF ANHYDROUS SODIUM ACETATE FROM AQUEOUS SOLUTION AT ROOM TEMPERATURE

Sir:

If the trihydrate of sodium acetate, $CH_3COONa\cdot 3H_2O$, is placed in a sealed tube and heated to 58°, it loses its water of crystallization and partially dissolves in this water. At 80° all the salt is dissolved. On cooling in the sealed tube, the writer, experimenting under the supervision of Professor Stuart Woodford Young, made the interesting and unexpected observation that the form crystallizing from this aqueous solution is anhydrous. This anhydrous form appears whether the solution be cooled rapidly or slowly, the only difference being in the appearance of the crystal. The slowly cooled solution will start crystallizing at only a few nuclei, from which there is a radial growth of thin needles. The rapidly cooled solution is immediately filled with small nuclei. Both of these are flattened and elongated orthorhombic crystals with the three indices of refraction lower than 1.45. This anhydrous form is shown by crystallographic observation, for which we are indebted to Professor A. F. Rogers, to be the same as the anhydride formed by direct dehydration, and the normal solubility curve is exhibited.

The crystals remain unaltered as long as the tube is kept sealed. Here, then, is a solution that is 2400% supersaturated and yet can be kept indefinitely in contact with the anhydrous form. Cooling below 0° has no effect, but cooling in liquid ammonia or liquid air brings about conversion to the stable trihydrate.

In 1904 and 1905 Dr. Young and W. E. Burke were able to form and identify ten new hydrates of sodium thiosulfate. At the beginning of the work on sodium acetate it was thought that some new hydrates might be produced, but so far none has been found.

This recent work of Dr. Young, who had been on the faculty of Stanford

University since 1892, was halted by his unexpected death on April 9, 1931, and is discontinued for the present.

DEPARTMENT OP CREMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CAL.
WILLIAM W. CONNER

RECEIVED JUNE 15 1931
PUBLISHED JULY 8,'1931

DISCONTINUITIES IN ADSORPTION ISOTHERMS

Sir:

In previous communications[1] we have shown that the adsorption of hydrogen by nickel and copper at low temperatures increases with pressure in a markedly discontinuous manner. Recently Allmand and Burrage[2] have reported a large number of isotherms for charcoal and silica gel which show discontinuities, and have suggested that the failure on the part of other investigators to detect this phenomenon is to be ascribed to an insufficient number of experimental points. In the course of an extended study, during the past four years, of the adsorption isotherms of hydrogen, nitrogen and carbon monoxide by nickel, copper and iron, at pressures up to one atmosphere and at temperatures which cover the range, —200 to +200°, we have found a considerable number of discontinuous isotherms, and have studied them in some detail, particularly from the standpoint of the effects produced by temperature and the presence of poisons.

The evidence now available points clearly to the conclusion that a step-wise increase of adsorption with pressure is a general characteristic of the physical, or "secondary," type of adsorption. There is no evidence that discontinuities ever occur in "chemical" adsorption. The steps have been found under conditions which preclude the existence of liquid films or of multimolecular layers of gas; further, the phenomenon appears to have no direct relation to the "active spots" of catalytic theory.

We have been led to advance a new hypothesis of physical adsorption, according to which the observed steps represent the formation of concentric rows of adsorbed molecules, first at the edges of each crystal face, and building up successively toward the center. The evidence in support of this hypothesis rests primarily on the uniformity in the volumes corresponding to successive steps, and on the actual magnitude of the individual step. The mechanism by which adsorption can occur in successive rows may readily be derived on the assumptions that neighboring adsorbed molecules evaporate from the surface less readily than isolated molecules,

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[1] Benton and White, THIS JOURNAL, 52, 2325 (1930); also paper read at the Atlanta meeting of the American Chemical Society, April, 1930.

[2] Allmand and Burrage, Proc. *Roy. Soc.* (London), A130, 610 (1931); *J. Phys. Chem.*, 35, 1692 (1931).

and that physically adsorbed molecules possess mobility in the plane of the surface.

Details will follow shortly.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
UNIVERSITY, VIRGINIA

ARTHUR F. BENTON
T. A. WHITE

RECEIVED JUNE 18, 1931
PUBLISHED JULY 8, 1931

HAZARDS IN CATALYTIC HYDROGENATION AT ELEVATED TEMPERATURES AND PRESSURES

Sir:

T. S. Carswell [THIS JOURNAL, **53**,**2417** (1931)] has reported an explosion which occurred while he was attempting to hydrogenate o-nitroanisole in the liquid phase with a nickel catalyst. He states that the purpose of his communication "is to call the attention of other investigators to the dangers of this type of reduction when carried out on other than a very small scale." There is no doubt that a warning is needed but in my opinion it should be against-the procedure used by him and not against catalytic hydrogenation at elevated temperatures and pressures. This general method has been in successful use in this Laboratory for the past three years [THIS JOURNAL, **52**, 4349, 5192 (1930); 53, 1091, 1095, 1402, 1425, 1868, 2012 (1931); **J.** Yhys. Chem., **35,** 1684 (1931)] using a wide variety of compounds and dealing with quantities similar to those used by Dr. Carswell. The procedure used by him is, in my opinion, ill-advised in several respects. The bomb was inadequate and sufficient information was not available to him before the attempt was made to hydrogenate 400 g. of nitroanisole. A bomb for experimental purposes 15 cm. in diameter should have a wall thickness several times as great as that (5 mm.) used by Carswell. Our own bombs have a wall thickness of 2 to 2.5 cm. and are only 6 cm. in internal diameter. They were bored out of properly annealed rolls of nickel–chromium steel [cf. Ernst, *Ind. Eng.* Chem., 18, 664 (1926)]. In order to control the rate of hydrogenation it is important that the bomb be provided with a thermometer or thermocouple well, so designed that there is little lag between the actual temperature of the liquid contents of the bomb and the reading of the temperature measuring device.

The temperature and amount of catalyst used by Carswell were excessively high for the compound to be hydrogenated, and apparently he made no attempt to control the rate of hydrogenation by control of the rate of shaking of the bomb. The reactions are quite exothermic and would result in local superheating if heat **was** being liberated more rapidly than it could be dissipated. In the hydrogenation of 100 *g.* of toluene with less than 0.5 *g.* of nickel, for example, we have observed a temperature rise of as much as 150° within two or three minutes. In the hydrogenation of only 20 g. of nitrophenol at 100° with **0.3** g. of nickel a temperature rise of 100° was observed. It is not surprising that in the hydrogenation at 250° of 400 g. of nitroanisole in the presence of perhaps 50 g. of nickel, the temperature of the contents of the bomb rose so high that there resulted an explosive decomposition.

There is little doubt that after suitable investigation the catalytic hydrogenation of such compounds as nitroanisole can be carried out on a commercial scale in relatively light equipment. However, one is not justified, as Carswell has demonstrated, in attempting to hydrogenate even so small a quantity as a few hundred grams of material without preliminary study and without having available a properly designed bomb.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
HOMER ADKINS

RECEIVED JUNE 20, **1931**
PUBLISHED JULY 8, **1931**

POSITIVE ION CATALYSIS IN THE KNOEVENAGEL REACTION

Sir:

Dakin [*J. Biol.* ***Chem.***, 7, 49 (1909)] found that amino acids might be employed in place of the amines usually used to effect condensations of the Knoevenagel type. In the presence of amino acids, the velocity of the condensation of cinnamic aldehyde with malonic acid in 50% alcohol was found to increase with increase in the hydrogen-ion concentration of the solution [D. L. Klein, Master's Thesis, New York University, 1930]. This result suggested the amino acid cation to be a more active catalyst than the other ions derivable from the ampholyte. As is well known, secondary aliphatic amines are preferable to primary amines for the catalysis of reactions of this type. Since, as a rule, such secondary amines are stronger bases than the corresponding primary amines, it appeared that with such substances the amine ion is the active catalyst. In agreement with this concept various amines have been found to be more active catalysts in acid solutions.

Extremely weak bases such as urea do not ordinarily appear to catalyze condensations of the Knoevenagel type in aqueous or alcoholic solution. When, however, the solutions are made strongly acid, such weak bases display some catalytic activity. By taking advantage of the fact that weak bases dissolved in acetic acid appear to be highly dissociated, it was found that in this solvent urea and similar substances are extremely efficacious catalysts for the condensation of aldehydes with substances containing an "active" methylene group.

On the basis of these results, it is concluded that condensations of the

Knoevenagel type are instances of positive ion catalysis. The details of this investigation will shortly be submitted to THIS JOURNAL.

BIOCHEMICAL LABORATORY
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK CITY

KENNETH CLARK BLANCHARD
DAVID L. KLEIN
JOSEPH MACDONALD

RECEIVED JUNE 18, 1931
PUBLISHED JULY 8, 1931

THE SEPARATION OF COLUMBIUM AND TANTALUM

Sir:

When columbium is reduced in acid solution from a valence of five to a valence of three the solution becomes blue. In the course of a study of the electrolytic reduction of columbium, with a view to the separation of this element from tantalum, reduction in alkaline solution was attempted. Although no color change was obtained, the formation of an amalgam at the mercury cathode was noted. This suggested the possibility of obtaining metallic columbium in the form of an amalgam by reduction in alkaline solution, Shortly thereafter the writer's attention was called to the article of Fink and Jones,[1] where they show that tungsten can be plated from a saturated solution of sodium carbonate at elevated temperature and high current density. Since that time, the writer has found that, at a current density of approximately 3 amp./sq. dm. and a temperature of 103°, columbium may be plated from a saturated solution of sodium carbonate containing ignited columbium oxide (Cb_2O_5). A copper cathode was used. Tantalum will not plate out from a similar bath under identical conditions of temperature and current density. Further, it has been found that a metallic plate is obtained from a carbonate bath containing a mixture of the ignited oxides of columbium and tantalum using the same temperature and current density as that indicated above. It seems to be a fairly safe conclusion that only columbium may be plated from a saturated solution of sodium carbonate containing a mixture of the ignited oxides of tantalum and columbium.

At present further studies are being made concerning the nature of the plates obtained by this method.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

D. D. PEIRCE

RECEIVED JUNE 20, 1931
PUBLISHED JULY 8, 1931

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[1] C. G. Fink and F. L. Jones, *Trans. Am. Electrochem. Soc.*, Preprint 59–27, 273 (1931).

NEW BOOKS

Das Buch der grossen Chemiker. (The Book of the Great Chemists.) **Vol. II. From Liebig to Arrhenius.** Edited by Dr. Günther Bugge. Verlag Chemie, G. m. h. H., Berlin W 10, Germany, 1930. x + 559 pages. 16 X 23.5 cm. Illustrated. Price, bound, M. 32.

This fine book is in every way a proper sequel to the first volume. The twenty-seven chapters, written by twenty different scholars, cover the history of chemistry from the beginning of organic synthesis to the triumphs of Fischer and Ehrlich, from the discovery of colloids and of the spectroscope to the periodic table and the theory of electrolytic dissociation, The two volumes complete the story to the point where the accomplishments of chemists now living must be discussed.

The work comes much nearer to being a history of chemistry than its title indicates, not because "history is a series of biographies" but, rather, because the authors of the various chapters have not confined themselves to biography but have placed each chemist in a setting of the chemistry of his time and have discussed his work in relation to the work of other chemists. The work is scholarly, attractive, readable and authoritative.

In addition to its own indexes, the second volume contains lists of the Nobel Prize winners in physics and chemistry, 1901–1930, and an extensive bibliography supporting the material of both volumes.

TENNEY L. DAVIS

A Short History of Atomism. **By** JOSHUA C. GREGORY, Lecturer in Chemistry in the University of Leeds. A. & C. Black, Ltd., London; New York Agents, The Macmillan Co., 60 Fifth Avenue, New York, 1931. 258 pp. 14 × 22 cm. Price, $3.50.

Due to the enormous flux of recent theory and experiment in the field of atomic structure, there exists a definite need for an historical survey of the entire subject. Unfortunately Professor Gregory's offering cannot be said to satisfy this need.

The subject matter of the present volume is delimited by the sub-title "From Democritus to Bohr," but the last chapter, entitled "Recent Atomism," is concerned with the developments of the last five years. An attempt has apparently been made to present an up-to-the-minute account in that the author mentions a number of researches that have been reported during the past year.

The description of Greek thought on atomism, its introduction into European philosophy, and finally its incorporation into chemistry to explain the laws of stoichiometry, have all been treated admirably. The author has taken pains to stress both the philosophical difficulties of the atomic concept and the large amount of cooperative research that was required to establish a detailed atomic theory, These chapters are clearly the product of a broad and well applied knowledge of the subject.

As the narrative proceeds to the closing decades of the nineteenth century, however, one feels that the author is about to commit two rather serious faults. The concluding chapters amply confirm these premonitions. In the first place, it seems that the author has shown greater partiality to the discoveries of British scientists than to those of other nations. For example, the names of Clausius, von Laue and Kossel do not appear in the book and, in general, non-British work is treated from the comments of English contemporaries rather than from the workers' own writings.

Rather more serious than this criticism, however, is the fact that Professor Gregory has neglected the more physical evidence in support of the atomic theory. The determinations of the Avogadro number are omitted and the results of the kinetic theory and of crystal structure are dismissed in a few paragraphs. These omissions assume even more startling proportions in the last chapter, which is composed for the most part of not too well selected excerpts from the recent popular books of Jeans and Eddington. Most surprising of all, the author barely mentions the corpuscular theories of light and confines the wave properties of matter to a single paragraph. Indeed, the problem of the dual aspects of both light and matter receives but casual mention. The discussion of recent work is confused and cannot but leave a blurred and uncertain picture in the mind of the reader.

Professor Gregory has written an excellent and scholarly account of the chemical aspects of nineteenth century atomism. The deficiencies of the remainder of the book lead one to suspect that the subject is now too extensive to allow comprehensive treatment by a single author. Perhaps it is too early to expect a balanced history of this field of thought, including the recent developments, but it is to be hoped that a complete account will be available in the near future.

HUGH M. SMALLWOOD

Inorganic Qualitative Chemical Analysis. By ALLAN R. DAY, Ph.D., Assistant Professor of Chemistry, University of Pennsylvania. The Chemical Publishing Company, Easton, Pennsylvania, 1930. ix + 197 pp. 15.5 X 23.5 cm.

This textbook can perhaps be best characterized as corresponding to an abbreviated compromise between the well-known textbooks of Stieglitz and of Treadwell Hall.

The reviewer fails to see that the author has achieved what he intended to do as expressed in the Preface, namely, "to realize a closer relationship between fact and theory." Though he treats, very briefly to be sure, oxidation–reduction from the ionic standpoint, the reactions in the laboratory section are written in the molecular form, just as they were written thirty years ago. This is not correlation of theory but, rather, neglect of it. This textbook also does not consider the modern aspects of the theory of electrolytic dissociation. Indeed, the author contends that "the student is unable to cope with the advancements which have been made in recent times in the theories of solutions." This has not been the reviewer's experience nor, judging from the numerous thoroughly modern texts that have appeared in the last few years, that of other teachers in Qualitative Analysis.

This book has no distinctive features to differentiate it from many similar manuals in existence. It will doubtless be useful in connection with a set of explanatory lectures and close laboratory supervision such as is evidently contemplated by the author, but can hardly be recommended to those who are looking for guidance in the newer paths.

The book is well printed and bound and free from typographical errors.

J. Enrique Zanetti

The Conductivity of Solutions and the Modern Dissociation Theory. By Cecil W. Davies, M.Sc. (Wales), A.I.C., Senior Lecturer in Physical Chemistry, Battersea Polytechnic. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1931. viii + 204 pp. 22 figs. 14.5 × 22.5 cm. Price, $4.00.

This is the first textbook on a branch of Electrochemistry in which the interpretation of the experimental facts is based mainly on the Debye–Hückel theory instead of on the older theory of Arrhenius, van't Hoff and Ostwald and should therefore be a distinct advance. The author apparently assumes that his readers are unacquainted with the calculus—at any rate no differential equations or integral signs appear in the entire book. To attempt an advance into the new realms of thought opened up by the Debye–Hückel theory with a mathematical equipment limited to algebra and analytical geometry can only result in a superficial and inadequate view. This method of treatment is defended by the author on the ground that "the chemist will judge the Debye–Hückel–Onsager equations not by the manner of their derivation, but by the degree of success with which they interpret and predict the results of experiment." Although, of course, the theory must meet this test if it is to survive, nevertheless the reviewer believes that the student should not be encouraged to ignore the derivations of the formulas merely because they are difficult, involve calculus and vector analysis and some principles of physics not familiar to most students of chemistry but should be aided in understanding the derivations.

The discussion of interionic attraction is by no means comprehensive. The Onsager modification of the conductance equation is discussed at considerable length; the variation of conductance at very high frequencies and the failure of Ohm's law at very high field strengths are also discussed. But very little is said about the application of the theory to solubility, or to the colligative properties of solutions, or to the viscosity of solutions. The early form of the equation for the activity coefficient of an ion which is applicable only to extremely dilute solutions is given but the modified form later derived by Hückel, which is apparently valid up to three normal solutions, is not mentioned.

The discussion of experimental methods is brief and lacks detail as to design of apparatus. The differences in technique required for direct current and alternating current bridges are treated in a most sketchy manner. The author apparently assumes that his readers are ignorant of alternating current theory and makes very little attempt to supply the deficiency. The figures given are purely diagrammatic. They show no arrangement for grounding the bridge, which is a matter of considerable importance for precise work. Nearly a page is devoted to a description of induction coils as a source of current while audion tube oscillators receive only a bare mention with a few references, although anyone who had ever used an audion tube oscillator would regard an induction coil as junk.

The discussion of polarization is especially weak. Kohlrausch developed a mathematical theory of polarization based on the idea that the electrode effects of alternating current electrolysis were electrically equivalent to a perfect condenser in series with the electrolytic resistance being measured. If this were the whole truth the effects of polarization could be compensated wholly by introducing a condenser into another arm of the bridge. Kohlrausch found experimentally that this device, although extremely helpful, is not a sufficient means of avoiding error due to polarization and suggested and used other experimental devices to minimize this error, but without revising his mathematical theory of polarization. Other investigators, some of them contemporaneous with Kohlrausch, including Wien, Warburg, Neumann, Reichinstein, Miller, and Haworth, have added much to our knowledge of the phenomena and have developed a theory which goes far beyond Kohlrausch. In this book the discussion of polarization is based on the ideas of Kohlrausch, although his mathematical theory is omitted, and contains no hint of the advances made by other authors.

In spite of its defects this book has points of merit. There is a good discussion of the correction for the conductance of the solvent, of the problem of the extrapolation of the conductance to infinite dilution, and of the application of conductance measurements to the solution of many chemical problems. The style is clear. It may be recommended to students ignorant of the calculus as interesting, instructive and easy reading.

GRINNELL JONES

Electrolytic Conduction. BY F. H. NEWMAN, D.Sc., A.R.C.S., F.Inst.P., Professor of Physics, University College of the South-West of England, Exeter. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1931. xii + 441 pp. 70 figs. 14.5 X 22.5 cm. Price, $6.50.

The title of this book is similar to Davies' "The Conductivity of Solutions" reviewed above, but the books are very different. Newman has chosen his title poorly because his work covers a far wider field than is indicated by the title. This book includes, in addition to subjects clearly covered by the title, a discussion of the first, second and third laws of thermodynamics, Clapeyron's equation, the phase rule, the colligative properties of solutions, the law of mass action, Gibbs' adsorption equation, the factors influencing the potential of voltaic cells, hydrogen electrodes, quinhydrone electrodes, the determination of the transference numbers by electromotive force measurements, oxidation–reduction potentials, dropping electrodes, electrocapillarity, overvoltage, passivity and some technical applications of electrolysis. Considered as a textbook on Electrochemistry the most serious omission is the absence of an explanation of the PH scale and a discussion of its significance in many diverse fields of science.

The book also differs radically from that of Davies in that the treatment is much more mathematical. Newman clearly prefers to state relationships and laws in mathematical form whenever feasible and the book gains in precision, clarity and brevity thereby. Of course he uses the calculus freely.

To write a textbook on Electrochemistry, which this book really is in spite of its title, or to teach the subject is especially difficult at the present time because the science is in a transition period. The older books and nearly all of the original literature are based on the classical theory. Now, thanks to the genius of Debye, we have a radically new point of view and method of attack which gives great promise of transforming the science. But the new theory is complicated and difficult mathematically—so much so that Debye and his school have been forced, or at least tempted, to introduce inexact mathematical procedures and approximate or incomplete premises for the frankly avowed purpose of simplifying the mathematics, with the result that the equations derived are in most cases only valid as limiting laws for extreme dilution or for "slightly polluted water." But the theory is yet in its infancy and it is to be hoped and expected that later developments will give equations which are valid in much more concentrated solutions and that the theory will be extended to problems, such as the electromotive force at liquid junctions, which have not yet been treated by the new method. In the meantime students must be taught the old theory in order that they may be able to understand the great bulk of the chemical literature and because of the considerable remnant of truth in the older although imperfect views. They must be taught the new point of view in order to move with the procession. This book by Newman gives a clearer and more nearly complete presentation of the newer theory than is available in any other book; nevertheless, large portions of the book are written from the old point of view, Thus, for example, there is a table occupying almost a full page comparing percentage ionization as computed from the freezing point and from the conductance for a large number of salts over a considerable range of concentration. This table is discussed at considerable length in a manner which might have been written twenty years ago. However this is not intended as a serious criticism because it is probably at least a decade too early to present the entire subject of electrochemistry in a logical and consistent manner in accordance with the theory of interionic attraction.

To an unusual degree this book by Newman gives the impression that it was written from the original literature rather than from older books. It has a wealth of tables of numerical data and of well-selected reading references. It may be recommended to students familiar with the calculus as interesting and instructive but not easy reading.

GRINNELL JONES

Theoretical Mechanics. The Theory of the Potential. By WILLIAM DUNCAN MACMILLAN, A.M., Ph.D., Sc.D., Professor of Astronomy, The University of Chicago. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1930. xiii + 469 pp. 112 figs. 15.5 × 23.5 cm. Price, $5.00.

This is an extensive and thorough treatment of one of the older and well-known branches of theoretical physics. The earlier chapters are elementary in their form of presentation and should provide a good introduction for the student, and the later chapters provide an enormous amount of useful material. The volume will be of use for chemists only in so far as they are working on the border line of physics. The book is well printed and arranged, and is provided with a bibliography and index.

RICHARD C. TOLMAN

An Outline of Wave Mechanics. By N. F. MOTT, Lecturer in Theoretical Physics, The University, Manchester. Cambridge, at the University Press; The Macmillan Company, 60 Fifth Ave., New York, 1930. 155 pp. 21 figs. 14 × 21.5 cm. Price, $2.80.

It has apparently been the author's aim in this outline to stress the physical aspects of the new quantum theory rather than the mathematical technique involved in its applications. Following a general discussion of waves and particles, the Schrodinger equation is introduced and used as a basis for a brief treatment of the scattering and reflection of electrons. Succeeding chapters deal with the uncertainty principle, radioactivity, absorption of radiation, the helium atom, the hydrogen molecule and a number of collision problems. The discussion of electron spin is postponed to the last chapter. No mention is made of topics chiefly of interest to the spectroscopist, that is, energy levels of atoms and molecules and intensities of spectral lines.

The developments of those subjects that are included are brief in the extreme, as may be judged from the size of the book. More disappointing, however, is the fact that the author has nowhere given a correlation between the theory and experiment. Some of the outstanding experimental work is mentioned but one is left with the feeling that the author has followed in the footsteps of the legendary mathematician who concluded a series of lectures with the remark: "And now gentlemen, since we see that the problem has a solution, we lose all further interest in it."

Dr. Mott has addressed his book primarily to physicists familiar with the older quantum theory and the classical theory of wave motion. To those who have this background, this outline will afford an excellent means of acquiring a general acquaintance with some of the methods and results of the new theory.

HUGH M. SMALLWOOD

Naphthenverbindungen, Terpene und **Campherarten inkl. Pinusharzsäuren** sowie **Körper** der Kautschukgruppe. (Naphthene Compounds, Terpenes and Camphors, Including the Rosin **Acids** and Substances in the Caoutchouc Group.) By OSSIAN ASCHAN. Walter de Gruyter und *Co.*, Genthinerstrasse **38,** Berlin W 10, Germany, 1929. xv + 378 **pp.** 17.5 × 25.5 cm. Price, unbound, RM. 30, bound, RM. **32.**

The contents of this book are adequately summarized in the sub-title which is "Original contributions to the chemistry of alicyclic compounds dealing in part with industrial applications and supplemented with suggestions concerning further research problems." The four main divisions of the work are: (1) alicyclic compounds with a simple carbon ring; (2) saturated bicyclic compounds; (3) alicyclic compounds with a tricyclic nucleus; (4) studies of caoutchouc and other condensation products of isoprene of high molecular weight (including a consideration of the possibility of large-scale manufacture). Among the many topics considered under these main divisions may be mentioned: naphthenic acids and their isolation from petroleum, naphthenes, camphoric acid and its relatives, dipentene, sylvestrene, camphor (including its synthetic production), the composition of crude wood spirits, the rosin acids, the artificial production of rubber. None of the topics mentioned are treated in a systematic or complete fashion and the volume will therefore be of little use to one who wishes to familiarize himself with any particular branch of alicyclic chemistry. It will be of interest, however, to investigators who themselves are working in any of the many fields of alicyclic chemistry which the author's manifold interest has embraced. The treatment consists of a discussion of each problem from the point of view of the author's own work, which in part has been published and which in part is given for the first time. The discussion is full and many of the suggestions concerning further work very interesting, but the lack of experimental detail would force many readers back to the author's original papers. This relatively small volume is not a collection of papers but rather a discussion of the results of the author's long years of research in alicyclic chemistry.

JAMES B. CONANT

BOOKS RECEIVED

May 20, 1931–June 15, 1931

HUGO BAUER. "Dehalogeniereu." Handbuch der biologischen Arbeitsmethoden, herausgegeben von Emil Abdcrhalden. Abt. I, Chemische Methoden, Teil 2, 2. Halfte, Heft 8. Urban and Schwarzenberg, Friedrichstrasse 105b, Berlin N 24, Germany. 108 pp. RM. 5.50.

ERNST BERL. "Liebig und die Bittersalz- und Salzsaurefabrik zu Salzhausen (1824–1831)." Nach neuen Funden herausgegeben von Prof. Dr. Ernst Berl im Auftrag der Vereinigung Liebighaus E. V., Darmstadt. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 65 pp. M. 3.50.

JACQUES CORBIÈRE. "Sur la Fixation des Matières Émulsionnées par les Fibres Textiles." Société Anonyme de l'Imprimerie A. Rey, 4 Rue Gentil, Lyon, France. 125 pp.

J. DAVIDSOHN. "Die Bleichung der Öle, Fette, Wachse und Seifen." Verlag von Gebrüder Borntraeger, W 35 Schöneberger Ufer 12a, Berlin, Germany. 269 pp. M. 18, unbound; M. 21, bound.

JOHN C. KRANTZ, Editor. "Fighting Disease with Drugs. The Story of Pharmacy." A Publication of the National Conference of Pharmaceutical Research. The Williams and Wilkins Company, Baltimore, Maryland. 230 pp. 12.00.

P. H. PRAUSNITZ AND J. REITSTÖTTER. "Elektrophorese, Elektroosmose, Elektrodialyse in Fliissigkeiten." Wissenschaftliche Forschungsberichte Naturwissenschaftliche Reihe, herausgegeben von Dr. Raphael Ed. Liesegang. Verlagsbuchhandlung Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 307 pp. RM. 18.50, unbound; RM. 20, bound.

LEOPOLD SCHMIDT. "Bernstein." Sonderausgabe aus Doelter-Leitmeier Handbuch Mineralchemie. Verlagsbuchhandlung Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 101 pp. RM. 7, unbound.

ROGER J. WILLIAMS. "An Introduction to Biochemistry." D. Van Nostrand Co., Inc., 250 Fourth Ave., New York. 501 pp. $4.00.

"Annual Reports on the Progress of Chemistry for 1930." Vol. XXVII. Issued by the Chemical Society, Burlington House, Piccadilly, London W I, England. 389 pp 10/6, net.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

HYSTERESIS IN THE WESTON STANDARD CELL[1]

BY WARREN C. VOSBURGH AND KELLY L. ELMORE

RECEIVED DECEMBER 6, 1930 PUBLISHED AUGUST 5, 1931

A theory of hysteresis in the Weston standard cell has been proposed by Niederhauser and Hulett[2] based on the formation of a supersaturated solution of mercurous sulfate at the cathode as a result of a decrease in temperature. This involves the assumption that the solubility of mercurous sulfate increases with temperature and that the rate of crystallization from a supersaturated solution is slow while the rate of dissolving in an unsaturated solution is rapid.[3]

Barre[4] found that the solubility of mercurous sulfate increases with the temperature, and it is probable that the solubility in a saturated cadmium sulfate solution would do the same. Calculation on the basis of the Nernst theory indicates that a concentration of mercurous ion 1% in excess of that of a saturated solution would account for an electromotive force about 1 mv. higher than the normal. The increase in solubility observed by Barre for a ten-degree increase in temperature was several times 1%, and so is sufficient to account for many, at least, of the hysteresis data.

Marc[5] showed that the velocities of crystallization of ammonium alum, potassium sulfate and potassium dichromate from their water solutions were slower than the velocities of dissolving under comparable conditions. Furthermore, Marc and Wenk[6] found that the presence of certain salts decreased the velocity of crystallization of potassium sulfate somewhat, and that certain dyes which were strongly adsorbed by the crystals of potassium sulfate greatly retarded the crystallization. In some cases no crystallization at all was observed during a period of six hours after seeding the super-

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[1] Thesis presented by Kelly L. Elmore in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

[2] Niederhauser and Hulett, THIS JOURNAL, 51, 2349 (1929).

[3] Hysteresis is observed with decreasing temperature, but usually not when the temperature increases.

[4] Barre, Ann. *chim. phys.*, [8] *24*, 202 (1911).

[5] Marc, Z. *physik. Chem.*, *67*, 493 (1909).

[6] Marc and Wenk, *ibid.*, 68, 104 (1910).

saturated solution. On the other hand, the dyes had little or no effect on the rate of dissolving of the crystals.

The results of Marc and Wenk support the supersaturation theory of hysteresis, which now seems preferable to that proposed by Vosburgh[7] based on a lag in the attainment of equilibrium between mercuric and mercurous ions and mercury.

A somewhat different mechanism than the one proposed by Niederhauser and Hulett is suggested by Marc's work. The rate of crystallization of the various salts from their supersaturated solutions as observed by Marc was rapid as compared with the change in electromotive force of many Weston cells after a decrease in temperature. However, in the light of the results of Marc and Wenk, adsorbed impurities on the surface of the mercurous sulfate might well account for the hysteresis phenomena, their effect being to retard crystallization.

The experiments described below were suggested by the theory of Niederhauser and Hulett and were undertaken with the object of obtaining more data on hysteresis.

Materials

Water.—For the preparation of other materials, water redistilled from alkaline permanganate was used. For the solutions used in the cells this water was again redistilled in a silica still,

Mercury.—Commercial redistilled mercury was passed several times through a column of mercurous nitrate solution and redistilled in a current of air.

Cadmium Amalgam.—By electrolysis with a cadmium sulfate electrolyte cadmium was transferred from c. p. sticks to mercury which had been washed with mercurous nitrate solution. It was again transferred to purified mercury by electrolysis, using the same electrolyte, forming a 12% amalgam to which was added enough mercury to give a 10% amalgam.

Cadmium. Sulfate.—Material of c. p. grade was dissolved and the solution treated with basic cadmium sulfate to precipitate impurities. The cadmium sulfate was then recrystallized twice by slow evaporation at room temperature,

Basic cadmium sulfate[8] was prepared from the normal salt by precipitation with ammonium hydroxide. It was washed free from ammonium salts by decantation, with the help of a small centrifuge.

Nitrogen and Oxygen.—Nitrogen from a tank of the compressed gas was passed through acidified potassium permanganate solution, alkaline pyrogallate solution. alkaline sodium thiosulfate solution, potassium hydroxide solution and then distilled water and a plug of cotton. Oxygen was passed through acidified potassium permanganate solution, potassium hydroxide solution, distilled water and a plug of cotton.

Mercurous Sulfate.—For the two similar preparations A and B, 400 g. of thrice recrystallized mercurous nitrate was dissolved in three liters of 0.1 M nitric acid solution, and this solution was added drop by drop to four liters of hot 2 M sulfuric acid solution. Preparation A was digested for twelve hours with the mother liquor on a hot-plate, and

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[7] Vosburgh, This Journal, **49**, 87 (1927).

[8] It is immaterial for present purposes whether this is a basic salt or a mixture of oxide and normal salt.

Preparation B was digested for one hour. Both were washed with 2 *M* sulfuric acid solution and Preparation *A* was not further treated. Preparation B was digested for another hour with *2* M sulfuric acid solution.

The crystals of Preparation A ranged in size from **30** to 2300μ, most of them being between **300** and 500μ. The crystals of Preparation B ranged from **15** to 1000μ, most of them being between 30 and 50μ.

Preparation C was made like Preparation B except that the mercurous nitrate solution was added rapidly to the sulfuric acid solution, and it was digested for a total of eight hours, three hours under the mother liquor and five hours under a fresh *2 M* sulfuric acid solution. The crystal size ranged from **15** to 40μ.

Preparation D was like Preparation C except that it was prepared from C. P. mercurous nitrate and ordinary distilled water.

Preparation E was made by the electrolytic method.[9] It was digested for three hours with *2* M sulfuric acid solution on a hot-plate. The crystals were about 9μ in length.

Preparation F was one made for an earlier investigation by reduction of mercuric sulfate by mercury. The crystals ranged from 20 to 40μ in length and the material contained much finely divided mercury.

Cell Vessels.—The vessels used were of soft glass with sealed-in platinum wires for connection to the electrodes. They were of the usual H form, the length of the vertical tubes being **11** cm. and that of the cross-arm **3.5** cm. Both had a diameter of **1.5** cm.. and the cross-arm was **3.5** cm. from the bottom.

Preparation of the Cells

The cells were prepared essentially as described previously.[10] For the protection from air the pipet described by Randall and Stone[11] was used.

When it was desired to prepare comparable groups of cells which differed more or less in materials or method of construction, care was taken to use as nearly the same procedure as possible. The method of washing the mercurous sulfate received special attention. In setting up a group of cells protected from air and a comparable group exposed to oxygen, all the cells were constructed from the same materials. Two portions of mercurous sulfate were filtered and washed in the same way, one in an atmosphere of oxygen with an electrolyte saturated with oxygen and the other in an atmosphere of nitrogen with an oxygen-free electrolyte.

In sealing the cells the tops of the tubes were flushed out with nitrogen (or in special cases oxygen) and the nitrogen was kept running into them as long as possible during the sealing process. It is not claimed that all oxygen was kept out by this process, but that its concentration was materially reduced.

In some of the earlier cells a little trouble was experienced with gas collecting above the amalgam. This trouble, at first thought to be caused by reaction of acid with the cadmium, was not confined to acid cells. It was probably caused by air trapped in and around the amalgam. Evacuation

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[9] Hulett, *Phys. Rev.*, **32**,262 (1911).

[10] Vosburgh, THIS JOURNAL, 47, **1257 (1925).**

[11] Randall and Stone, *ibid.*, **51,1753 (1929).**

of the vessel with the amalgam in place and a little electrolyte above it overcame the trouble.[12]

Electromotive Force Measurements

The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer, the measuring system being properly shielded. The standards were the previously described Cells 353–6 and 496[10,13] to which an electromotive force of 1.01805 v. was assigned. The five cells agreed within 0.01 mv. A cell of larger capacity than the standards was used as the working standard, and a value was assigned it that would lead to the assumed value for the standards when they were measured. The absolute values of the standards were checked by means of two portable cells certified by the Bureau of Standards. The value found for the portable cells on the basis of the assumed values for the standards agreed with the certified value within 0.01 to 0.02 mv. There was evidence of a slight change in the portable cells, perhaps as a result of shipment.

Since the unknown electromotive forces were measured in the same manner as the standards and since the electromotive forces differed little from those of the standards, the errors of measurement must have been less than 0.01 mv. in most cases. Although in many standard cell investigations the precision attained is better than 0.01 mv., this was considered sufficient because the objective was to investigate relatively large deviations from constancy rather than to establish conditions for the preparation of cells of the highest quality.

Experimental Results

The cells were kept in an oil thermostat at $25 \pm 0.02°$ (fluctuations of temperature were usually not more than $\pm 0.005°$) for some" time after their preparation. Subsequently they were kept at room temperature, but put into the thermostat for measurements. In such a case their constancy was tested by at least three measurements made a day or more apart before final results were recorded. Care was taken that a change from room temperature to the thermostat was an increase in temperature rather than a decrease.

The electromotive forces were measured at intervals and the change of electromotive force with time is shown in the tables below. An hysteresis test was made from one to three and a half months after the cells were set up. A second hysteresis test was made later, all the cells being tested at one time. The ages of the cells at the time of the second test varied from three to eight months and are given in the tables. A third test was made four months after the second and a fourth three months after the third.

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[12] It was learned later that Dr. Marion Eppley (private communication) had previously discovered the same remedy.

[13] Vosburgh, THIS JOURNAL, 49, **85 (1927).**

Hysteresis tests were made by transferring the cells to a thermostat at 35°, leaving them there for at least three days, then transferring back to the thermostat at 25° and measuring after one hour and six hours. The hysteresis was measured by the difference between the electromotive force at the time in question and that at 25° previous to the test.

Acid **Cells.—A** number of cells with slightly acid electrolytes were prepared to test the materials and technique and to act as controls for the other cells. The concentration of acid was 0.01 mole per liter. The electromotive forces of these cells over a period of twelve to sixteen months are shown in Table I and the results of four hysteresis tests carried out at different times are given in Table II.

TABLE I

CELLS WITH ACID ELECTROLYTES

Cells	Hg_2SO_4	E − 1018.00 mv., 25°						
		1 mo.	3	5	7	8–9	11–13	16
531–5[a]	A	0.05	0.05	0.05	0.05	0.05	0.04	0.04
626–8	B	..	.06	..	.06	..	.08[b]	
615–7	C	.07	.07	..	..	.06	.08	
605–6	D	.07	.07	.04	..	.06	.06	
607–8	D	.01	.05	.07	..	.05	.05	
632, 634	E	.11	..	.10	..	..	..	

[a] Cell 533 cracked and oil from the thermostat entered. After eight months the electromotive force became variable, and the results are omitted from the average. [b] Hysteresis caused too high a value for cell 626.

TABLE II

HYSTERESIS OF ACID CELLS

Cells	Hysteresis I		Hysteresis II			Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.	Age, mo.	1 mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
531–4[a]	−0.06	−0.06	8	−0.05	−0.06	−0.03	−0.05	−0.02	−0.05
535	....	....	8	+ .04	+ .04	+ .11	+ .06	+ .13	+ .08
626–8[b]	+ .14	+ .04	3	.20	.08	.39	.20	.52	.30
615–7	.11	.06	4	.15	.07	.19	.10	.23	.12
605–6	.14	.06	5	.15	.06	.17	.07	.17	.08
607–8	.03	.02	5	.04	.02	.05	.03	.05	.02
632, 534	.06	.03	5	.04	.02	....			

[a] The hysteresis of Cell 533 (see note *a*, Table I) was omitted from the average. It was much larger than that of the others. [b] Cell 626 showed larger hysteresis and a more rapid increase than the other two.

The effect of impurities on the hysteresis of acid cells was investigated by making cells comparable with certain of those described above except that impurities were introduced. The impurities tried were formaldehyde, urea, material extracted from cork and gelatin. The formaldehyde was suggested by the fact that the coarse mercurous sulfate preparation found by Vosburgh and Eppley[14] to lead to more hysteresis than various finer

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[14] Vosburgh and Eppley, THIS JOURNAL, 46, 109 (1924).

preparations was made by reduction of mercuric sulfate by formaldehyde.[15] Urea was tried because it affects the growth of sodium chloride crystals.[16] That material extracted from cork had the effect of increasing hysteresis was shown by Vosburgh and Eppley.[17] The present experiment was a repetition of theirs, except that the cork material was introduced in a different manner.

The methods of introducing the impurities were the following. For Cells 620 and 622 mercurous sulfate was allowed to stand overnight under an acid solution containing 2 g. of formaldehyde per liter. For Cells 636–638 the mercurous sulfate was untreated, but 0.04 g. of formaldehyde was added to 100 *g.* of the electrolyte. For Cells 623–625 and 644–646 the electrolyte was shaken with finely divided cork which had been digested previously with two portions of boiling water. In the former group some of the cork was included in the cells also. Cells 639–641 contained 0.1 g. of urea per 100 g. of electrolyte. For Cells 642–643 the electrolyte was heated with gelatin, 0.05 g. of the latter to 100 g. of electrolyte, and approximately half dissolved. The results are shown in Tables III and IV.

TABLE III

EFFECT OF IMPURITIES ON THE ELECTROMOTIVE FORCE OF ACID CELLS

Cells	Hg_2SO_4	Impurity	E − 1018.00 mv., 25°				
			1 mo.	3	5	8-9	12
620,622	B	HCHO	0.05	0.06	..	0.05	0.06
636–8	E	HCHO	.01	..	0.01	.01	..
623–5	B	Cork	..	.11	..	.14	.27
644–6	E	Cork	.08	..	.09	.08	..
639–41	E	Urea	.05	..	.07	.07	..
642–3	E	Gelatin	.19	..	.03	.07	..

TABLE IV

HYSTERESIS IN CELLS CONTAINING IMPURITIES

Cells[a]	Hysteresis I		Hysteresis II		Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
620,622	0.15	0.07	0.24	0.11	0.33	0.17	0.38	0.20
636–8	.01	.01	.01	.00	.03	.01	..	..
623–5	.38	.19	.62	.35	.75	.45	.76	.44
644–6	.08	.04	.13	.06	.16	.08	..	..
639–41	.03	.02	.05	.03	.09	.03	..	..
642–3	1.09	.82	1.53	1.22	1.91	1.64	..	..

[a] The age at the time of the first hysteresis test was one or two months and at the time of the second test was four or five months.

As far as hysteresis is concerned, formaldehyde seems to have a favorable effect, if any. Cells 620 and 622 differed little from Cells 626–628 (Table II)

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[15] Since formaldehyde did not increase hysteresis, the conclusions of Vosburgh and Eppley are not affected by the present work.

[16] Neuhaus, *Z. Krist.*, 68, 15 (1928), cited in *Chemical Abstracts*, 24, *9* (1930).

[17] Vosburgh and Eppley, *J.* Optical *Soc. Am.*, *9*, 70 (1924).

in this respect, while 636–638 showed less hysteresis than Cells 632 and 634 (Table II). With respect to electromotive force, Cells 636–638 were abnormal, though constant, as far as observed.

The material extracted from cork by the solution undoubtedly caused some hysteresis. This is unmistakable in the case of Cells 623–625. The hysteresis of Cells 644–646, however, is not large as compared with many of the other groups, but it is the largest of any of the cells made with Mercurous Sulfate E.

Urea had little or no effect, but there can be no doubt that gelatin had a very pronounced effect.

The behavior of gelatin toward mercurous sulfate was tested qualitatively in another way. If gelatin prevents crystallization from a supersaturated solution, it should interfere with the growth of crystals in the precipitation of mercurous sulfate. Accordingly, mercurous sulfate was precipitated by the addition of mercurous nitrate solution drop by drop to a portion of dilute cadmium sulfate solution containing 0.01 mole of sulfuric acid per liter. Gelatin was dissolved in a second portion of the cadmium sulfate solution (0.025 g. per 100 cc.) and the mercurous nitrate solution added as before. Much more of the mercurous nitrate solution was added before precipitation started in the second case than in the first. Examination of the first mercurous sulfate under the microscope showed that it consisted of clusters of thick needle-like transparent crystals, while the second consisted of much smaller particles of roughly circular cross section.

Neutral **and Basic** Cells.—Hysteresis in acid cells has been found to increase with decreasing acid concentration.[17,18] If the supersaturation theory of hysteresis is to be applied to this case, a mechanism must be assumed to account for the effect of decreasing acidity on the velocity of crystallization. Such a mechanism might be based on the observation of Gardiner and Hulett[19] that mercurous sulfate becomes covered with a surface layer of basic mercurous sulfate when in contact with a cadmium sulfate solution. How large a concentration of sulfuric acid must be present to prevent such an action is uncertain.

It was thought that some data on the effect of a surface layer of basic mercurous sulfate might be obtained by comparing the hysteresis of groups of cells made with different opportunities for hydrolysis. **A** number of cells without added acid were made, and some others were made at the same time and of the same materials, but with the inclusion of some basic cadmium sulfate.8 The basic cadmium sulfate was placed either above the mercurous sulfate, separated from it by a layer of fine crystals of the normal sulfate, or in a similar position on the amalgam side of the cell.

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[18] Ref. 10, p. 1265.

[19] Gardiner and Hulett, *Trans. Am Electrochem. Soc.*, 56, 121 (1929).

The results are given in Tables V and VI. For convenience, the cells containing no added acid are called neutral cells and those containing basic cadmium sulfate are called basic cells.

TABLE V

VARIATION OF ELECTROMOTIVE FORCE OF NEUTRAL AND BASIC CELLS

Cells	Hg_2SO_4	Basic salt	E − 1018.00 mv., 25° 1 mo.	3	5	8–10	12	16
546–50	A	None	0.06	0.04	0.03	−0.01	−0.03	−0.07
556–60	A	Hg leg	.03	−.01	.00	+.01	.00	.00
561–4	A	Cd leg	.03	.00	.00	.00	−.01	−.01
584–6	B	None	.06	+.05	−.31	−.57	−.81	....
590–4	B	Cd leg	.02	.04	+.03	+.03	+.04	....

The cells containing basic cadmium sulfate were less variable in electromotive force than the neutral cells, and the various groups agreed fairly well with each other. The average variation from the group mean of the individual cells within the groups was about ±0.01 mv. It is quite evident that the inclusion of basic cadmium sulfate has in these cases led to better cells than its omission. This recalls the precaution taken by Shaw and Reilley[20] to make the electrolyte in standard cells slightly basic.

It was observed at the end of the twelfth month (the eighth month for Cells 590–4) that the cells containing the basic salt all had a thin layer of gray material above the layer of fine cadmium sulfate crystals which covered the mercurous sulfate. A few contained spots of yellow basic mercurous sulfate in the paste, but no other changes were noticed. In order to learn to what extent basic cadmium sulfate can hydrolyze mercurous sulfate, a nearly saturated cadmium sulfate solution was shaken with a mixture of mercurous sulfate and basic cadmium sulfate. The first result was hydrolysis of the mercurous sulfate to yellow basic mercurous sulfate. On standing in the dark, the mixture turned gray in color, indicating further hydrolysis to oxide. If basic cadmium sulfate can hydrolyze mer-

TABLE VI

HYSTERESIS OF NEUTRAL AND BASIC CELLS

	Hysteresis I[b]		Hysteresis II[b]		Hysteresis III		Hysteresis IV	
Cells	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
546–9"	0.34	0.23	0.52	0.36	0.70	0.39	0.64	0.38
557–9"	.25	.15	.11	.08	.06	.05	.03	.03
561–4[a]	.12	.07	.04	.01	.03	.01	.03	.00
584–6	1.43	.86	3.48	2.99	2.70	2.17	3.07	2.57
590–4	0.62	.37	0.23	0.12	0.14	0.08	0.11	0.05

[a] In the first two hysteresis tests Cells 547 and 563 and the others indicated were omitted. At the time of the third test these cells agreed with the others as well as could be expected. [b] The age at the time of the first hysteresis test was one and a half to three months, and at the time of the second test five and a half to eight months.

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[20] Shaw and Reilley, *Trans.* Roy. *Soc. Canada* [III], 13, 174 (1919).

curous sulfate to this extent, equilibrium was not attained in the basic cells. The constancy of electromotive force must have been the result of a local equilibrium or a steady state of change.

Cells made with Mercurous Sulfate B had more hysteresis than similar cells made with Mercurous Sulfate A, regardless of whether the electrolyte was acid, neutral or basic. It is uncertain what the difference between these two preparations was.[21] It is believed that in the preparation of the neutral and basic cells made with Mercurous Sulfate B, the mercurous sulfate was washed more thoroughly with the neutral electrolyte than in the case of Mercurous Sulfate A. This would lead to a thicker layer of basic salt on the surface.

The basic cells showed less hysteresis than the cells containing no added acid or base. In the basic cells the hysteresis decreased with the age of the cells. Hysteresis in the first group of neutral cells increased with age at first but after a year it was practically constant. In the second group a maximum seems to have been attained, after which there was a decrease to a more or less variable value.

Basic cadmium sulfate was also added to some cells made with an electrolyte containing 0.004 mole of acid per liter. Their behavior and that of some control cells made at the same time are shown in Tables VII and VIII.

TABLE VII

ELECTROMOTIVE FORCES OR SLIGHTLY ACID AND BASIC CELLS

Cells	Hg_2SO_4	Basic salt	E − 1018.00 mv., 25°					
			1 mo.	3	5	7	12	16
543–5	A	None	0.08	0.07	0.07	0.07	0.07[a]	[b]
537–9	A	Hg leg	.05	.00	.00	.02	.01	0.00
540–2	A	Cd leg	.03	.03	.03	.02	.00	.00

[a] The agreement of the three cells was not good at this time. [b] Hysteresis interfered with the measurement.

In this case slightly acid cells are compared with basic cells. In electromotive force the basic cells agreed better with the other basic cells shown in Table V than with the acid cells. Any important differences between the acid and basic cells must have been caused by changes which took place after the cells were set up, because acid cells are easy to reproduce. Such changes were doubtless accompanied by a decrease in the acid concentration in the vicinity of the mercurous sulfate—or were the result of it. The hysteresis results for these cells are given in Table VIII. The results for the separate cells are given rather than the average for the groups because of the lack of agreement.

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[21] All the digestion of Mercurous Sulfate A was carried out in a solution containing nitric acid, while the last part of the digestion of Mercurous Sulfate B was carried out in sulfuric acid solution. A portion of the latter preparation was given an additional digestion in a sulfuric acid solution containing nitric acid, and two acid cells were made. The hysteresis was very small. Whether or not this was fortuitous was not determined.

TABLE VIII

HYSTERESIS OF SLIGHTLY ACID AND BASIC CELLS

Cells[a]	Hysteresis I 1 hr., mv.	Hysteresis I 6 hr., mv.	Hysteresis II 1 hr., mv.	Hysteresis II 6 hr., mv.	Hysteresis III 1 hr., mv.	Hysteresis III 6 hr., mv.	Hysteresis IV 1 hr., mv.	Hysteresis IV 6 hr., mv.
543	..	..	..	..	0.45	0.27	0.70	0.46
544	0.13	0.06	0.26	0.13	.50	.39	.46	.27
545	.10	.06	.18	.10	.31	.16	.31	.15
537	..	..	..	..	− .01	+ .01	− .02	.00
538	.12	.08	.00	.01	.00	.00	− .01	.00
539	.19	.12	.14	.10	+ .07	.06	.04	.04
540	.15	.12	.06	.06	.03	.03	.00	.01
541	.32	.23	.27	.19	.16	.11	.10	.08
542	..	..	..	..	.03	.01	.02	.00

[a] The age of the cells at the time of the first hysteresis test was one and a half months and at the time of the second test eight months.

At the beginning, the acid cells were definitely superior with respect to hysteresis. Their hysteresis increased with age, and by the time of the third hysteresis test, ten months after the first, the basic cells were definitely superior. During the early life, the acid cells agreed among themselves in electromotive force better than the basic cells. At the end of a year, however, the basic cells were superior in this respect. After a year, some of the basic cadmium sulfate was still present, though less than in the basic cells made with a neutral electrolyte.

It is of interest to consider the behavior of some neutral cells made with mercurous sulfate that had been washed with water (Cells **598–600)** or a very dilute sodium carbonate solution (Cells 572–4) before the cells were set up, and so presumably hydrolyzed on the surface. In the latter case there was a slight change of color.

TABLE IX

ELECTROMOTIVE FORCE OF CELLS MADE WITH HYDROLYZED MERCUROUS SULFATE

Cells	Hg_2SO_4	$E - 1018.00$ mv., 25° 1 mo.	3	5	7	9–11	15
572–4	A	−0.01	−0.05	−0.11	−0.14	−0.27	−0.39
598–600	C	+1.20	+ .97	+ .88	....	+ .80	....

TABLE X

HYSTERESIS OF CELLS MADE WITH HYDROLYZED MERCUROUS SULFATE

Cells	Hysteresis I[a] 1 hr., mv.	Hysteresis I[a] 6 hr., mv.	Hysteresis II[b] 1 hr., mv.	Hysteresis II[b] 6 hr., mv.	Hysteresis III 1 hr., mv.	Hysteresis III 6 hr., mv.	Hysteresis IV 1 hr., mv.	Hysteresis IV 6 hr., mv.
572–4	0.50	0.40	1.01	0.78	1.89	1.41	2.18	1.65
598–600	.52	.32	0.74	0.55	0.86	0.65	0.89	0.67

[a] The cells were one month old. [b] The cells were seven months old.

Cells **572–4** made with hydrolyzed mercurous sulfate A showed considerably more hysteresis than Cells **546–50** (Table V) made in the usual way. The hysteresis increased with age in both groups made with the hydrolyzed mercurous sulfate.

It seems to be pretty well established[18] that in slightly acid cells the hysteresis increases with decreasing acid concentration. The increase of hysteresis as the quantity of added acid approaches zero must either parallel or be caused by hydrolysis of the mercurous sulfate. The same might be said of the decrease of electromotive force with time. Tables IX and X show that hydrolysis of the mercurous sulfate previous to setting up the cells leads to a still more rapid decrease in electromotive force, or to an initially high and decreasing electromotive force, and to increased hysteresis. However, as shown above, the introduction of basic cadmium sulfate leads to smaller hysteresis than in neutral cells, and the hysteresis in this case decreases with the age of the cells. The difference must have been in the extent of the hydrolysis. As shown above equilibrium could not have been attained in the basic cells and hydrolysis of the mercurous sulfate must have gone on continuously from the time the cells were set up. It is hoped that research now in progress will throw light on why basic cells have so little hysteresis.

The Effect of Oxygen.—Conflicting opinions have been expressed as to the effect of the exclusion of oxygen in the preparation of cells. Vosburgh[22] and Eppley[23] considered this precaution necessary, while Gardiner and Hulett[24] considered that it did not help any. Hydrolysis of the mercurous sulfate by washing seems to have been a very important factor in the results of the latter investigators, and its effect may have masked a smaller effect of the oxygen.

If oxygen has any chemical effect, the ultimate result must be to make the cell contents more basic. This could result either from direct union with cadmium or mercury, or the oxidation of mercurous ion to mercuric ion with subsequent reduction by mercury. If this is true, the reported good effect of exclusion of oxygen may have resulted from preventing the neutralization of a small quantity of acid present in the cell. It might be predicted, however, on the basis of the above results and discussion, that in a cell with an electrolyte containing very little free acid, oxygen might have a beneficial effect, making the electrolyte more basic.

Two groups of cells were made with Mercurous Sulfate A, two with Mercurous Sulfate B and two with Mercurous Sulfate F. In each case the two groups were made by as nearly the same procedure as possible except that air was excluded by means of nitrogen in one group and oxygen was used in place of nitrogen in the other. The results are shown in Tables XI and XII.

In the first two groups little effect of oxygen on the constancy is apparent. The oxygen-containing cells were more nearly constant over a period of

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[22] Ref. 10, p. 1259.

[23] Eppley, *Trans. Am. Electrochem. Soc.*, 53, 149 (1928).

[24] Gardiner and Hulett, *ibid.*, 56, 138 (1929).

TABLE XI

EFFECT OF OXYGEN ON CONSTANCY

Cells	Hg_2SO_4	Gas	$E - 1018.00$ mv., 25° 1 mo.	3	5	6-8	9	12	16
546–50	A	N_2	0.06	....	0.04	−0.01	....	−0.03	−0.07
551–5	A	O_2	.05	0.01	.00	.00	....	− .05	− .08
584–6	B	N_2	.06	.05	− .31	....	−0.57	− .81	....
587–9	B	O_2	.03	− .02	....	− .09	− .22	− .31	....
579–80	F	N_2	− .04	....	− .56	− .65	− .72	− .73	....
5813	F	O_2	+ .03	.00	....	− .27	− .22	− .32	....

three or four months, but later decreased to a slightly lower value. On the other hand, the decrease in electromotive force of the nitrogen-containing cells was slower during the first three or four months, and the electromotive force was nearer the normal. In the other four groups there is no question as to the oxygen-containing cells being less variable in the long run, though none of the cells can be called good. Cells 584–6 had an electromotive force nearer the normal for the first three months than the comparable oxygen-containing cells.

TABLE XII

HYSTERESIS OF CELLS CONTAINING OXYGEN

Cells	Hysteresis I[c] 1 hr., mv.	6 hr., mv.	Hysteresis II[d] 1 hr., mv.	6 hr., mv.	Hysteresis III 1 hr., mv.	6 hr., mv.	Hysteresis IV 1 hr. mv.	6 hr.. mv.
546–9[a]	0.34	0.23	0.52	0.36	0.69	0.39	..	..
551–4[b]	.43	.31	.89	.69	.31	.17	0.33	0.18
584–6	1.43	.83	3.48	2.32	2.70	2.17	..	..
587–9	1.38	.76	1.56	0.87	1.86	1.10	2.14	1.31
579–80	3.26	2 66	3.47	2.93	3.03	2.33	3.10	2.40
581–3	3.23	2 86	2.31	1.91	1.72	1.24	1.84	1.26

[a] See note *a*, Table VI. [b] Cell 553 was omitted; it agreed with the others in the third and fourth hysteresis tests, as did Cell 555 also. [c] The age of the cells was one to three and a half months. [d] The age of the first two groups was eight months and that of the last four groups was six months.

In the first hysteresis test the presence or absence of oxygen seemed to make no appreciable difference; the groups that were comparable agreed as well as could be expected. In the other hysteresis tests the oxygen-containing cells showed less hysteresis than the others, except in the cells made with Mercurous Sulfate A in the second test. The presence of oxygen, if enough time is allowed, seems to bring about a reduction of hysteresis. The effect of oxygen is in the same direction as the effect of the addition of basic cadmium sulfate, though not as pronounced.

Discussion

Hysteresis does not in all cases increase with the age of a cell, In some of the acid cells the increase was small, while in some of the basic cells the hysteresis decreased rather than increased. The mechanism of the change is probably more complicated than that proposed by Niederhauser and Hulett. Instead of an approach toward perfection of the crystal surfaces it seems that adsorption of impurities, or of basic mercurous sulfate, on the surface may be at least a partial explanation.

If the surface is covered with basic mercurous sulfate as a result of hydrolysis, the case is more complicated than when gelatin or a similar material is adsorbed. A layer of basic mercurous sulfate would not necessarily prevent the deposition of mercurous ions from a supersaturated solution, but might make it necessary for these to be deposited as the basic salt rather than the normal salt.

Whether or not protection from oxygen can be considered beneficial depends on the point of view. Slightly acid or neutral cells made with care to avoid appreciable hydrolysis are more likely to give an electromotive force near the normal at the beginning if oxygen is absent. Oxygen in neutral cells seems to cause a more rapid decrease at first, but less variation later. However, the addition of basic cadmium sulfate (or cadmium hydroxide) to the electrolyte helps more in this respect than the addition of oxygen. In a basic cell oxygen should do no harm.

If the action of oxygen in a cell results in the addition of basic material, it follows that its presence in a slightly acid cell is undesirable. Hysteresis increases with a decrease of acidity, and if the added acid should be used up, the electromotive force would be likely to vary. If acid cells are made without protection from the air, enough acid should be added so that after the clean-up of the oxygen present a sufficient excess of acid will still remain. Other sources of basic material, such as cadmium oxide introduced with the amalgam, should be eliminated or taken into account.

Summary

Gelatin and material extracted from cork increased the hysteresis in acid Weston cells considerably. An explanation based on adsorption is suggested.

Cells with no added acid or basic material (neutral cells) had more hysteresis than cells containing basic cadmium sulfate.

The electromotive forces of cells to which basic cadmium sulfate was added were less variable over a period of several months and more reproducible than those of similar cells with no added basic material (or acid). The electromotive forces of the basic cells were lower than what is considered normal, however, after the first month.

The presence of oxygen caused a decrease of hysteresis in two groups of neutral cells and an increase at first in a third group, with a subsequent decrease. The electromotive forces of most of the cells containing oxygen decreased less than corresponding nitrogen-containing cells.

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[CONTRIBUTION NO. 664 OF THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

CHEMICAL KINETICS. II. THE INFLUENCE OF RELATIVE POSITION OF ELECTRIC CHARGE AND REACTING GROUP ON THE VELOCITY OF THE BROMOPROPIONATE-THIOSULFATE REACTION

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I. Introduction

It is well known that the velocities of bimolecular ionic reactions are markedly influenced by the number of ions present as well as by the sign and magnitude of the excess charge upon them. These kinetic effects designated by Bronsted as primary salt effects are the result of the relatively greater opportunity for collision between ions of opposite sign than between ions of the same sign. They have been accounted for successfully in dilute solutions by the theory of inter-ionic attraction.

Except for two papers[1] (which will be considered later), giving relevant but not complete data, no measurements exist for a consideration of the more detailed problem of the possible kinetic effect arising from the structural position of the charge of the ion in relation to the structural position, within the ion, of the specific group which reacts chemically with the second ion. Except for a remark by Bjerrum[2] that the problem is not without interest and a brief discussion by Christiansen, no one appears to have even considered this possibility. The reactions between thiosulfate ion and the various brominated fatty acids furnish a type of reactions capable of answering this question. Thus, if we consider the reaction

$$CH_2BrCOO^- + S_2O_3^{--} \longrightarrow CH_2(S_2O_3)COO^{--} + Br^- \qquad (1)$$

which has been studied, previously, in this Laboratory,[3] and elsewhere,[4] and the analogous reactions

$$CH_3CHBrCOO^- + S_2O_3^{--} \longrightarrow CH_3CH(S_2O_3)COO^{--} + Br^- \qquad (2)$$

$$CH_2BrCH_2COO^- + S_2O_3^{--} \longrightarrow CH_2(S_2O_3)CH_2COO^{--} + Br^- \qquad (3)$$

it is evident that the chemical reaction involves the exchange of bromine for thiosulfate in each case. From electrostatic considerations, (3) should be more rapid than (2) because the electrical field of force repelling the entering negative thiosulfate ion is less intense in the beta position than in the alpha position. Chemical theory, alone, without electrostatic considerations would predict the opposite effect.

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[1] (a) H. Euler, *Ber.*, 39, 2726 (1906); (b) H. J. Backer and W. H. Van Mels, *Rec. trav. chim.*, 49, 177 (1930).

[2] N. Bjerrum, *Z. physik. Chem.*, 113, 82 (1924); J. A. Christiansen, *ibid.*, 113, 35 (1924).

[3] Victor K. La Mer, THIS JOURNAL, 51, 3341 (1929); Paper No. 1 of this series.

[4] (a) A. Slator, *J. Chem. Soc.*, 87, 481 (1905); (b) S. Krapiwin, *Z. physik. Chem.*, 82, 439 (1913); (c) A. N. Kappana, *J. Indian Chem. Soc.*, 6, 45 (1929); 6, 419 (1929).

In order to determine quantitatively the role which relative position of charge and reacting group plays, it is necessary to eliminate the various influences upon the reactivity of the bromine atom which are dependent upon its structural position but independent of the presence of a neighboring charge. This can be accomplished by determining the rates of reaction of thiosulfate with the corresponding esters of the brominated fatty acids.

$$CH_2BrCOOCH_3^\circ + S_2O_3^{--} \longrightarrow CH_2(S_2O_3)COOCH_3^- + Br^- \qquad (4)$$
$$CH_3CHBrCOOCH_3^\circ + S_2O_3^{--} \longrightarrow CH_3CH(S_2O_3)COOCH_3^- + Br^- \qquad (5)$$
$$CH_2BrCH_2COOCH_3^\circ + S_2O_3^{--} \longrightarrow CH_2(S_2O_3)CH_2COOCH_3^- + Br^- \qquad (6)$$

Then, by comparing the ratios of ion rate/ester rate in each case, we measure the influence which the electric charge exercises in determining the rate of reaction.[5]

As the investigation proceeded, it became apparent that reactions (2) and (3) are not as simple as represented. Although the rate of the simultaneous water reaction

$$CH_2BrCOO^- + HOH \longrightarrow CH_2OHCOO^- + Br^- + H^+ \qquad (7)$$

is quite negligible as compared with the thiosulfate reaction (1), when bromoacetate ion is employed, this simplicity does not obtain in the spontaneous water reactions of the homologous acids—the water reactions being sufficiently rapid, in the case of the propionates, to be appreciable. These two reactions to be discussed later are[6]

$$CH_3CHBrCOO^- + HOH \longrightarrow CH_3CH(OH)COO^- + Br^- + H^+ \qquad (8)$$
$$CH_3BrCH_2COO^- + HOH \longrightarrow CH_2(OH)CH_2COO^- + Br^- + H^+ \qquad (9)$$

II. Preparation and Purification of Reagents

For an investigation of this kind purity of reagents is important. A redistilled sample of Kahlbaum's bromoacetic acid, m. p. 50.6–50.9° (Beilstein 50–51°), yielded kinetic results almost identical with those obtained with the bromoacetic acid used in the previous investigation. The propionic acids were Eastman's products and were redistilled at 10 mm. pressure before use. The esters were prepared according to the directions of Lepercq,[7] Lederer,[8] and Drushel and Hill,[9] by heating on a sandbath a mixture of the brominated acid with an excess of methyl alcohol and refluxing for two hours. The product was neutralized with sodium carbonate, poured into a large volume of water and after washing was

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[5] Except for one value of Slator's, *J. Chem. Soc.*, 87, 481 (1905), for the rate of reaction between methyl bromoacetate and thiosulfate, there are no data in the literature for these last three reactions.

[6] Reactions (8) and (9) have been studied by Senter [*ibid.*, 91, 460 (1907)], but only at 52.4 and 79°, and the results of Simpson [THIS JOURNAL, 40, 674 (1918)] were obtained at 70°.

[7] M. G. Lepercq, Bull. *soc. chim.*, [3] *11*, 297 (1894).

[8] L. Lederer, *J. prakt. Chem.*, *42*, 384 (1890).

[9] W. A. Drushel and J. W. Hill, *Am. J. Sci.*, **180**, 72 (1910).

dried over calcium chloride and fractionated. The esters of bromoacetic and bromopropionic acids were distilled at reduced pressure to prevent decomposition. Table I gives a summary of the properties indicating the purity of the compounds used. The figures for bromine content were determined by the micro Carius method.[10]

TABLE I

PURITY OF COMPOUNDS

Compound	Final purification	Bromine content, % Calcd.	Bromine content, % Found
Bromoacetic acid	Distn., 79° 10 mm.	57.52	56.58 ± 0.02
α-Bromopropionic acid	Distn., 73–75" 10 mm.	52.24	53.12 ± 0.03
β-Bromopropionic acid	Distn., 94–95° 10 mm.	52.24	52.26 ± 0.01
Me ester bromoacetic acid	Distn., reduced pressure	52.24	53.09 ± 0.08
Me ester α-bromopropionic acid	Distn., 147–150°	47.86	48.94 ± 0.06
Me ester β-bromopropionic acid	Distn., reduced pressure	47.86	48.10 ± 0.10
Sodium hydroxide	Concentrated solution of Kahlbaum product was filtered according to directions of Clark[11]		
Sodium thiosulfate	C. P. salt was recrystallized and air dried		

It has been found by Slator and Twiss[12] and by La Mer[13] that one equivalent of sodium bromoacetate reacts with one equivalent of sodium thiosulfate, and in the present investigation that one equivalent of sodium β-bromopropionate reacts with 0.98 equivalent of sodium thiosulfate when the latter is in excess. Under the same conditions one equivalent of sodium α-bromopropionate was found to react with not more than 0.935 equivalent of sodium thiosulfate before the solution showed signs of decomposition, due to the exceedingly long time (more than thirty days) required for the completion of the reaction. There is no valid reason to doubt that the results would have been similar to those for the salt of the @-acid had it not been for this interference.

In the case of the esters it was observed by Slator that one equivalent of methyl bromoacetate reacts with one equivalent of sodium thiosulfate[4]" and that the ethyl ester of α bromopropionate reacts with only 0.93 equivalent of sodium thiosulfate.[12]

III. Experimental

All experiments were made at 25 ± 0.01". Volumetric apparatus was calibrated. Distilled water, freed from carbon dioxide by boiling, was used in the reaction mixtures.

For thiosulfate reactions (1), (2) and (3) the required amount of bromi-

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[10] These bromine determinations were made in duplicate by the Research Service Laboratories. 37 East 28th Street, New York City.

[11] W. M. Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, p. 195.

[12] A. Slator and D. F. Twiss, J. *Chem. Soc.*, **95,** 93 (1909).

[13] Victor K. La Mer, THIS JOURNAL. 51,3341 (1929).

nated acid was weighed out, neutralized with sodium hydroxide solution, using phenolphthalein, and, in some cases, brom thymol blue as an indicator, and made up to volume. The desired amount of sodium thiosulfate solution was pipetted into each reaction flask (200-cc. capacity, fitted with ground-glass stopper and trough for potassium iodide solution when needed to prevent loss of vapor if the flask contained iodine solution). With both salt and thiosulfate solutions at 25° the former was added to the latter in the reaction flask, taking into account the time of delivery of the pipets. The stopwatch was frequently checked against Naval Observatory Time. The reaction was stopped by adding an excess of iodine solution. The excess (approximately 0.01 N) was back titrated at once with dilute sodium thiosulfate solution.

For reactions (4), (5) and *(6)* the procedure was the same, the ester solution replacing the salt solution.

To study reactions (7), (8) and (9) solutions of the sodium salts of the brominated acids were kept in the thermostat and portions removed for titration with standard sodium hydroxide solution.

In a second series of experiments, to avoid the catalytic effect of the hydrogen ion liberated, the standard base was added at frequent intervals to a large volume of the solution to keep the solution neutral to brom thymol blue as an internal indicator—that is, the hydrogen ion was titrated as soon as it was liberated.

IV. Analytical

The iodine solutions containing 4% of potassium iodide were kept in dark bottles. They were standardized against Kahlbaum's arsenious oxide according to the directions of Washburn.[14]

Sodium thiosulfate was made up in 0.1 M solutions from which more dilute solutions were prepared and standardized against iodine. The use of stock bottles which had been dried at a high temperature, boiled water, and a minimum time of contact of solutions with air made possible quite stable solutions of thiosulfate, although frequent restandardizations were performed as a check. We have many data to show that 0.01 N thiosulfate solutions when so prepared retain their titer to within one part per thousand for at least a week. With weight burets a precision of one part per thousand is easily obtained.

The 0.5% starch solutions were prepared from potato starch by boiling for two hours, filtering through cotton and sterilizing at eighteen pounds' pressure in cotton stoppered tubes. Under the conditions of our experiments we find that $6 \cdot 10^{-7}$ equivalent of iodine is sufficient to produce a detectable color. This correction is negligible except for the most dilute solutions; the blank correction was applied whenever it was significant.

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[14] E. W. **Washburn,** THIS JOURNAL, **30,** 31 (1908).

The stability of the very dilute thiosulfate solutions under the exact conditions of the experiments was controlled by blank experiments. After four thousand minutes we recovered 99.99% at *P*H 6.5 and 99.96% at PH 4.5. In the more acid solutions necessary for studying the rate of reaction of the undissociated brominated fatty acid, the instability of thiosulfate becomes important. and the necessary corrections for blanks were made in these cases. These data for very acid solutions, however, are used only in a qualitative sense.

Although the *P*H of the brominated ion plus thiosulfate ion reactions was initially 7, owing to access of carbon dioxide from the air and the liberation of traces of hydrogen bromide, the PH at the time of titration was more often 6 than 7. Moreover, even at *P*H 7 recovery of thiosulfate from 0.002 N thiosulfate solutions (by adding excess iodine and back titrating with thiosulfate) was 100.9%, the initial amount present having been determined by a 0.01 *N* thiosulfate, 0.03 N iodine standardizaiton.

We have been unable to detect any perceptible difference in the velocity constants when the reaction is stopped by titrating the residual thiosulfate with standard iodine as against the method of adding excess iodine and back titrating with thiosulfate. It is important to note that any minute error due to the course of the iodine–thiosulfate reaction in 0.01 N solution is canceled out since the thiosulfate was always standardized by the same iodine solution at the time of making the experiment.

It has been shown that the constants for the β-bromopropionate–thiosulfate reaction, in the most dilute region, obtained when the reaction was carried on under nitrogen and with the reaction mixture brought to a *P*H of approximately 5, immediately before the addition of iodine (run number 83), show no significant difference from those obtained in the other runs.

For the second order reactions (1), (2), (3), (4), (5), (6)

$$k = \frac{1}{(a-b)} \cdot \frac{1}{t} \cdot \ln \frac{b}{a} \frac{(\text{"}a\text{"} - x)}{(\text{"}b\text{"} - x)} \qquad \text{when } a > b$$

$$k = \frac{1}{t} \frac{1}{a} \frac{x}{(a-x)} \qquad \text{when } a = b$$

where k is velocity constant: a is initial concentration in moles per liter of thiosulfate; b is initial concentration in moles per liter of salt, or ester; x is equivalents of b converted = equivalents of thiosulfate used; "a" and "*b*" are equivalents present, at beginning of reaction; *t* is time in minutes. For the first order reactions (7), (8) and (9), $k = (1/t) \ln [a/(a - x)]$, where a is equivalents of salt present, at beginning of reaction; x is equivalents of H^+ titrated with alkali = equivalents of salt converted by water reaction.

Since so far as we are aware no one has worked out the kinetics of first and second order reactions proceeding independently and simultaneously in a solution, we give the following development by R. W. Fessenden of this Laboratory.[15] Let k_1 be velocity constant for first order reaction; k_2, velocity constant for second order reaction; a, substance disappearing by two reactions; b, substance disappearing by second order reaction only; dx/dt be rate of first order reaction; dy/dt be rate of second order reaction; then

$$\frac{dx}{dt} = k_1(a - x - y) \tag{10}$$

$$\frac{dy}{dt} = k_2(a - x - y)(b - y) \tag{11}$$

where a is concentration of salt in moles per liter; b is concentration of thiosulfate in moles per liter; x is moles per liter of salt transformed by water reaction; and y is moles per liter of salt transformed by thiosulfate reaction. Dividing *(10)* by *(11)* we obtain

$$\frac{dx}{dy} = \frac{k_1}{k_2(b - y)} \tag{12}$$

which gives

$$-x = \frac{k_1}{k_2} \ln (b - y) + C \tag{13}$$

When $x = 0$ and $y = 0$, then $C = -(k_1/k_2) \ln b$, or

$$x = \frac{k_1}{k_2} \ln \frac{b}{(b - y)} \tag{14}$$

Substituting this value of x in *(11)* we obtain

$$\frac{dy}{dt} = k_2 \left[a - y - \left(\frac{k_1}{k_2} \ln \frac{b}{(b - y)}\right)\right] (b - y) \tag{15}$$

By use of the calculus of finite differences, dy/dt can be evaluated for any given time, t. All other quantities except k_2 are known, and the equation is solved for k_2. This formula applied to the β-bromopropionate–thiosulfate runs in the dilute region gives a corrected bimolecular constant greater than the uncorrected constant. The correction is negligible in concentrated solutions. Evidence will be given later to show that the assumption that the two simultaneous reactions are proceeding independently is not warranted and that the k_1 values obtained in the absence of thiosulfate are much larger than those obtained in its presence. The correction consequently becomes negligible even in dilute solution. It is important, however, to note that this water reaction correction is of the wrong sign to account for the anomalous results for the β-ion to be discussed later.

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[15] The formula of Bronsted, Kilpatrick and Kilpatrick, [THIS JOURNAL, 51, 428 (1929)], for the disappearance of epichlorohydrin in a buffer solution, by two paths—that is, by reaction with water and with an anion—was developed for a case in which the concentration of anion remains constant. This cannot be applied to reactions in which brominated fatty acid ion reacts with water and with thiosulfate, since the concentration of the thiosulfate ion does not remain constant throughout the reaction.

V. Typical Runs

TABLE II

RUN 8. SODIUM BROMOACETATE AND THIOSULFATE

$\sqrt{\mu} = 0.493$ "a" $= 2.094 \times 10^{-3}$ $a = 0.0698$
μ = ionic strength "b" $= 1.000 \times 10^{-3}$ $b = 0.0333$

Time, min.	10^3 Equiv. thio. used	k
8	0.294	0.674
12	.399	.680
16	.488	.692
23	.602	.694

Av. k = 0.685 ± 0.008

TABLE III

RUN 81. SODIUM or-BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.408$ "a" $= 2.102 \times 10^{-3}$ $a = 0.04204$
"b" $= 2.000 \times 10^{-3}$ $b = 0.04000$

Time, min.	10^3 Equiv. thio. used	10^3 k
1529	0.494	5.03
1652	.515	4.92
2618	.708	4.92
2973	.771	4.94
3355	.832	4.98
4081	.931	4.98

Av. k = $4.96 \pm 0.035 \times 10^{-3}$

TABLE IV

RUN 33. SODIUM α-BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.237$ "a" $= 2.108 \times 10^{-3}$ $a = 0.01622$
"b" $= 1.000 \times 10^{-3}$ $b = 0.00769$

Time, min.	10^3 Equiv. thio. used	10^3 k
4036	0.231	4.25
5489	.299	4.31
6894	.357	4.35
9753	.455	4.38
12,738	.534	4.35

Av. k = $4.33 \pm 0.04 \times 10^{-3}$

TABLE V

RUN 79. SODIUM or-BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.153$ "a" $= 2.018 \times 10^{-4}$ $a = 0.006727$
"b" $= 1.000 \times 10^{-4}$ $b = 0.003333$

Time, min.	10^4 Equiv. thio. used	10^3 k
3928	0.093	3.78
12,905	.3222	4.91
13,227	.3249	4.84
13,925	.3503	5.09
16,906	.3961	4.98
21,180	.4625	5.02

Extrapolated $k = 3.23 \times 10^{-3}$

TABLE VI

RUN 30. SODIUM β-BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.494$ "a" $= 2.108 \times 10^{-3}$ $a = 0.0703$
"b" $= 1.000 \times 10^{-3}$ $b = 0.0333$

Time, min.	10^3 Equiv. thio. used	10^2 k
248	0.205	1.38
285	.236	1.43
468	.346	1.42
597	.412	1.42
1336	.663	1.44
1404	.677	1.43
1682	.730	1.42

Av. $k = 1.42 \pm 0.01 \times 10^{-2}$

TABLE VII

RUN 31. SODIUM β-BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.237$ "a" $= 2.108 \times 10^{-3}$ $a = 0.01622$
"b" $= 1.000 \times 10^{-3}$ $b = 0.00769$

Time, min.	103 Equiv. thio. used	10^2 k
617	0.192	2.22
1288	.348	2.24
1404	.375	2.28
1668	.419	2.25
2742	.581	2.33
3117	.621	2.34

TABLE VIII

RUN 74. SODIUM β-BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.0937$ "a" $= 2.010 \times 10^{-4}$ $a = 0.002512$
"b" $= 1.000 \times 10^{-4}$ $b = 0.00125$

Time, min.	104 Equiv. thio. used	10^2 k
1148	0.212	8.77
1529	.260	8.44
2574	.386	8.46
5464	.612	8.47
6932	.663	7.86

Av. k $= 8.40 \pm 0.27 \times 10^{-2}$

TABLE IX

SUMMARY OF VELOCITY CONSTANTS OF THIOSULFATE AND BROMINATED ION (IN THE PRESENCE OF Na^+) AS A FUNCTION OF THE SQUARE ROOT OF IONIC STRENGTH

Run	$\sqrt{\mu}$	k	Log k + 1
		Bromoacetate	
27[a]	0.0447	0.298 ± 0.001	0.474
26"	.0516	.304 ± 0.0008	.483
25"	.0632	.371 ± 0.003	.501
22[a]	.0816	.325 ± 0.004	.512
20[a], 21"	.1000	.354 ± 0.003	.549
23[a], 19[a], 6, 4[a]	.1414	.385 ± 0.005	.585
2[a], 5[a]	.2000	.445 ± 0.002	.648
7	.493	.690 ± 0.006	.839
8	.493	.685 ± 0.008	.836

TABLE IX *(Concluded)*

a-Bromopropionate

Run	$\sqrt{\mu}$	*k*	log k + 3
18	0.495	5.12±0.06 X 10^{-3}	0.709
29	.494	4.86f0.09 X 10^{-3}	.687
81	.408	4.96f0.04 X 10^{-3}	.695
33	.237	4.33±0.04 × 10^{-3}	.636
80	.182	3.75 X 10^{-3} (extrap.)	.574 (?)
79, 38	.154	3.23 X 10^{-3} (extrap.)	.509
78, 82	.0939	2.64 X 10^{-3} (extrap.)	.422 (?)

β-Bromopropionate

			log k + 2
72	0.526	1.59±0.08 × 10^{-2}	0.201
30	.494	1.42±0.01 X 10^{-2}	.152
35	.462	1.63±0.05 X 10^{-2}	.212
31	.237	2.28±0.04 X 10^{-2}	.358
36	.189	3.79±0.12 X 10^{-2}	.579
83	.0961	8.01±0.21 X 10^{-2}	.904
32	.0937	9.05 X 10–˙˙extrap.)	.957 (?)
74	.0937	8.40±0.27 X 10^{-2}	.924
37	.078	13.2 X 10^{-2} (extrap.)	1.121 (?)
77	.0759	13.5±0.5 X 10^{-2}	1.130

[a] Victor K. La Mer, THIS JOURNAL, 51,3341 (1929): see correction, page 3678.

The plots of these data are shown in Figs. 1, 2 and **3.** The following tables show typical runs for thiosulfate–ester reactions.

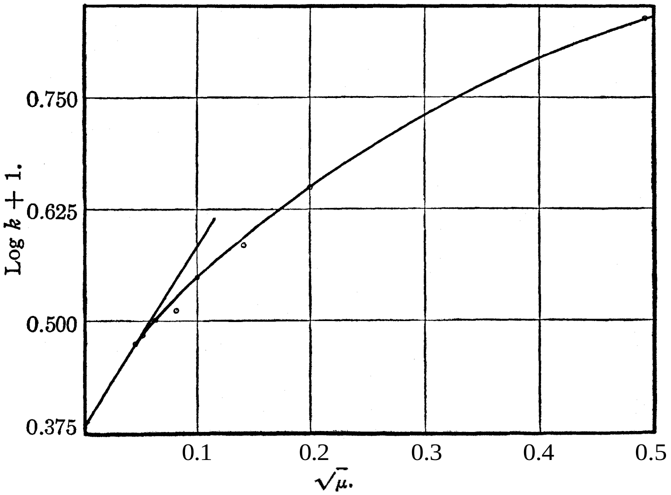


Fig. 1.—Bromoacetate ion and thiosulfate ion.

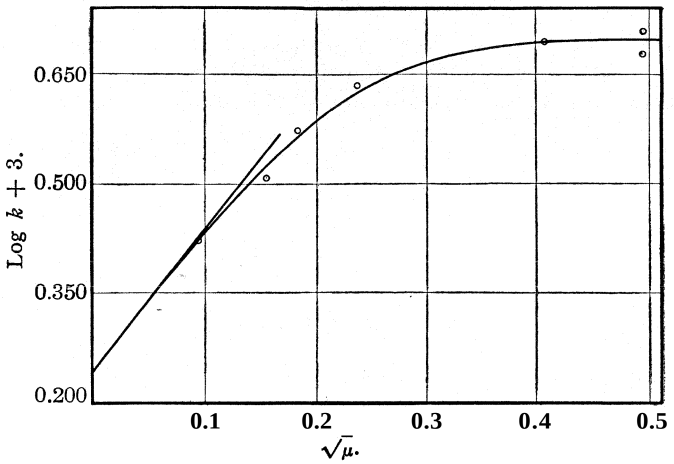


Fig. 2.—a-Bromopropionate ion and thiosulfate ion.

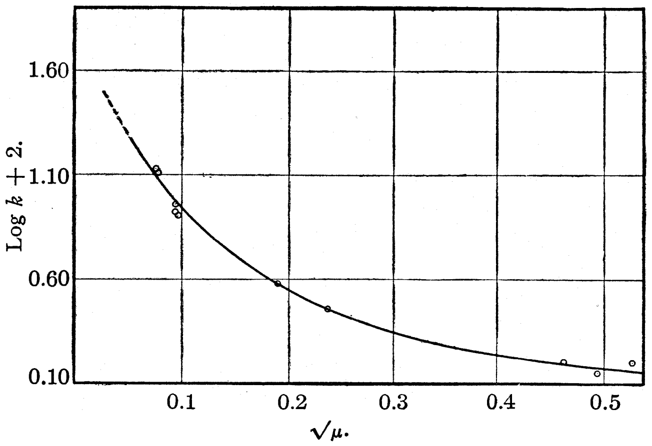


Fig. 3.—β-Bromopropionate ion and thiosulfate ion.

TABLE X

RUN 50. METHYL ESTER OF BROMOACETIC ACID AND THIOSULFATE

$\sqrt{\mu} = 0.0580$ Concentration of ester, mole per liter = 0.000416

Time, min.	10^4 Equiv. thio. used	k
18	0.092	13.8
27	.126	13.5
36	.153	13.2
47	.190	13.8
60	.226	14.4

Av. k = 13.7 ± 0.3

TABLE XI

RUN 53. METHYL ESTER OF a-BROMOPROPIONIC ACID AND THIOSULFATE

$\sqrt{\mu} = 0.399$ Concentration of ester, mole per liter = 0.00912

Time, min.	10^3 Equiv. thio. used	k
15	0.026	0.197
32	.049	.190
51	.069	.183
73	.088	.179
81	.092	.172

Extrapolated k = 0.202

The graph for this extrapolation is shown in Fig. 4.

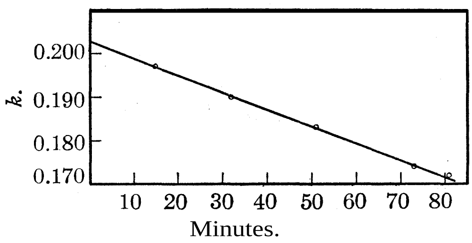


Fig. 4.—Extrapolation for run No. 53.

TABLE XII

RUN 59. METHYL ESTER OF β-BROMOPROPIONIC ACID AND THIOSULFATE

$\sqrt{\mu} = 0.163$ Concentration of ester in mole per liter = 0.002245

Time, min.	10^4 Equiv. thio. used	k
1023	0.297	0.0282
1313	.398	.0312
1464	.437	.0315
2494	.619	.0297
2879	.673	.0292

Av. k = 0.030 ± 0.001

TABLE XIII

SUMMARY OF ESTER–THIOSULFATE RUNS

Run	$\sqrt{\mu}$	Concentration of ester in moles per liter	Average k
		Methyl Ester of Bromoacetic Acid	
42	0.0669	0.00078	13.2 ± 0.2
43	.0674	.00085	14.6 ± 0.65
44	.0674	.00083	13.8 ± 0.8
45	.0677	.00052	15.3 ± 0.3
48	.0675	.00043	14.0 ± 0.3
49	.0580	.00055	12.9 ± 0.3
50	.0580	.00042	13.7 ± 0.3
51	.0516	.00029	13.8 ± 0.3
52	.0469	.00042	14.1 ± 0.2

TABLE XIII (*Concluded*)

Run	**$\sqrt{\mu}$**	**Concentration of ester in moles per liter**	**Average k**
	Methyl Ester of a-Bromopropionic Acid		
53	0.399	0.00912	0.203 (extrap.)
58	.399	.00334	.166 **(extrap.)**
71	.301	.00368	.178f0.008
21 (a)	.229	.0111	.169 (extrap.)
54	.146	.00367	.233 (extrap.)
24	.145	.00554	.217 (extrap.)
55	.066	.00369	.218 (extrap.)
	Methyl Ester of β-Bromopropionic Acid		
57	0.461	0.00449	0.0297 ± 0.0015
60	.461	.00197	.0387 ± 0.002
20	.460	.00741	.036 ± 0.000
21 (b)	.224	.00741	.0266 ± 0.0007
59	.163	.00225	.0300 ± 0.001
62	.070	.00098	.0306 ± 0.0003
63	.070	.00171	.0299 (one value)

The plots of these data are shown in Fig. 5.

TABLE XIV
TYPICAL "SPONTANEOUS WATER REACTION" RUNS

Time, min.	**Salt converted according to NaOH titration, %**	***k***
	Run 13. 0.05 M Na Bromoacetate	
. . . . .[a]		
60, 544	15.2	2.71×10^{-6}
. . . . .		
86, 116	21.2	2.76×10^{-6}
149, 510	34.1	2.79×10^{-6}
207, 060	45.1	2.90×10^{-6}
	Run 14. 0.1 M Na a-Bromopropionate	
9, 793	11.8	1.29×10^{-5}
. . . . .		
18,770	21.1	1.26×10^{-5}
. . . . .		
24,442	26.3	1.24×10^{-5}
76, 335	58.8	1.16×10^{-5}
	Run 26.[b] **0.1** *M* Na β-Bromopropionate	
. . . . .		
1, 329	16.5	1.35×10^{-4}
. . . . .		
1,823	22.2	1.38×10^{-4}
2,815	31.5	1.34×10^{-4}
. . . . .		
3, 150	34.2	1.33×10^{-4}
4, 585	42.8	1.22×10^{-4}

[a] **. . . . .** indicates that a number of determinations were made at these times but are omitted here to save space.

[b] **Alkali was** added at short time intervals to maintain the PH at approximately 7.0.

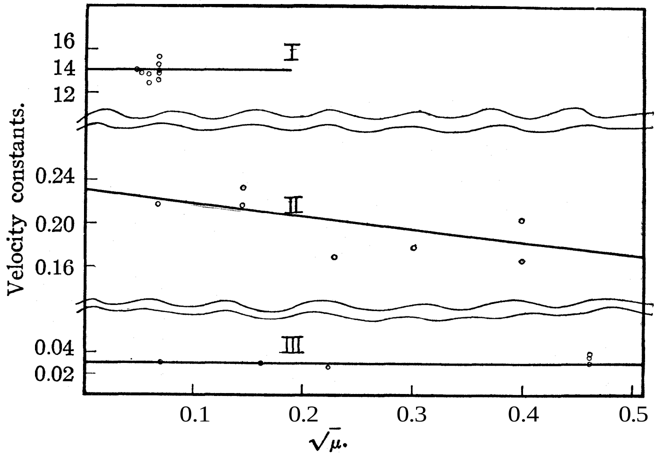


Fig. 5.—Data for reaction of thiosulfate with methyl esters of: I, bromoacetic acid; II, α-bromopropionic acid; III, β-bromopropionic acid.

TABLE XV

SUMMARY OF "SPONTANEOUS WATER REACTION" RUNS

Run	Salt	$\sqrt{\mu}$	k
12	0.1 M Na bromoacetate	0.316	$3.37 \pm 0.14 \times 10^{-6}$
13	0.05 M Na bromoacetate	.224	$2.78 \pm 0.06 \times 10^{-6}$
14	0.1 M Na a-bromopropionate	.316	$1.27 \pm 0.03 \times 10^{-5}$
15	0.05 M Na a-bromopropionate	.224	$1.24 \pm 0.04 \times 10^{-5}$
73"	0.3 *M* Na β-bromopropionate	.548	1.21×10^{-4}
25"	0.1 M Na β-bromopropionate	.316	1.53×10^{-4}
26[a]	0.1 M Na β-bromopropionate	.316	1.35×10^{-4}
27[a]	0.1 M Na β-bromopropionate	.316	1.27×10^{-4}
28[a]	0.1 M Na β-bromopropionate	.316	1.24×10^{-4}
16	0.1 M Na β-bromopropionate	.316	1.42×10^{-4} (extrap.)
17	0.05 M Na β-bromopropionate	.224	1.59×10^{-4} (extrap.)

[a] Alkali was added at short time intervals to maintain the P_H at approximately 7.0.

TABLE XVI

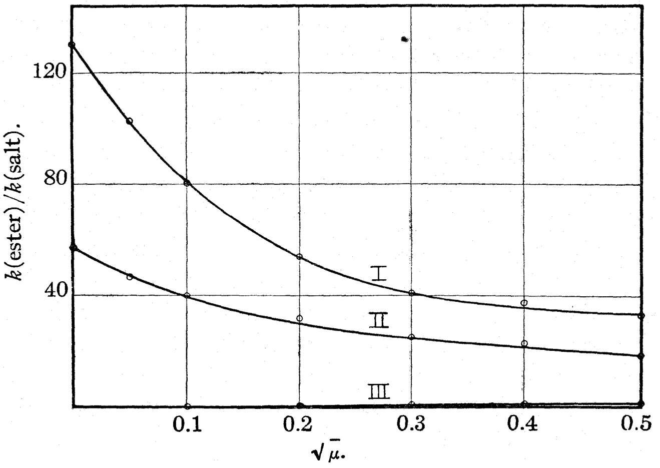
SUMMARY

$\sqrt{\mu}$	0.00	0.05	0.10	0.20	0.30	0.40	0.50
$\frac{k_{\text{ester}}}{k_{\text{salt}}}$[a] Bromoacetate	(58)	46	40	32	26	23	20
$\frac{k_{\text{ester}}}{k_{\text{salt}}}$[a] a-Bromopropionate	(131)	102	81	53	42	36	34
$\frac{k_{\text{ester}}}{k_{\text{salt}}}$[a] β-Bromopropionate	...	...	0.4	0.9	1.4	1.9	2.2
$\frac{k_{\text{ester}}}{k_{\text{salt}}}$ α-Bromopropionate / $\frac{k_{\text{ester}}}{k_{\text{salt}}}$ β-Bromopropionate	...	...	218	58.5	28.9	19.7	15.7
k_{salt} β-Bromopropionate / k_{salt} α-Bromopropionate	...	...	32.2	9.1	4.8	3.5	3.0
k_{salt} β-Bromopropionate / k_{salt} Bromoacetate	...	...	0.25	0.08	0.04	0.03	0.02

[a] A plot of these data is shown in Fig. 6.

VI. Discussion

Position of Charge in Relation to Velocity.—From Table XVI and Fig. 6, where the value of k for the methyl ester is compared with that for the salt, we find in the case of bromoacetate and a-bromopropionate that the rate of reaction of the negative thiosulfate ion is twenty to a hundred and thirty-fold faster with the ester than with the ion, depending upon the concentration of the reactants. When the bromine is in the @-position, thiosulfate ion reacts about as rapidly with the ester as with the salt, since in this case the number of impacts of the thiosulfate upon the bromine is less influenced by the presence or absence of a charge on the carboxyl group.



Pig. 6.—I, α-Bromopropionic acid; II, bromoacetic acid; III, β-bromopropionic acid.

Although the *a-ester* reacts five to seven times faster than the *β-ester* in harmony with the rule that the a-position is more reactive than the @-position,the velocity of reaction of the β-bromopropionate ion greatly exceeds that for the a-bromopropionate ion. The recent data of Backer and Van Mels[1b] on the rate of reaction of the negative sulfite ion with the β-bromopropionate ion show it to be double that for the corresponding a-ion at the 0.1 M concentration used. These data, consequently, support our view that the electrostatic interaction is the dominant factor in regulating the rates of ionic reactions.

With reactions between ions of opposite sign, a reverse result should be obtained. Euler,[1a] studying the reaction $ClCH_2COO^- + H_2O + Ag^C \longrightarrow AgCl + (OH)CH_2COOH$, actually found that the rate of reaction of the corresponding ester of chloroacetic acid is only about one-eighth that for the sodium salt. Here the presence of the negative charge increases the probability that a positive silver ion will collide with the chlorine atom and react. Euler's data show also that sodium thiosulfate reacts fourteen times as rapidly with the ester as with the sodium salt of chloroacetic acid.

Concentration Dependence of the Ratios in Table XVI.—We had hoped to determine the values of k_0 for each reaction, *i. e.*, k, freed from interionic effects, by extrapolating the values of log k plotted against $\sqrt{\mu}$ to infinite dilution in accordance with the limiting slope predicted by the Debye–Hückel limiting theory; namely, $\log k_{\text{obs}} = \log k_0 + Z_AZ_B \sqrt{\mu}$. This limiting slope of $Z_AZ_B = 2$ is approached in the case of bromoacetate and also by the α-bromopropionate reaction as shown in Figs. 1 and 2. Much to our surprise, however, we found that the observed values for k for the β-bromopropionate salt, instead of decreasing with concentration, actually increased! The β-bromopropionate–thiosulfate reaction is the only one in dilute solution which, to our knowledge, is in direct contradiction to this prediction of the Bronsted theory. The cause of the discrepancy is, consequently, a matter of considerable theoretical interest.

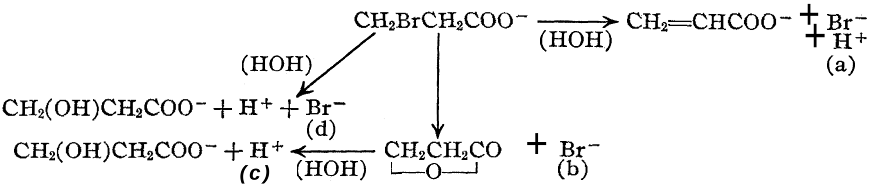
Several factors which might be relevant have been investigated. Experiments to detect errors in procedure were first carried out. The data have been confirmed in a second series of experiments performed nine months after the first. Reaction flasks, scrupulously cleaned with soap and chromic acid, before rinsing with distilled water and finally steamed, showed no difference in reaction rate for their contents as compared with the rate in cases where flasks had been merely cleaned with cleaning mixture and rinsed with distilled water. The possibility of traces of catalyst from the glass affecting the dilute solutions is not likely. Results no different from the others were obtained when the reactants were protected from the action of light.

In those experiments extending over several days where perceptible drifts in k occurred with time, the possibility was considered that the liberation of hydrogen bromide from concurrent water reaction might produce an analytical error in the iodine–thiosulfate titration. Some experiments were therefore made in which the reaction mixture was brought to a P_H of 7 using brom thymol blue as indicator, immediately before the iodine was added to stop the progress of the reaction. This did not eliminate the drifts in the case of a-salts (which will be discussed later) but gave for the β-bromopropionate–thiosulfate reaction values which showed no drift with time and were not appreciably different (Nos. 32, 74 and 37, 77) from the extrapolated values of the earlier runs in which neutralization of the hydrogen bromide before addition of iodine was omitted. This precaution is unnecessary for the runs at higher $\sqrt{\mu}$ values, since in the more concentrated solutions the iodine–thiosulfate reaction is less sensitive to acidity, and the reaction time being less there is a quite negligible accumulation of hydrogen ion. Moreover, the rate of development of acidity in the concentrated β-bromopropionate–thiosulfate reaction mixtures is enough less than the rate in the dilute mixtures that the actual titratable hydrogen ion formed is less in the former solutions, for a given period of time.

It has been found that the rate of formation of hydrogen ion in water solution by sodium β-bromopropionate in the absence of thiosulfate is considerably greater than the rate for the same concentration of salt in the presence of sodium thiosulfate. For instance, Run 72 shows that after 1523 minutes in the presence of thiosulfate of about twice its concentration, titratable hydrogen ion equivalent to only 0.2% of the original salt present (0.0375 M) has been formed, while in the absence of thiosulfate about one hundred times this amount would be formed. This can hardly be considered a salt effect in the ordinary sense. It would appear that the bromine atoms in the activated state react preferentially with thiosulfate rather than with water. Another fact pointing to this conclusion is that we found that 98% of the sodium β-bromopropionate present in a 0.0333 M solution reacted with thiosulfate as calculated from the disappearance of the latter. Reaction 9 therefore proceeds more slowly in the presence of Reaction **3** than in its absence. *These observations cast considerable doubt upon the validity of corrections for side reactions based upon the rate of the side reaction in the absence of the main reaction.* Therefore, the previously mentioned correction of the bimolecular reaction due to the monomolecular side reaction (water reaction) has not been used.

Since owing to its monomolecular character the rate of the water reaction is relatively greater then the bimolecular thiosulfate reaction in the dilute solutions of sodium β-bromopropionate, and it is these same solutions which show the unusually large value of k for the thiosulfate reaction, the question arises as to whether the accumulation of the hydrolysis products, either by catalytic action or by reaction with the thiosulfate, can cause this increase in velocity. Run 74, with concentration of thiosulfate 0.002512 M and sodium β-bromopropionate 0.00125 M ($\sqrt{\mu} = 0.0937$), performed by adding thiosulfate to salt immediately after its preparation and making up to volume, gave a velocity constant of $8.40 \pm 0.27 \times 10^{-2}$. A portion of the same salt solution was kept in the thermostat until the water reaction had converted 74.6% of the original salt (as determined by titration of hydrogen ion formed). To this neutralized solution, thiosulfate to give the same final concentration as above was added, and the mixture made up to the same volume. The velocity constant of this run was $6.61 \pm 0.39 \times 10^{-2}$ (calculated on the basis of concentration of salt remaining unchanged by water reaction). A similar experiment using more concentrated solutions also showed that the presence of the water reaction products *decreases* the rate of the reaction of sodium β-bromopropionate with thiosulfate and, therefore, their presence (which even in the runs of greatest dilution and longest time never approaches the large concentration, here) can be eliminated as the cause of the increase in velocity constants in the dilute region.

Possible courses of the water reaction of sodium β-bromopropionate are



The velocity of the water reaction as determined by the titration of hydrogen ion indicates how much salt has been converted to (a), (c) or (d) but if (b ⟶ *c)* is slower than (salt ⟶ b), this fact is not detected by acid titration, alone. Difference in concentration of bromide ion and hydrogen ion would be an index of whether more of (b) than (c) exists, but since silver nitrate reacts to some extent with the salt itself this does not promise to be a very satisfactory procedure. It has been found,[16] however, that at 70° solutions of a-bromopropionate and of β-bromopropionate show a negligible excess of bromide ion over hydrogen ion. We found in Run 11 that 0.98 equivalent of thiosulfate disappeared per equivalent of sodium p-bromopropionate present originally. It appears, then, that whatever water reaction products had accumulated, reacted (within two parts per hundred) with thiosulfate in the same ratio as postulated for the original salt. Whether the reaction took place through the intermediate step of lactone, hydroxy compound or even unsaturated compound should not influence the interpretation of the results since one equivalent of each is formed from one equivalent of salt. If the (b ⟶ c) conversion is slower than the formation of (b), then lactone accumulates and the water reaction products mixture should contain enough to make the velocity constant exceed that of the usual runs if the lactone reacted very rapidly with thiosulfate. That no appreciable thiosulfate was used up as soon (after *a* few minutes) as the reactants were mixed is evidence that the water reaction mixture contains no very reactive substance which could account for the increase in velocity of the dilute β-bromopropionate–thiosulfate runs.

In order to isolate the reaction product, equivalent amounts of sodium β-bromopropionate and thiosulfate were allowed to react for a sufficient time to approach completion of the reaction (adding sodium hydroxide occasionally to neutralize acidity). After proceeding according to the directions of Purgotti[17] for preparation of the barium salt of the thio deriva-

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[16] G. S. Simpson, THIS JOURNAL, 40,674 (1918).

[17] A. Purgotti, *Gazz. chim. ital.*, 22,416 (1892).

tive of chloroacetic acid, a fine, white crystalline substance was obtained. After recrystallization, analysis[18] showed 19.60% sulfur. The theoretical sulfur content of $CH_2(S_2O_3)\overline{CH_2COOBa}$ is 19.94%. The corresponding sodium salt has been postulated as the reaction product in the thiosulfate reactions studied in this paper. **A** solution of the barium salt prepared had no perceptible action on an iodine solution.

The dissociation constant of a-bromopropionic acid is 108 X 10^{-5}, that of β-bromopropionic acid is 9.8 × 10^{-5}. Can the acidity resulting from hydrogen ion liberated by the reaction of the salt with water, by repressing the ionization of these rather weak acids, particularly the latter, cause thiosulfate to react with undissociated acid molecules as well as with the ion? By the use of citric acid–phosphate buffer solutions, the reacting mixtures for salts of the above acids were maintained at various ***PH*** values and the rate of thiosulfate reaction determined. In the more acid solutions the stability of the thiosulfate was determined by "recovering" it by iodine titration in control experiments from buffer mixtures of the same ***PH*** value and these values were used as the initial concentration of thiosulfate in calculating the velocity constant. With sodium β-bromopropionate 0.00125 M and thiosulfate 0.0027 M, the velocity constant decreased rapidly as the solutions became more acid than ***PH*** 4.5 and at **3.5** had fallen to a value but slightly more than half that at ***PH*** 6.5. The plot of these results has the form of a titration curve and shows that the undissociated molecule of β-bromopropionic acid reacts more slowly than does the ion with thiosulfate. This possibility of explaining the anomalous rise in velocity constant with decreasing $\sqrt{\mu}$ value is thus eliminated.

In the case of a-bromopropionate in buffered solutions (salt 0.0125 *M*, thio controls, varying slightly about the value 0.0266 M), the velocity constant is increased markedly with increasing acidity and at ***PH*** 4.0 has more than doubled its value at PH 6.5. The plot of these results also takes the form of a titration curve. The upward drift of the constants in runs of low concentrations of the a-salt can be accounted for by the increasing acidity which occurs during the many days required for a run. On this basis, then, it seems justifiable to extrapolate the results to determine the a-bromopropionate–thiosulfate velocity constant at zero time, for any run which shows a drift with time.

The fact that repression of the ionization of the acid increases more markedly the velocity of the reaction of the a-acid with thiosulfate than it decreases the velocity of the β-acid is in harmony with what we have found in comparing the effect of removal of charge in forming a methyl ester.

[18] Analysis by Research Service Laboratories, **37** East **28th** Street, New York, N. Y.

An Orientation Theory of Reaction Velocity.[19]—Having exhausted the possible chemical explanations, we present a physical explanation which is in harmony with the known facts and at the same time does not entail rejection of the Brönsted–Debye theory. In order to test Bronsted's theory it is necessary to introduce the Debye–Hückel limiting law. This law is derived on the simplifying assumption that the charges on the ions may be considered as symmetrically distributed upon a sphere of radius "b" so that the distance of closest approach of their centers equals the parameter "a." This assumption appears to be sufficiently valid to account for the bromoacetate–thiosulfate data and for the α-bromopropionate–thiosulfate data but can hardly be considered valid for β-bromopropionate if we are to consider the formulas of structural organic chemistry as representing even the approximate positions of the bromine atom and the charge on the carboxyl group. Since a reaction occurs only when a thiosulfate ion collides with the bromine in the β-position, our molecular model should be revised to take the form of one spherical ion (thiosulfate) and a long chain ion with a negative charge at one end and reacting bromine atom at the opposite end. From this model of structural organic chemistry, we contend that an orientation effect should be superimposed upon the effect predicted for spherical ions on the basis of the Brönsted–Debye equation.

Although the influence upon the activity coefficient produced by superimposing a dipole upon an excess charge has never been worked out quantitatively, it is generally recognized that the contribution of the dipole to the free energy should be small and vanish more rapidly with dilution than the contribution of the excess charge.[20] The influence of the dipole upon the reaction velocity, however, is not exactly comparable, for in reaction velocity we measure only the frequency of those collisions which occur between a thiosulfate ion and a β-bromopropionate chain when the chain is oriented within a given critical solid angle such that a chemical reaction will occur. Thus, the comparatively minute contribution to

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[19] In his important paper on reaction kinetics, Christiansen [Z. *physik. Chem.*, **113**, **35** (1924)], in a carefully worded sentence, considers the possibility of orientation but expresses the opinion that it is of less importance than that of deactivating collisions. Christiansen, however, was, apparently, drawing primarily on his experience with gaseous reactions where the possibility of the orienting effect of the net charge of one ion upon another ion is remote as contrasted with the case of aqueous ionic solutions. We do not believe his analogy applicable in the present case. He does mention, however, the importance of attention to electrical forces in calculating concentration dependence of the velocity constant especially in treating a reaction in which large organic molecules are concerned, representing the organic molecule as being a chain and burdened with a charge at one place and at a proportionally great distance from the center of reaction. His reference to Holmberg's acetylglycolic acid experiments does not make clear, however, his point as we would interpret it.

[20] Discussion of one of us with Professor Debye in 1926.

the activity coefficient arising from the orientation due to dissymmetry of the charge in the β-bromopropionate ion may become the predominant factor in such a specific process as the oriented collision necessary for a chemical reaction.

That the molecular model, spherical ion and non-spherical ion with the point of attack at a great distance from the excess charge, should lead to a decreased velocity on increasing ionic concentration, may be shown as follows. Consider the extreme case of a volume of solution containing only one thiosulfate ion and one β-bromopropionate ion. Collisions will be very infrequent but, when they do occur, the bromine end will collide with the thiosulfate owing to the repulsive effect of the negative charges on the two ions. Every collision having a velocity sufficient to exceed the critical increment should, therefore, be fruitful. As we pass to slightly more concentrated solutions, the rapidly fluctuating fields produced by the thermal movement of the neighboring ions, will disturb the ideal orientation of the collisions that prevails at extreme dilution. Many of the collisions predicted by the term $C_A \cdot C_B$ in the rate equation $dx/dt = k \cdot C_A \cdot C_B$ will no longer occur with an orientation represented as lying within the critical solid angle necessary for chemical reaction. The result will be a decrease in the value of the velocity constant with increasing concentration which will be most pronounced in the highly dilute region. Since this effect will be superimposed upon the Debye–Hückel effect arising from the net charges on the ions, it is clear that we have a plausible explanation of the anomaly which does not conflict with the Bronsted theory.

It is hoped that theoretical physicists will essay a solution of this problem suitable for numerical evaluation. In the meantime, we are testing the idea by studying the rates of reaction in a homologous series of brominated compounds. Our theory requires a greater change in the temperature coefficient for the β-reaction as compared with the a-reaction, with variation in concentration, since an orientation effect should be more sensitive to temperature changes than is the Brönsted–Debye effect.

VII. Summary

1. Data are given for the rates of reaction of bromoacetate, α-bromopropionate and β-bromopropionate ions, and of their methyl esters, with sodium thiosulfate over a wide range of concentrations. The rates of the corresponding spontaneous water reactions have been investigated.

2. At all concentrations the velocity constant for the reaction of negatively charged thiosulfate ion with bromine in the β-position to a negatively charged carboxyl group greatly exceeds that for the reaction with bromine in the a-position to the carboxyl group. The converse is true when the esters are used in place of the salts.

3. Removal of the negative charge on the brominated ion either by

ester formation or by repression of ionization increases the velocity constant over a hundred fold when the bromine is in the a-position to the group bearing the charge, but has little effect when the bromine is in the β-position. All of these facts are in accord with the predictions of the electrostatic theory of reaction velocity.

4. For the α-bromopropionate–thiosulfate reaction, the limiting slope predicted by the Brönsted–Debye theory is approached for concentrations less than $\sqrt{\mu} = 0.06$. For the β-bromopropionate–thiosulfate reaction the velocity constant contrary to this theory **increases** with decreasing $\sqrt{\mu}$ values, the effect being most marked in the very dilute region.

5. As an explanation of this anomalous result for the β-bromopropionate, a theory based on the assumption of oriented collision is submitted.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE CRYSTALLINE FORM OF SOME NEW COBALTAMMINES[1]

BY LESTER W. STROCK[2] AND THOMAS P. McCUTCHEON

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Introduction

The recent work of V. M. Goldschmidt on crystal chemistry has shown that crystal structure is determined by the relative numbers, size and deformability of the constituent particles[3] These results are based largely on x-ray investigation, but deal primarily with relatively simple compounds. The structure of a compound consists of an interpenetration of a definite anion and cation arrangement, whose mutual influence on each other determines the final structure of the compound. A given cation structure is expanded by the introduction of various anions, but this expansion has a limit, at which the fundamental cation arrangement alters. The substitution of various cations similarly influences the structure of the anion.

The cation of a complex cobaltammine must represent the largest and most determining part of the final structure of compounds containing this cation in combination with a simple anion. The structure of compounds of

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[1] This paper is a thesis submitted to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Acknowledgment is made to the George Leib Harrison Foundation of the University of Pennsylvania for fellowships granted for 1929–1930 and 1930–1931.

[3] V. M. Goldschmidt, *Skrifter Norske Videnskap. Akad. Oslo*, **1926**, No. 2; *ibid.*, **1926**, No. 8; *Naturwissenschaften*, 14, 477 (1926); *Trans. Faraday Soc.*, 25, 253–83 (1929).

this type is determined to a large extent by the cation, whose fundamental arrangement can be altered only with great difficulty. The axial ratio of suitable cobaltammines containing various simple anions should offer a means of determining the effect which an anion produces on a given cation structure. It must be remembered that when the structure of the cation does not represent a large portion of the final structure, and when the cation is not complex and heterogeneous, the axial ratio will be inadequate to measure the effect which the anion produces, as is seen from Fig. 1.

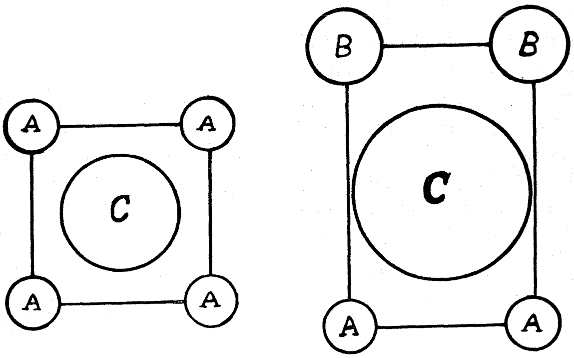


Fig. 1.—If the substitution of (C) increases the absolute dimension of the cell from 5×5 to 10×10, the axial ratio is not changed.

Fig. 1a.—If the substitution of (C) increases the absolute dimension of the cell from 4×10 to 8×12, the axial ratio changes from 1:2.5 to 1:1.5.

Fig. 1.—Illustrating the type of atomic arrangement, whose expansion may be detected by axial ratio determinations.

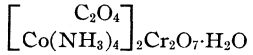
The figures show that the effect of the anion can be measured by a determination of the axial ratios only in the second case, where various anions (C) expand the cation structure (AABB) to different extents in different directions depending upon the atoms involved in the expansion. Only x-ray measurements will ascertain the absolute expansion in either of the above cases, but any irregular expansion in different directions may be detected in the axial ratios as determined by geometrical crystallography. The acido cobaltammines are compounds of the type shown in Fig. 1a, and should be well suited for testing this view. The introduction of various anions will not produce any regular differences on the crystalline form of the compound if the new anion causes a change in structural type to occur. However, the structural type of the compounds reported in this paper appears to be the same, and regular differences in the crystalline form should be and are observed.

Experimental

Preliminary work showed that compounds in the oxalato series were very stable and could be obtained in measurable crystals; therefore, several oxalato tetrammines were prepared, analyzed and their crystalline form determined. None of the compounds studied, except the perchlorate, has been previously described; therefore their methods of preparation and properties are included in this paper.

Preparation of Compounds.—Oxalato tetrammine cobalti sulfate was first prepared by the method of Schramm, and this was used to prepare the other compounds in the oxalato series.[4]

1. Oxalato Tetrammine **Cobalti Dichromate.**—A saturated solution of potassium dichromate at 30 to 40° is added slowly and with stirring to a saturated solution of the oxalato sulfate. A few drops of acetic acid or a little ammonium acetate is added to the oxalato sulfate solution to prevent decomposition. A bright orange-red precipitate is formed, which is filtered off at once, washed with cold water and alcohol, then dried in the air. The precipitate is a mass of minute but perfect crystals.

Composition 

$$\left[\overset{C_2O_4}{Co(NH_3)_4}\right]_2Cr_2O_7\cdot H_2O$$

Constituent	Calcd., %	Found, %
Cr	15 66	15.69
Co	17.76	18.21
NH_3	20.513	20 55
H_2O	2.712	2.71
C_2O_4	Not determined	

The salt was found to be more soluble in a solution of ammonium acetate than in water. Since a more concentrated solution of the salt could be obtained in ammonium acetate than in water, this was used as a means of obtaining crystals suitable for measuring. The following procedure was followed. A 5 to 30% solution of ammonium acetate was carefully saturated with the salt at 40°. The excess salt was removed, and the saturated solution was allowed to cool very slowly (fifteen hours) down to room temperature while immersed in a large thermostat. This produced many small, but extremely perfect, deep ruby-red crystals. The crystals were always distorted when the concentration of the ammonium acetate was above 30 to 40%. The composition of the recrystallized and precipitated salt was found to be the same on analysis, showing that the treatment with ammonium acetate did not alter the composition of the salt.

2. Oxalato **Tetrammine** Cobalti Chromate.—All attempts to prepare this salt by the direct action of potassium chromate upon oxalato sulfate failed, but a small amount of acetic acid present caused the slow formation of the dichromate. When a small amount of ammonium carbonate was present no reaction occurred, and on evaporation the reactants were deposited unchanged. It was found that when the orange-red oxalato dichromate was boiled with ammonium carbonate it was transformed to a salt of a more nearly pure red color. An excess of the oxalato dichromate was then boiled with ammonium carbonate, and the salt, after boiling, was filtered off and used to saturate a 5 to 10% solution of ammonium carbonate at 40°. By slowly cooling this solution as described above, perfect deep red crystals were obtained which proved to be the oxalato chromate. Therefore even though the chromate cannot be made directly, it can be obtained by crystallizing the dichromate from ammonium carbonate.

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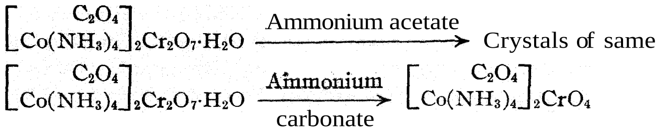
[4] Schramm, *Z. anorg. Chem.*, 180,179 (1929).

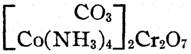


$$\left[\begin{matrix} C_2O_4 \\ Co(NH_3)_4 \end{matrix}\right]_2 Cr_2O_7\cdot H_2O \xrightarrow{\text{Ammonium acetate}} \text{Crystals of same}$$

$$\left[\begin{matrix} C_2O_4 \\ Co(NH_3)_4 \end{matrix}\right]_2 Cr_2O_7\cdot H_2O \xrightarrow[\text{carbonate}]{\text{Ammonium}} \left[\begin{matrix} C_2O_4 \\ Co(NH_3)_4 \end{matrix}\right]_2 CrO_4$$

From several ammonia determinations the composition of the chromate was found to correspond to the formula written above. The ammonia required by the formula is 24.92% and the average found from four determinations was 24.94%.

3. **Carbonato Tetrammine** Cobalti **Dichromate.**—A saturated solution of potassium dichromate at 30 to 40° is added to a solution of carbonato sulfate at 60° in the presence of a little ammonium acetate. The mixture is stirred vigorously under running water, cooled quickly and filtered at once. The filtrate after removing the precipitate, and frequently even before, turns very dark brown in color, and on standing deposits crystals of similar color. These crystals could not be obtained pure for analysis. If the carbonato sulfate solution is not completely saturated, and if the potassium dichromate solution is much above 40° and also unsaturated, no precipitate will form, but the solution turns at once dark brown in color. The bright red salt changes to this dark brown substance on standing in water solution, acetic acid, ammonium acetate, potassium and ammonium dichromate, and most attempts to recrystallize it formed this brown solution.

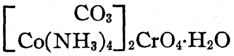
Composition 

$$\left[\begin{matrix} CO_3 \\ Co(NH_3)_4 \end{matrix}\right]_2 Cr_2O_7$$

Constituent	Calcd., %	Found, %
Cr	17.62	17.63
NH3	23.08	23.00
Co	19.98	20.79
CO_3	Not determined	

The carbonato dichromate could not be crystallized, since all solutions of the salt change in composition before crystals form.

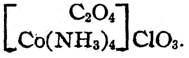
4. Carbonato **Tetrammine** Cobalti Chromate.—A solution of ammonium carbonate of almost any strength is saturated with the carbonato dichromate at 30 to 40° and allowed to stand. Large individual crystals deposit on cooling which are deep red in color.

Composition 

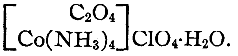
$$\left[\begin{matrix} CO_3 \\ Co(NH_3)_4 \end{matrix}\right]_2 CrO_4\cdot H_2O$$

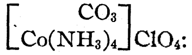
Constituent	Calcd., %	Found, %
Cr	10.23	10.17
NH_3	26.81	26.76
Co	23.21	23.98
H_2O	3.54	3.45
CO_3	Not determined	

As in the oxalato series the chromate could not be prepared directly, but was obtained by crystallizing the dichromate from ammonium carbonate.

5. Oxalato **Tetrammine** Cobalti **Chlorate.**—This salt, not previously described, was prepared in order to study the crystalline form of a compound containing the oxalato cation combined with a univalent anion. Oxalato sulfate was treated with the calculated quantity of barium chlorate, the barium sulfate was filtered out, and the oxalato chlorate crystallized from the filtrate in measurable crystals after several days. The cobalt found in these crystals was 19.92%, and the cobalt required by the formula is 19.83% 

$$\left[\begin{matrix} C_2O_4 \\ Co(NH_3)_4 \end{matrix}\right] ClO_3.$$

6. Oxalato **Tetrammine** Cobalti Perchlorate.—This salt was prepared by Bronsted, and used by him in his studies on solubility. It forms readily on mixing saturated solutions of ammonium perchlorate and oxalato sulfate. Measurable crystals were obtained by slowly cooling an aqueous solution of the salt:  $\left[\begin{matrix}C_2O_4\\Co(NH_3)_4\end{matrix}\right]ClO_4\cdot H_2O$. Cobalt found, 17.78%; calcd., 17.74%.

7. **Carbonato** Tetrammine Cobalti Perchlorate.—This salt was prepared by mixing solutions of ammonium perchlorate and oxalato sulfate. The crystals were more difficult to obtain in measurable form, but were not investigated since other salts in this series could not be crystallized.  $\left[\begin{matrix}CO_3\\Co(NH_3)_4\end{matrix}\right]ClO_4$: Cobalt found, 20.69%; calcd., 20.59%.

Remarks on the Oxalato Tetrammine Ion

Solutions of salts containing a complexly bound acido group usually undergo hydrolysis, whereby a water molecule is exchanged for the acido group. The oxalato and the carbonato tetrammine ions show a marked difference in this respect. The carbonato dichromate changes to the diaquo compound rapidly, but the chromate ions which are produced in the hydrolysis of the dichromate group immediately replace the water molecules from the complex, so that the result of the hydrolysis of the unstable carbonato group is the formation of a chromato complex compound, which is the cause of the dark brown solutions previously mentioned. Briggs[6] has prepared compounds of this series by reactions involving the replacement of water by the CrO_4^{--} group.

Oxalato dichromate is very different from the carbonato dichromate, and hydrolyzes, producing the brown chromato compound only to a small extent after several days. Lamb has shown that the carbonato tetrammine base is as highly ionized as the alkali bases.[6] The presence of the carbonato ion in solution appears to favor the formation of hydroxyl ions, which in turn produces a high concentration of chromate ions when the carbonato dichromate is dissolved in water. These chromate ions either replace the CO_3 directly or replace the water molecule which had previously replaced the CO_3 group. Lamb did not determine the strength of the oxalato tetrammine base, so that we can make no prediction as to whether the oxalato tetrammine ion will favor hydroxyl-ion formation. From the behavior of oxalato dichromate solutions, it appears that very few chromate ions are formed. This would indicate that the oxalato ion favors hydrogen-ion formation. Solutions of oxalato dichromate do not change to the chromato compound, either because of the failure of the oxalato group to be replaced by water, or because the oxalato complex prevents the formation of chromate ions from the dichromate group. In the event that the aquo compound is formed there is no evidence that the dichromate group becomes com-

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[5] Briggs, J. *Chem. Soc.*, **115**, 67 (1919); 685 (1929).

[6] Lamb and Yngve, THIS JOURNAL, 43, **2352** (1921).

plexly bound as does the chromate group. Rây and Sarkar have described a compound which contains a complexly bound Cr_2O_7 group, but this has a very complex structure and is not comparable to the type of compounds considered here,[7]

Solubility of the Salts in Water

The solubility was determined by the same method used by Bronsted.8

Cobalt tetrammines	Solubility at 25° G. of salt per 100 cc. of satd. soln.	Specific gravity at 25°
Oxalato sulfate	0.7712	....
Oxalato dichromate	.0734	2.0995
Oxalato chromate	.3156	1.9790
Oxalato perchlorate	.4403 (At 20°, Bronsted)	....
Carbonato sulfate	6.061	....
Carbonato dichromate	Decompose rapidly in water and could not be determined	2.0300
Carbonato chromate		2.0135

The composition of the salts was ascertained by determining the constituents in the following way. Chromium was determined by the lead chromate method, ammonia by the method of Bronsted, and cobalt by the nitroso beta naphthol method, not igniting the precipitate in hydrogen.

Crystallography

Crystals of the compounds studied were obtained suitable for measuring by methods already mentioned. They were, as desired, very small and did not exceed 0.1 to 0.2 mm. in their greatest dimension. A crystal which was typical of the compound was selected and accurately sketched. This sketch was used to make the final drawing from the measured angles, so that each drawing would be a faithful portrait of the compound and not a drawing of the ideal form. A small piece of wax, fastened on a spindle, was drawn out to a thin thread, which was then attached to a suitable point on the crystal. The crystal when mounted on the wax was placed on a Goldschmidt two-circle goniometer and measured with a prominent zone vertical.

The average values from the measurement of a number of crystals were used to calculate the crystallographic elements. These elements and symbols were calculated by the method of Victor Goldschmidt from a gnomonic projection.[9] Care was taken to select the unit face so that

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[7] Rây and Sarkar, *J. Indian Chem. Soc.*, 1,289 (1925).

[8] J. N. Bronsted and Agnes Petersen, THIS JOURNAL, 43,2265 (1921).

[9] A series of papers edited by Edgar T. Wherry and Charles Palache describes these calculations and covers the important bibliography of the subject [*Am. Mineral.*, 5, Nos. 2–12 (1920)].

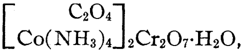
similar faces on different compounds would have similar indices, and so that the orientation of the various crystals would be comparable. The same plan was followed in assigning letters to the faces.

The crystal tables which follow contain the measurements, calculations and results of the compounds studied. The figures are reproductions of drawings made from the gnomonic projections of the average values obtained, and are in all cases real portraits and not drawings of the ideal crystal, as Victor Goldschmidt insists is the best procedure.

CRYSTAL TABLE NO. I

OXALATO TETRAMMINE COBALTI DICHROMATE

Measurement of a typical crystal, see Figs. 2 and 3


$\begin{bmatrix} C_2O_4 \\ Co(NH_3)_4 \end{bmatrix}_2 Cr_2O_7 \cdot H_2O$, Monoclinic.

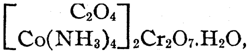
$H_0 = 144°16'$
$V_0 = 34°56'$

No	Let.	Symbols		Measured		Orientated		Calcd.	Av. top and bot.	
		G.	M.	H	V	$V - V0$	$H - H_0$	φ	φ	ρ
1	c	0	001	141°44′	124°56′	90°00′	2°32′	90°00′	89°59′	2°35′
4	p	½	112	186 29	176 29	143 33	42 13	38 27	38 26	42 42
5	p	½	112	186 57	73 20	38 14	42 41	38 14	38 26	42 42
17	$\bar{e}$	$\bar{1}0$	$\bar{1}01$	190 54	305 27	270 31	46 38	$\bar{9}0$ 31	$\bar{9}0$ 31	46 38
2	f	01	011	199 44	213 16	178 20	55 28	1 40	1 47	55 33
3	f	01	011	19945	3658	2 02	55 29	2 02	1 47	55 33
16	g	1	111	205 31	72 23	37 27	61 15	37 27	37 45	61 11
14	$\bar{h}$	$\bar{2}0$	$\bar{2}01$	209 01	305 06	270 10	65 45	$\bar{9}0$ 10	$\bar{9}0$ 10	64 45
15	h	20	201	209 44	125 01	90 05	65 28	90 05	90 01	65 25
8	b	0 ∞	010	234 21	214 54	179 58	90 05	0 02	00 00	89 58
12	b	0 ∞	010	234 16	35 09	0 13	90 00	0 13	00 00	89 58
7	m	∞1	110	23403	251 11	216 15	89 47	36 15	3636	8958
9	m	∞1	110	234 18	178 25	143 29	90 02	36 31	3636	8958
11	m	∞1	110	23420	7056	**36** 00	90 04	36 00	36 36	89 58
13	m	∞1	110	234 14	357 57	323 01	89 58	36 59	36 36	89 58
6	a	∞0	100	234 00	305 00	270 04	89 44	90 04	9001	8958
10	a	∞0	100	234 19	124 58	90 02	90 03	90 02	90 01	89 58

CRYSTAL TABLE NO. II

OXALATO TETRAMMINE COBALTI DICHROMATE

Results and table of forms


$\begin{bmatrix} C_2O_4 \\ Co(NH_3)_4 \end{bmatrix}_2 Cr_2O_7.H_2O$, Monalinic

142 of the best faces from
10 crystals averaged

Form	Symbol, M	Angles		Form	Symbol, M	Angles	
		φ	P			φ	ρ
c	001	90°00′	2°35′	h	201	90°00′	65°35′
p	112	3840	4243	$\bar{h}$	$\bar{2}01$	$\bar{9}0$ 00	64 45
$\bar{e}$	$\bar{1}01$	$\bar{9}0$ 07	46 35	b	010	00 00	89 56
f	011	144	5534	m	110	36 32	89 58
g	111	3727	6127	a	100	90 06	90 00

Forms (p), (f) and ($\bar{h}$) uniformly excellent and used to calculate p_0 and q_0.

CRYSTAL TABLE NO. II (Concluded)

POLAR ELEMENTS

$\epsilon' = 0\ 04512$ ha $= 1.0000$ $q_0 = 1.4484$

$p_0' = 1.0683$ $\epsilon = 0.04307$ $r_0 = 1.0000$

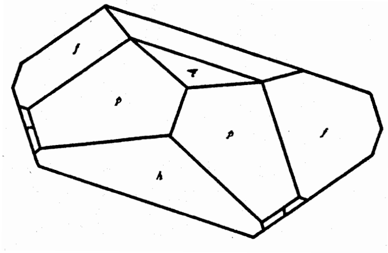
$q_0' = 1.4499$ $p_0 = 1.0672$ $\mu = 87°25'$

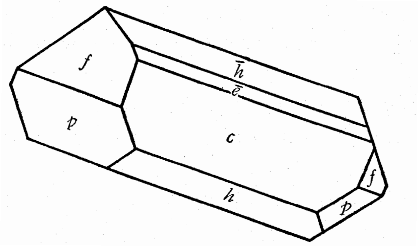
LINEAR ELEMENTS

$a : b : c$ $\beta = 92°35'$

$1.3586:1:1.4484$

The legend used is the usual one of Goldschmidt. (ρ) is the angle of the face normal from the vertical pole or may be thought of as the co-latitude (φ) is the angle from a suitable horizontal meridian, and may be thought of as the longitude.





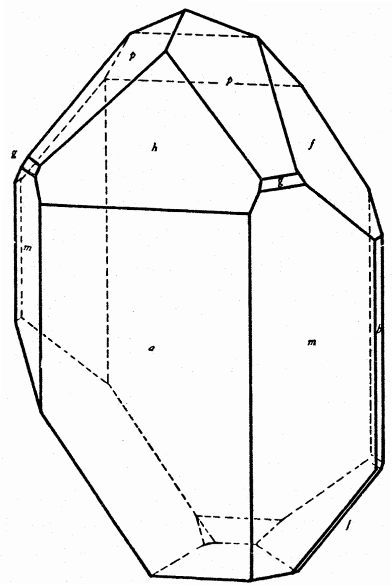


Fig. 2.—Oxalato tetrammine cobalti dichromate, monoclinic (hemihedral habit).

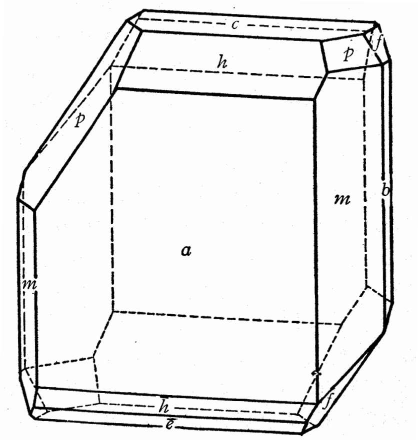


Fig. 3.—Oxalato tetrammine cobalti dichromate, monoclinic (regular habit).

CRYSTAL TABLE NO. III

OXALATO TETRAMMINE COBALTI CHROMATE

Measurement of a typical crystal, see Fig. 4

$\left[\begin{matrix}C_2O_4\\Co(NH_3)_4\end{matrix}\right]_2CrO_4$, Triclinic

$H_0 = 144°14'$
$V_0 =$ **(see below)**

No.	Let.	Symbols G.	Symbols M.	Measured H	Measured V	V − Vo	Av. angles from 12 crystals (φ)	Av. angles from 12 crystals (ρ)
1	c	0	001	**176°18'**	**43°48'**	89°40'	89°40'	32°25'
2	$\bar{O}$	$\bar{\tfrac{1}{2}}\,\bar{1}$	$\bar{1}\bar{2}1$	**188 17**	**136 37**	182 14	$\bar{2}$ 14	44 25
3	h	20	201	**Not** on **this crystal**			90 05	73 23
7	0	$\bar{\tfrac{1}{2}}\,\bar{1}$	$\bar{1}21$	**185** *25*	**313 13**	357 58	$\bar{1}77$ 58	44 45
20	ē	$\bar{1}0$	$\bar{1}01$	**179 24**	**224 26**	270 40	$\bar{9}0$ 40	35 12
4	M	$\infty\bar{1}$	$1\bar{1}0$	**234 10**	**100 38**	146 00	146 00	90 00
5	a	$\infty 0$	100	**234 30**	**44 23**	90 15	90 15	90 00
6	m	$\infty 1$	110	**234 13**	**348 50**	34 19	34 19	90 00
8	M	$\infty\bar{1}$	$1\bar{1}0$	**234 10**	**281 00**	326 00	146 00	90 00
9	a	$\infty 0$	100	**234 28**	**224 18**	270 15	90 15	90 00
10	m	$\infty 1$	110	**234 15**	**167 07**	214 19	34 19	90 00

No actual values for V_0 were obtained, but the (V) values were orientated by getting the best average angle between like faces from twelve different crystals. Face *(5)* was then set at 90° and from the angles obtained all other faces were orientated with respect to this one. The plot of these values (V') showed that it was necessary to move all these values clockwise 0.15' in order that zone (0–01) be parallel to the horizontal meridian. This gave at once the necessary known terms to calculate the polar elements. This procedure was necessary because no (010) face was present on any of the crystals examined. Even though these crystals appeared to be very brilliant, they gave many blurred and ghost signals. For this reason the calculations were made entirely from averaged values. The compound was at first thought to be monoclinic, and faces 5, 1, **3,** 20 and 9 to be in the plane of symmetry. Because of the blurred signals the variation of the measurements from monoclinic values were within the limit of reading error. That the crystal was triclinic was demonstrated by examining it with polarized light. With crossed nicols an extinction angle of 8° was obtained for all faces whose face poles were parallel with the supposed symmetry plane. Hence the measurements were averaged and calculated as triclinic. The symmetry of the crystal is very close to monoclinic since angles alpha and gamma are near 90°.

A special form table for the oxalato chromate is not included, since almost each face is a separate form. The last two columns of Table III give the average angles from the measurement of twelve different crystals instead of the angles from one typical crystal for, as mentioned above, the signals from many of the faces were so poor that the calculations had to be made solely from average values. Reference to Fig. 4 will show the prominence of the forms. The results are listed below.

POLAR ELEMENTS

$x'_0 = 0.6350$	$x_0 = 0.53607$	$v = 90°15'$
$y'_0 = 0.00203$	$y_0 = 0.00172$	$\lambda = 89\ 54$
$p'_0 = 1.3434$	$p_0 = 1.1341$	$\mu = 57\ 35$
$q'_0 = 0.9864$	$q_0 = 0.8326$	$\varphi_0 = 89\ 45$
$h_0 = 1.0000$	$r_0 = 1.0000$	$\rho_0 = 32\ 25$

LINEAR ELEMENTS

$a : b : c$
$1.5767 : 1 : 1.3434$

$\alpha = 90°16'$ $\gamma = 89°30'$
$\beta = 122°26'$

CRYSTAL TABLE NO. IV

OXALATO TETRAMMINE COBALTI CHLORATE

Measurement of a typical crystal, see Fig. 5

$\left[\begin{matrix} C_2O_4 \\ Co(NH_3)_4 \end{matrix}\right]ClO_3$, Triclinic

$H_0 = 00°00'$
$V_0 = 148°07'$

		Symbol		Measured		Orientated	**Calculated**	
No.	Let.	G.	M.	H	V	V − V0	φ	ρ
1	b	0	010	90"00'	328°07'	180°00'	0°00'	90°00'
2	n	$1\bar{1}$	$1\bar{1}0$	90 00	291 44	142 37	142 37	90 00
3	t	$\infty 1\bar{\frac{1}{2}}$	$2\bar{1}0$	90 00	273 11	125 04	125 04	90 00
4	a	$\infty 0$	100	90 00	238 11	90 04	90 04	90 00
5	r	$\infty 1\frac{1}{2}$	210	90 00	203 05	55 28	55 28	90 00
6	m	$\infty 1$	110	90 00	185 03	36 56	35 56	90 00
7	n	$\infty 1\bar{1}$	$1\bar{1}0$	9000	11146	323 39	142 39	90 00
8	t	$\infty 1\bar{\frac{1}{2}}$	$2\bar{1}0$	90 00	92 41	304 34	124 34	90 00
9	a	$\infty 0$	100	90 00	57 49	269 42	89 42	90 00
10	r	$\infty 1\frac{1}{2}$	210	90 00	23 37	235 30	55 30	90 00
11	m	$\infty 1$	110	90 00	4 29	216 20	36 22	90 00
12	$\bar{P}$	$\frac{1}{2}$	$\bar{1}\bar{1}2$	41 36	359 48	211 41	$\bar{3}1$ 41	41 36
13	P	$\frac{1}{2}$	$\bar{1}12$	4202	11544	327 37	$\bar{1}47$ 35	42 02
14	c	0	001	458	23601	87 54	87 54	4 58

CRYSTAL TABLE NO. V

OXALATO TETRAMMINE COBALTI CHLORATE

Results and table of forms

$\left[\begin{matrix} C_2O_4 \\ Co(NH_3)_4 \end{matrix}\right]ClO_3$, Triclinic

Average of 80 best faces
from six crystals

		Angles			Symbol,	Angles	
Form	Symbol, M	φ	ρ	Form	M	φ	ρ
a	100	89°58'	90°00'	r	210	55°34'	90°00'
b	010	00 00	90 00	t	$2\bar{1}0$	124 29	90 00
c	001	87 45	4 58	$\bar{P}$	$\bar{1}\bar{1}1$	$\bar{3}1$ 46	41 36
m	110	36 52	90 00	P	$\bar{1}11$	$\bar{1}47$ 35	42 08
n	$1\bar{1}0$	143 20	90 00				

POLAR ELEMENTS

$x'_0 = 0.08683$	$p'_0 = 1.1260$	$(\varphi_0) = 87°45'$
$y'_0 = 0.00341$	$q'_0 = 1.5185$	$(\rho_0) = 4°58'$
$x_0 = 0.08651$	$p_0 = 1.1218$	$(\lambda) = 89°48'$
$y_0 = 0.00340$	$q_0 = 1.5128$	$(\mu) = 85°02'$
$h_0 = 1.0000$	$r_0 = 1.0000$	$(v) = 89°58'$

CRYSTAL TABLE NO. V (Concluded)

LINEAR ELEMENTS

$a : b : c$	
1.3536 : 1 : 1.5185	**(*a*)** = 90°12′ (γ) = 79°26′ (β) = 98°52′

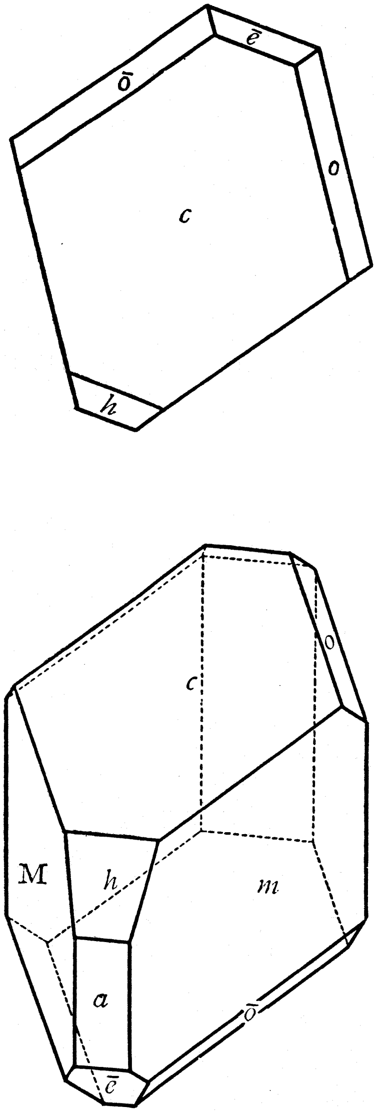


Fig. 4.—Oxalato tetrammine cobalti chromate, triclinic.

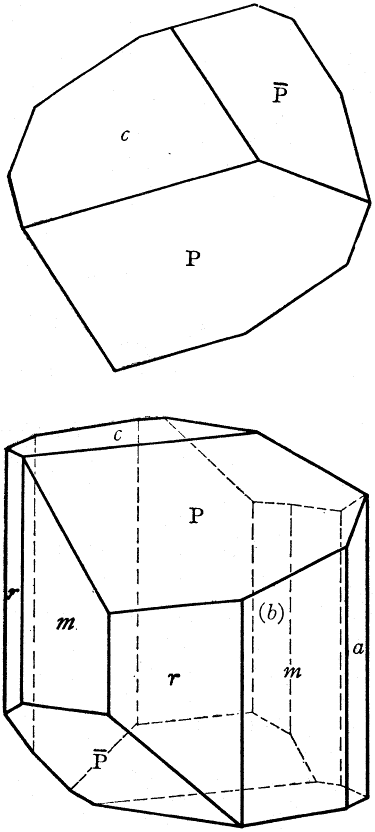


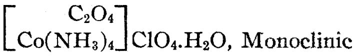
Fig. 5.—Oxalato tetrammine cobalti chlorate, triclinic (drawn with *b* front).

CRYSTAL TABLE NO. VI

OXALATO TETRAMMINE COBALTI PERCHLORATE

Results and table of forms

The number of forms developed on this compound is so small that all the necessary data can be included in one table.



$\left[\begin{matrix}C_2O_4\\Co(NH_3)_4\end{matrix}\right]ClO_4.H_2O$, Monoclinic

Form	Symbol, M	Angles φ	ρ	Form	Symbol, M	Angles φ	ρ
a	100	90°00′	90°00′	ē	$\bar{2}01$	$\bar{9}0$°00′	38°06′
b	010	00 00	90 00	m	110	33 26	90 00
c	001	90 00	9 58	**r**	210	52 45	90 00
d	012	13 15	35 57				

See Fig. 6 for **face development.**

POLAR ELEMENTS

$\epsilon' = 0\ 1740$ $\epsilon = 0.1714$

$p_0' = 0.4791$ $p_0 = 0.4719$ $\mu = 80°02'$

$q_0' = 1\ 4634$ $q_0 = 1.4414$

$h_0 = 1.0000$ $r_0 = 1.0000$

LINEAR ELEMENTS

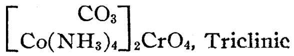
$a : b : c$ $\beta = 99°58'$

1.5508: 1 : 1.4634

CRYSTAL TABLE NO. VII

CARBONATO TETRAMMINE COBALTI CHROMATE

Measurement of a typical crystal, see Fig. 7



$\left[\begin{matrix}CO_3\\Co(NH_3)_4\end{matrix}\right]_2CrO_4$, Triclinic

$H_0 = 234°10'$

$V_0 =$ **(see below)**

No.	Let.	Symbol G.	M.	Measured H	V	Orientated V⁻	V⁺	Calculated φ	ρ
1(18)	**c**	0	001	165°17′	3°50′	91°38′	88°22′	88°22′	21°07′
2(17)	**e**	10	101	204 16	3 39	91 27	88 33	88 33	60 04
3(16)	ē	$\bar{1}0$	$\bar{1}01$	188 54	185 05	271 12	268 48	$\bar{8}8$ 48	44 23
4	G	$\bar{1}1$	$\bar{1}11$	201 00	132 16	219 30	320 30	$\bar{1}40$ 30	56 58
6(13)	$\bar{f}$	$0\bar{1}$	0 i l	195 49	230 35	17 46	162 14	162 14	51 31
20(15)	$\bar{P}$	$\bar{\frac{1}{2}}$	$\overline{11}2$	178 36	246 37	357 07	205 53	25 53	34 23
21(14)	$\bar{G}$	$\bar{1}$	$\overline{11}1$	201 46	234 18	321 53	218 07	$\bar{3}8$ 07	57 45
7	b	0 m	010	234 23	92 07	180 00	0 00	00 00	90 00
8	m	∞1	110	234 13	44 48	132 33	47 27	47 27	90 00
9	M	$\infty\bar{1}$	$1\bar{1}0$	234 17	321 38	49 16	130 44	130 44	90 00
10	**b**	0 m	010	234 08	272 22	00 00	180 00	00 00	90 00
11	m	∞1	110	234 11	225 00	312 33	227 27	47 27	90 00
12	M	$\infty\bar{1}$	$1\bar{1}0$	234 05	140 35	229 16	310 44	130 44	90 00
19	**a**	∞0	100	234 10	182 51	91 20	88 40	88 40	90 00
22	a	∞0	100	234 57	**3** 33	271 20	268 40	88 40	90 00

The ordinary methods for determining (V_0) could not be employed here. After plotting, faces (7) and (10) were found to be (010) and when correctly rotated should have a (φ) angle of zero and be at zero on the projection. The angles between all forms measured were determined and the values in each case averaged. By this means the best average angle between that form and (010) was found. This gave a set of vertical readings which are recorded in column (V^-) of Table VII. By examining the plot it was found that the negative end of the crystal had been measured and sketched. The (V^-) values, therefore, were adjusted to their complementary position.

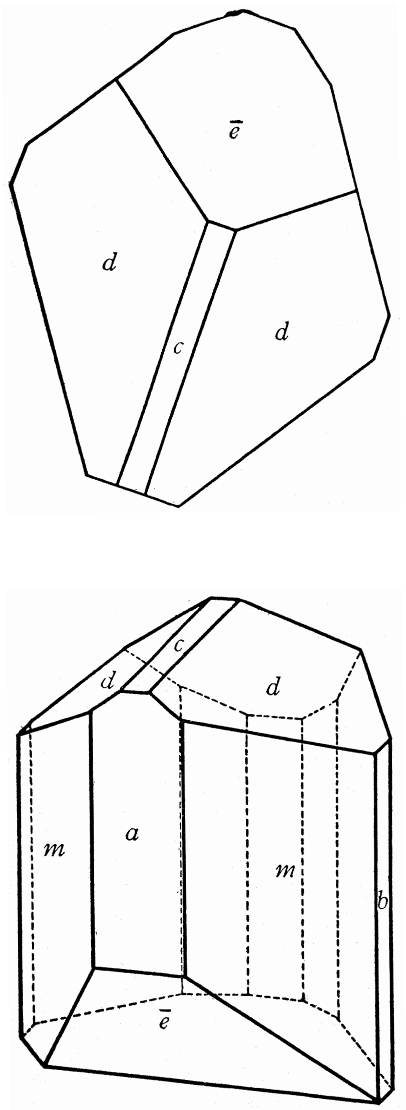


Fig. 6.—Oxalato tetrammine cobalti perchlorate, monoclinic.

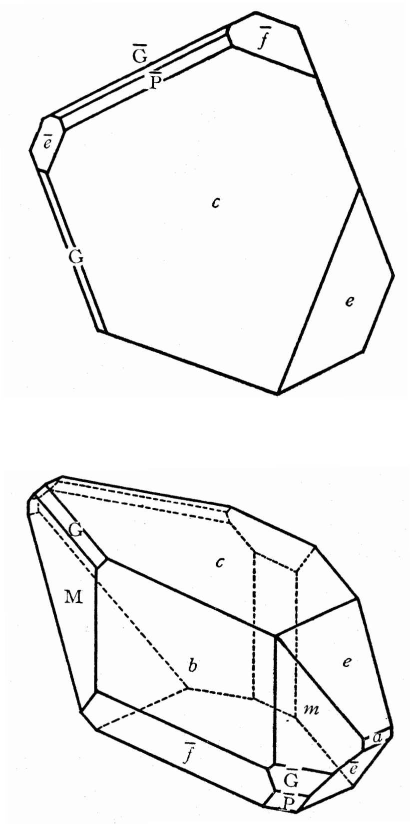


Fig. 7.—Carbonato tetramtnine cobalti chromate, triclinic (drawn with *b* front).

The values in column ($V+$) are the results of this readjustment, and from them the (φ) values were calculated.

CRYSTAL TABLE NO. VIII

CARBONATO TETRAMMINE COBALTI CHROMATE

Results and table of forms

Form	Symbol, M	Angles φ	ρ	Form	M	Angles φ	ρ
a	**100**	88°40′	90°00′	$\bar{G}$	$\bar{1}\bar{1}1$	$\bar{3}$8°07′	57°45′
b	010	00 00	**90** 00	**$\bar{f}$**	$0\bar{1}1$	**162 41**	**51 31**
c	**001**	**88 22**	**21 07**	$\bar{P}$	$\bar{1}\bar{1}2$	$\bar{2}$5 53	**34 23**
e	**101**	**88 33**	**60 04**	**m**	**110**	**47 27**	**90 00**
ē	**$\bar{1}$01**	**88 48**	**44 23**	**M**	**110**	**130 44**	**90 00**
G	**$\bar{1}$11**	**$\bar{1}$40 30**	**56 58**	**See figure for development of forms.**			

POLAR ELEMENTS

$x_0' = 0.3718$ $p_0' = 1.3497$ $(\varphi_0) = 88°22'$

$y_0' = 0.0104$ $q_0' = 1.2060$ $(\rho_0) = 21°07'$

$x_0 = 0.3632$ $p_0 = 1.2592$ $(\tau) = 89°27'$

$y_0 = 0.00967$ $q_0 = 1.1250$ $(\mu) = 68°42'$

$h_0 = 1.0000$ $r_0 = 1.0000$ $(\nu) = 88°40'$

LINEAR ELEMENTS

$a : b : c$ $(\alpha) = 90°05'$ $(\gamma) = 91°14'$

0,9589 : 1 : 1.5197 $(\beta) = 111°17'$

Conclusions

As anticipated, the crystalline form and habit of a compound was affected as one of the groups was substituted. It appears that the structural type of all the oxalato tetramine compounds studied is the same, because the symmetry of their crystalline forms bear simple relations to one another. If this is correct, then the deforming influence of the substituted anions upon the structure of the oxalato group may be stated as having the following increasing order: Cr_2O_7, ClO_4, ClO_3 and CrO_4.

From infra-red absorption data, Rawlins[10] has suggested that in compounds of the type ABX, the AB portion of the compound may preserve a well-defined skeleton structure in various compounds as various atoms or groups are substituted for the X portion. Similarly, the oxalato tetrammines described in this paper may be given a type formula as follows—AXY. In the compounds described by Rawlins the two cations preserve a definite structure in various combinations. In the oxalato complexes, or in any acido ammonia complex, it is entirely possible that the AX portion of the molecule preserves a definite skeleton structure which is merely altered or deformed as various substitutions of (Y) are performed. This is merely another definition of a complex ion, and states that two atoms or groups which under some conditions exist as a single anion and cation are now combined in some way so that the combination acts as a definite new ion.

[10] **Rawlins, *Trans. Faraday Soc., 25* 283 (1929).**

Complex ions are usually considered in the same way as more simple ions, *i. e.*, to be more or less spherical. Pauling[11] has discussed the ionic radii of a few complex ions and their radius ratios. There is no literature which is opposed to assigning a definite skeleton structure to a complex ion of the type $AX^{\pm}$, and indeed such a structure appears to exist. Quantitative verification of the exact effect of the substituted anion in these oxalato complexes will be possible only after an x-ray determination of their structural types and cell dimensions. If the structural type is not altered by the substitution of the anion, then, as stated in the introduction, the axial ratios of a series of compounds which contain a complex ion will be adequate to measure the effect produced by the substituted anion.

Summary

1. The following new compounds have been prepared and analyzed: the chromate, dichromate and chlorate of the oxalato tetrammine series of cobalt, also the chromate and dichromate of the carbonato series.

2. Crystals of all the above compounds, except the carbonato dichromate have been prepared. These crystals, in addition to the oxalato perchlorate, were measured and the crystalline forms determined.

3. The difficulty encountered in preparing the oxalato chromate suggests an interesting example of the manner in which affinity of ions for each other may limit their deforming influence.

4. It is suggested that the complex oxalato cobalti tetrammine ion, and other acido complexes, may have a definite skeleton structure in crystals containing this complex ion, and that the substitution of various anions merely alters the shape and dimensions of this structure.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A PERIODIC ARRANGEMENT OF THE ATOMIC NUCLEI. THE PREDICTION OF ISOTOPES

BY HERRICK L. JOHNSTON

RECEIVED APRIL 29, 1931 PUBLISHED AUGUST 5, 1931

Interesting and suggestive regularities in the existence and abundance of mass numbers have been called to attention by various authors in recent years.[1] The most thorough tabulations of such empirical regularities are those of Harkins. The discovery of such relationships is useful not only in

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[11] L. Pauling, THIS JOURNAL, 49, 765 (1927).

[1] (a) Harkins, *ibid.*, 39, 859 (1917); 42, 1976 (1920); 43, 1050 (1921); 45, 1426 (1923); *Phil. Mag.*, 42, 331 (1921); *Phys. Rev.*, 15, 85 (1920); *J. Franklin Institute*, 195, 554 (1923). *Chem. Reviews*. 5, 371 (1928); (b) Beck, *Z. Physik*, 47, 407 (1928); (c) Barton, *Phys. Rev.*, 35, 408 (1930); (d) Latimer, THIS JOURNAL, 53, 981 (1931).

offering a basis for the prediction of new isotopes but also in providing a key to the as yet obscure nature of nuclear structure. In these two respects such empirical tabulations play a role entirely analogous to that of the Periodic Table in the search for new elements and in the explanation of the structure lying outside the nucleus.

A new arrangement of the atoms in order of isotopic mass numbers is presented in Table I, which may be referred to as a Periodic Table of the nucleus. We believe that this arrangement possesses the advantage of easy comprehension and is, at the same time, suggestive both of unambiguous predictions of many undiscovered isotopes and of significant relationships with respect to nuclear structure.

In this table the atoms are first classified into four main types, differing in respect to the numbers of "free" protons in the respective nuclei. These four types are: the 4 N type, with atomic weight evenly divisible by four, which may be arbitrarily regarded as composed of exactly *N* alpha particles; the 4 N + 1 type, made up of N alpha particles plus one "free" proton; the 4 N + 2 type, consisting of N alpha particles with two additional protons; and the 4 *N* + **3** type, with three extra protons. This classification is made arbitrarily from consideration of mass number alone and is not regarded as precluding the possibility that in some nuclei four or more "free" protons may exist without combination into an alpha particle. N, of course, differs for various atoms and, in general, may assume any value from 0 to about 60, the latter corresponding to the mean value of N for isotopes of uranium. Successive rows in the table are characterized by successive values of N, given for convenience at the extreme left of the columns for each main type. A further classification is carried out, based on the numbers of "free" electrons in respective nuclei. The numbers which stand at the heads of columns represent the numbers of *nuclear* electrons in *excess* of 2 *N*. These may be arbitrarily taken as nuclear electrons outside of alpha particles.

Atoms experimentally observed and reported in the literature[2] are shown in bold-faced type. O^{17} and O^{18},[3] C^{13},[4] N^{15},[5] Be^8,[6] and Cl^{39},[7] were observed

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[2] It is perhaps worthy of comment that about twenty-five isotopes have been reported since this table was prepared in its present outline several months ago. That these have fitted into the table without exception, as the reader may observe, inspires confidence in the use of the table for further predictions.

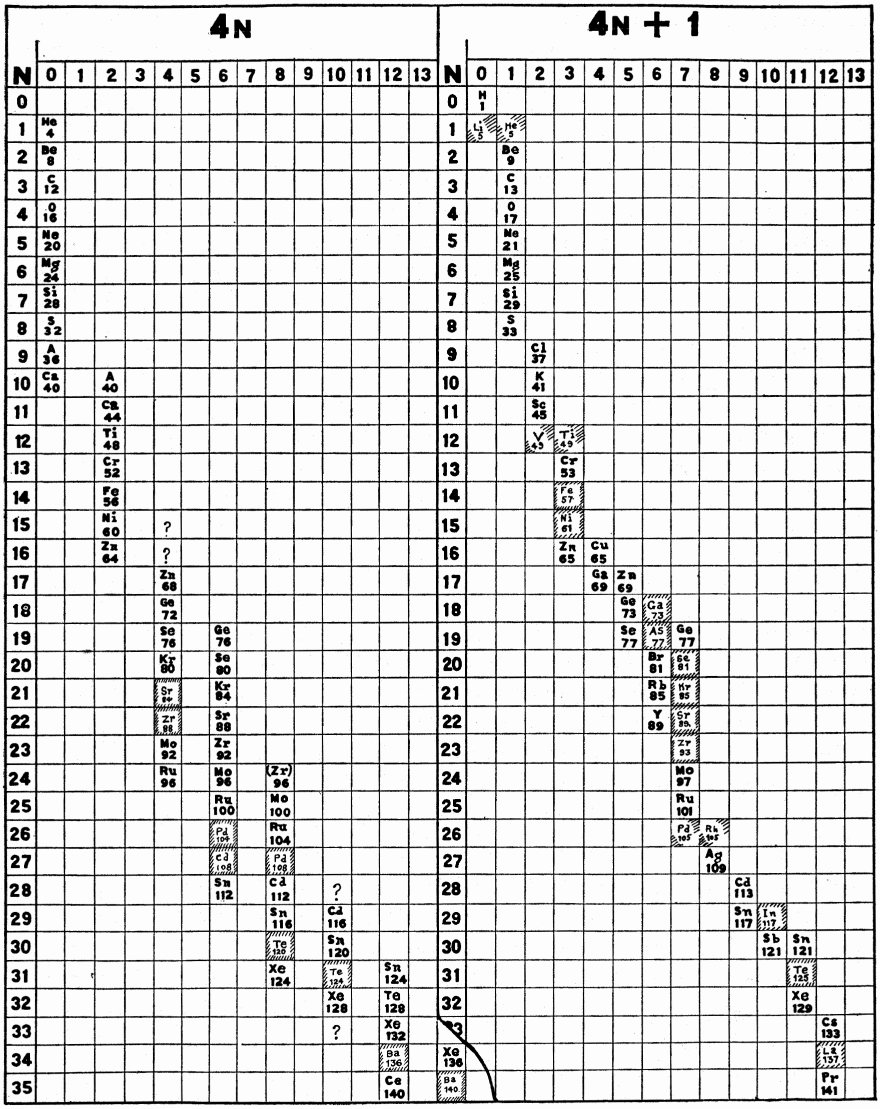
[3] Giauque and Johnston, THIS JOURNAL, 51, 1436, 3528 (1929). See also reference 5 and Ruchardt, *Naturwiss.*, 18, 534 (1930).

[4] King and Birge, *Nature,* 124, 127 (1929); *Astrophys. J.*, *72,* 19 (1930); Birge, *Nature,* 124, 182 (1929).

[5] Naude, *Phys. Rev.*, *36,* 333 (1930); see also Herzberg, *Z. physik. Chem.*, [B] 9, 43 (1930). Note. Herzberg's prediction of N^{16} on a "theoretical" ground, and which he failed to find experimentally, is ruled out by Table I.

Watson and Parker, *Phys. Rev.*, **37,** 167 (1931).

[7] Becker, *Z. Physik,* 59, 583 *(1930).* Ashley and Jenkins failed to confirm this iso-



4N

N	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0														
1	He 4													
2	Be 8													
3	C 12													
4	O 16													
5	Ne 20													
6	Mg 24													
7	Si 28													
8	S 32													
9	A 36													
10	Ca 40		A 40											
11			Ca 44											
12			Ti 48											
13			Cr 52											
14			Fe 56											
15			Ni 60		?									
16			Zn 64		?									
17					Zn 68									
18					Ge 72									
19					Se 76		Ge 76							
20					Kr 80		Se 80							
21					Sr 84		Kr 84							
22					Zr 88		Sr 88							
23					Mo 92		Zr 92							
24					Ru 96		Mo 96		(Zr) 96					
25							Ru 100		Mo 100					
26							Pd 104		Ru 104					
27							Cd 108		Pd 108					
28							Sn 112		Cd 112		?			
29									Sn 116		Cd 116			
30									Te 120		Sn 120			
31									Xe 124		Te 124		Sn 124	
32											Xe 128		Te 128	
33											?		Xe 132	
34													Ba 136	
35													Ce 140	

4N + 1

N	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	H 1													
1	Li 5	He 5												
2		Be 9												
3		C 13												
4		O 17												
5		Ne 21												
6		Mg 25												
7		Si 29												
8		S 33												
9			Cl 37											
10			K 41											
11			Sc 45											
12			V 45	Ti 49										
13				Cr 53										
14				Fe 57										
15				Ni 61										
16				Zn 65	Cu 65									
17					Ga 69	Zn 69								
18						Ge 73	Ga 73							
19						Se 77	As 77	Ge 77						
20							Br 81	Se 81						
21							Rb 85	Kr 85						
22							Y 89	Sr 89						
23								Zr 93						
24								Mo 97						
25								Ru 101						
26								Pd 105	Rh 105					
27									Ag 109					
28										Cd 113				
29										Sn 117	In 117			
30											Sb 121	Sn 121		
31												Te 125		
32												Xe 129		
33													Cs 133	
34	Xe 136												La 137	
35	Ba 140												Pr 141	

A PERIODIC TABLE OF

spectroscopically. The remainder were found with the mass spectrograph.[8,9]

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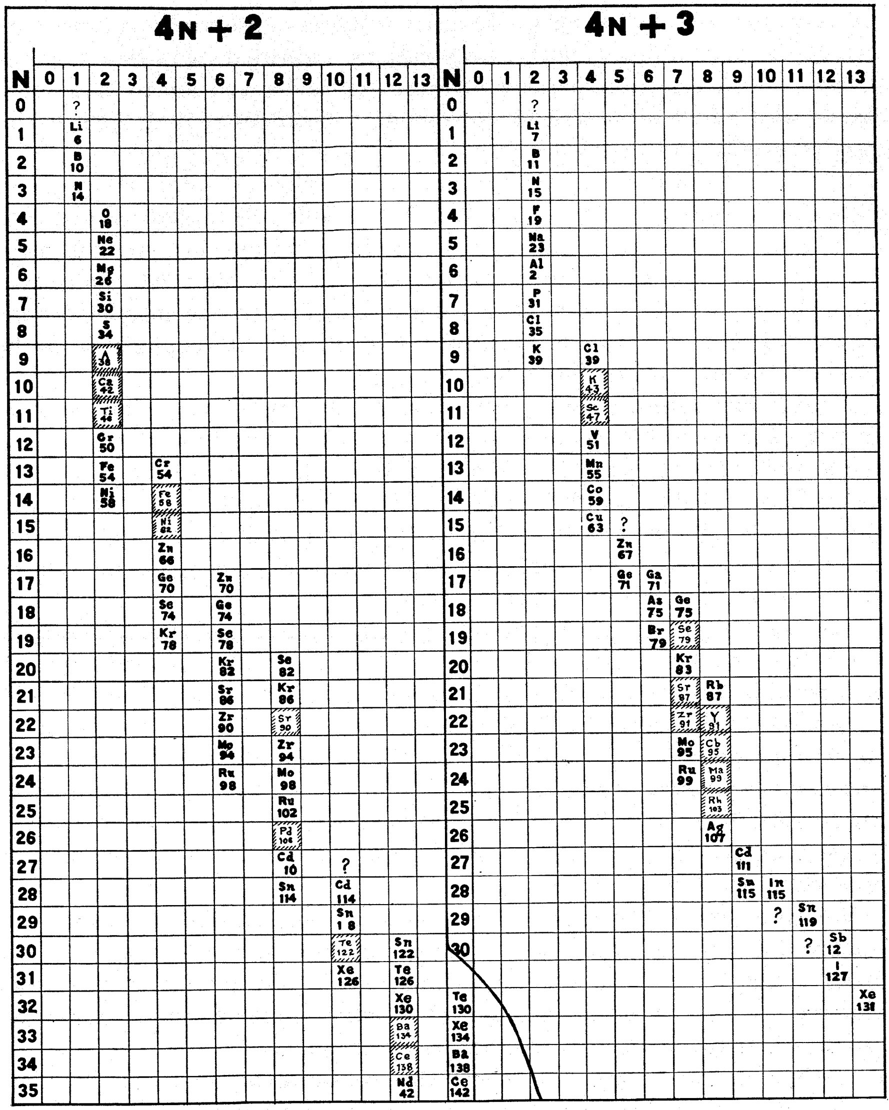
tope in the band spectrum of AgCl [Washington meeting of the American Physical Society, April 30 to May 2 (1931)]. On the other hand, Hettner and Bohme [*Naturwiss.*, **11**, 252 (1931)] claim to have confirmed Cl^{39} by new measurements on the 1.7μ band of HCl.

[8] Hogness and Kvalnes, *Nature*, **122**, 441 (1928).

[9] Aston, *Phil. Mag.*, 49, 1199 (1925); *Proc. Roy. Soc.* (London), [A] **115**, 487 (1927); [A] **130**, 302 (1931); *Nature*, **122**, 167, 345 (1928); **126**, 200, 348 (1930); **127**, 233 (1931).



4N + 2

N	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0		?												
1		Li 6												
2		B 10												
3		N 14												
4			O 18											
5			Ne 22											
6			Mg 26											
7			Si 30											
8			S 34											
9			A 38											
10			Ca 42											
11			Ti 46											
12			Cr 50											
13			Fe 54		Cr 54									
14			Ni 58		Fe 58									
15					Ni 62									
16					Zn 66									
17					Ge 70		Zn 70							
18					Se 74		Ge 74							
19					Kr 78		Se 78							
20							Kr 82		Se 82					
21							Sr 86		Kr 86					
22							Zr 90		Sr 90					
23							Mo 94		Zr 94					
24							Ru 98		Mo 98					
25									Ru 102					
26									Pd 106					
27									Cd 10		?			
28									Sn 114		Cd 114			
29											Sn 1 8			
30											Te 122		Sn 122	
31											Xe 126		Te 126	
32													Xe 130	
33													Ba 134	
34													Ce 138	
35													Nd 42	

4N + 3

N	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0			?											
1			Li 7											
2			B 11											
3			N 15											
4			F 19											
5			Na 23											
6			Al 2											
7			P 31											
8			Cl 35											
9			K 39		Cl 39									
10					K 43									
11					Sc 47									
12					V 51									
13					Mn 55									
14					Co 59									
15					Cu 63	?								
16						Zn 67								
17						Ge 71	Ga 71							
18							As 75	Ge 75						
19							Br 79	Se 79						
20								Kr 83						
21								Sr 87	Rb 87					
22								Zr 91	Y 91					
23								Mo 95	Cb 95					
24								Ru 99	Ma 99					
25									Rh 103					
26									Ag 107					
27										Cd 111				
28										Sn 115	In 115			
29											?	Sn 119		
30												?	Sb 12	
													I 127	
Te 130														Xe 131
Xe 134														
Ba 138														
Ce 142														

THE ATOMIC NUCLEI

Isotopes as yet undiscovered but whose existence is predicted unambiguously by the regularities in the table, are marked lightly in squares bordered with hachuring. In three instances which occur in the 4 N + 1 column it is safe to predict only that either one, or perhaps both, of a pair of atoms must exist. These qualified predictions are indicated by means of hachuring at diagonally opposite corners. We do not feel that there is, in general,' sufficient basis to predict either upward or downward extrapolations of members of columns. In a few instances observed regularities increase the probability of such extrapolations, indicated by question marks. However, the question marks which represent extrapolation to mass numbers 2 and **3** in positions which correspond to isotopes of hydrogen are intended literally as question marks.

The table is carried only to mass numbers of about 140 since the group of elements with mass numbers ranging from about 140 to 200 has received very little investigation. Lead, mercury, tungsten and bismuth fall regularly in order in the positions surrounding mass number 200, indicating that the regularities observed in the table persist to the heavier atoms. La^{139}, Nd^{144}, Nd^{145} and Nd^{146} are also known, and fit regularly into the table, but were omitted through an oversight.

Aston[9] has recently called attention to the existence of an isobaric triplet of mass 96. This table predicts the existence, as well, of isobaric triplets of masses 77 and 124. It is probable that several others exist in the latter half of Table I, although the uncertainty as to the upper and lower limits of the members of the columns does not permit definite predictions in other cases. It is not improbable that isobaric quadruplets may make their appearance among the heavy atoms.

We wish to point out certain very obvious regularities characteristic of the respective four chief nuclear types. The 4 N group is made up of a staggered progression occupying all *even-numbered* columns. The 4 N + 1 group, on the other hand, occupies *all* columns. The 4 N + 2 group makes its first progression in the manner of the preceding group *and then continues in the fashion of the 4 N group.* The *4 N +* **3** group makes its first progression like the 4 N group, *and then continues like the 4 N + 1 group.* These regularities must possess some significance with respect to structural relationships within the nuclei.

We were at first inclined to doubt the authenticity of Ge^{77} until we observed at approximately the same position in column 7 of the 4 N + **3** group a sequence of at least seven atoms. We do not know what significance can be attached to these rather long sequences in the midst of groups consisting ordinarily of much shorter sequences.

In the light of the table we believe that we can make some modification of Harkins' abundance rules[10] in a way which improves the usefulness of the latter. Thus Harkins' statement that atomic species which contain even numbers of nuclear electrons are much more plentiful than those which contain odd numbers can be better expressed as follows: Atoms made up of even numbers of protons as a rule do not contain odd numbers of nuclear electrons, while atoms of odd mass are distributed between even and odd nuclear electron types without essential distinction as to abundance. Likewise the distinction between species abundance (not gross abundance) of even and **add** mass numbers seems to be overemphasized. Eighty-six known isotopes of even mass are listed in the table and nineteen more predicted with certainty. Sixty-four known isotopes of odd mass number are listed and twenty-three more are predicted. Nor is there any essential difference between the numbers of atomic species in the 4 N and the 4 N + 2 groups. In terms of gross abundance, of course, O^{16} and Si^{28} alone furnish approximately three-fourths of matter as has been pointed out by Harkins[1a] and, in general, the prevalence of even mass types is well established. Even here there are frequent instances, particularly in higher atomic weights, in which the percentage of a particular species of odd mass among isotopes of a given element is considerably higher than one would be led to predict from a statement of the more general abundance ratios.

Since preparing the present table we have observed that the tabulation of Beck[1"] is capable of leading to the same predictions of isotopes as is the present arrangement, since it contains the same sequences of atoms which appear in the columns of Table I although the general plan of arrangement is quite different and, we believe, more difficult to comprehend. For atoms of mass 4 N, Latimer's[1d] tabulation is closely analagous to the present one. Professor Urey[10] has recently arrived at a, formally, quite different graphical plot of mass numbers which he informs us leads to predictions of isotopes nearly identical with those in this table.

We are at present engaged in the program of searching for predicted isotopes by means of spectroscopic analysis.

We do not attempt to offer, at present, any theoretical explanation of the observed arrangement.

Summary

A tabular arrangement of known isotopic species of atoms is presented, being essentially a Periodic Table of the Atomic Nuclei.

On the basis of the table, many undiscovered isotopes are predicted. The probable existence of certain isobaric triplets is pointed out.

Attention is called to significant relationships between the numbers of "free" protons and "free" electrons in atomic nuclei.

Certain of Harkins' abundance rules are restated in an amended form.

No theoretical explanation is offered for the observed regularities.

COLUMBUS, OHIO

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[10] Urey, THIS JOURNAL, 53, 2872 (1931).

[CONTRIBUTION NO. 660 FROM THE DEPARTMENT OF CHEMISTRY. COLUMBIA UNIVERSITY]

THE NATURAL SYSTEM OF ATOMIC NUCLEI

BY HAROLD C. UREY

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Recently Barton[1] has shown several interesting regularities in the known atomic nuclei when these are plotted with the numbers of nuclear protons and electrons as coordinates. The known nuclei lie on this diagram between two lines whose slopes are 2 and 1.61,[2] the points for nuclei of low mass lie on or near the first line while, with increasing mass, the points approach the second line so that the occupied region of the diagram is a band, narrow near the origin and wider for nuclei of higher masses. Barton pointed out that several well-defined groups of nuclei, which he called "clusters," appear in this diagram such that each cluster possesses an approximate center of symmetry. These centers of symmetry he places at P = 24, E = 12; P = 80, E = 45; and P = 124, E = 72, while Urey and Miss Johnston[3] showed that there are indications of another cluster of radioactive nuclei with a center at P = 222, E = 136. In this paper it will be shown that there are indications of another cluster with center at P = **38,** E = 20, that there is probably no cluster in the region of the diagram below A^{36}, and a correlation of these clusters with the stability of the nuclei as indicated by radioactivity and relative abundances of nuclei may exist. Further, a suggestion is made in regard to nuclei, as yet unknown, to be expected in the region from A to Cu.

Figure 1 is the proton–electron plot of the known nuclei from hydrogen to neodymium. The numbers of protons and electrons are plotted as abscissa and ordinate, respectively, with the scale drawn near the nuclei to facilitate comparison. Figure 2 is a similar plot of the radioactive nuclei in which it has been assumed that the nuclei of the actinium series have odd mass numbers.[4]

It is evident that the number of kinds of nuclei per unit length of the occupied band varies greatly with especially large numbers between P = 65 and P = 100 and between P = 110 and P = 150. There is another dense region near the radioactive elements shown in Fig, 2. The pattern of the nuclei from Li^6 to A^{36} is very regular and leads one to postulate that all possible nuclei of this region are known or that any unknown ones are very rare. Between A^{36} and Cu^{63} is a region having a very low density of points scattered in what appears to be a very irregular way on the diagram.

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[1] Barton, Phys. *Rev.,* 35, 408 (1930).

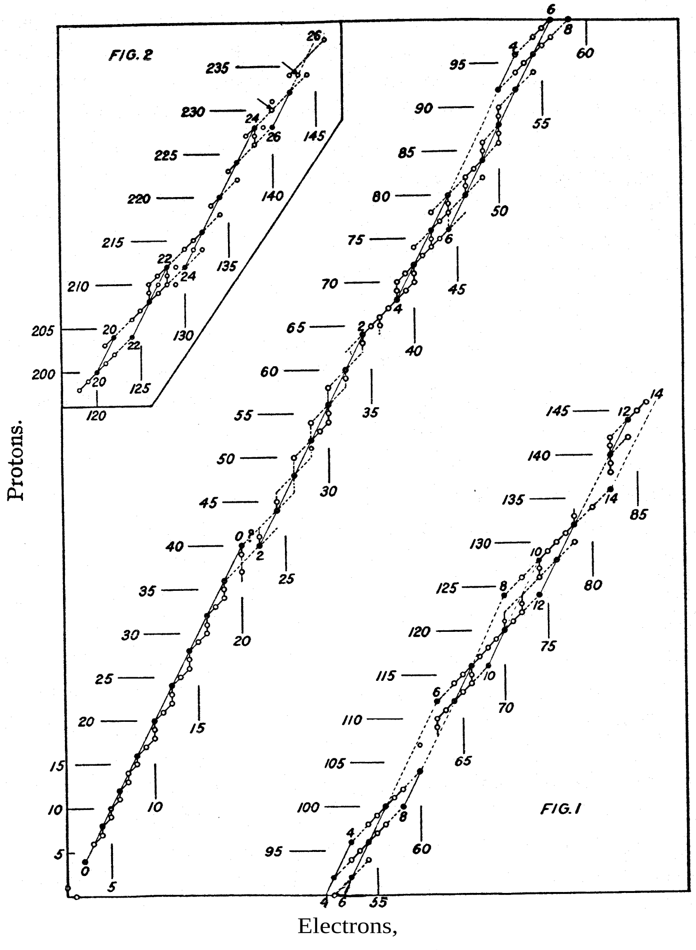
[2] Harkins, *Chem. Rev.,* 5,371–435 (1928). See this article for the many preceding references.

[3] Urey and Johnston, *Phys. Rev.,* 35,869 (1930).

[4] Aston reports that Pb^{207} is present in sufficient amounts in Norwegian broeggerite to indicate that this lead is the end-product of the actinium series.

It is almost a certainty that all possible types of nuclei in this region have not yet been detected. The removal of Be^S, C^{13}, N^{15}, O^{17}, O^{18} and Ne^{21}[5] from the diagram would cause the plot in the region of these atoms to

Fig. 2.—The proton--electron plot of the radioactive nuclei and of Hg, Pb and Bi. Io and UY both occupy the point of P = 230, *E* = 140 and UX_2 and UZ probably the point P = 234, E = 143.



Fig, 1.—The proton–electron plot of non-radioactive nuclei. There may be a Ca^{41} since K^{41} is radioactive.

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[5] Be^8, Watson and Parker, *Phys.* **Rev.,**37, **167 (1931).** C^{13}, Birge and King, ***Nature,*** 124, 127 and **182 (1929);** *Astrophys.* **J., 72, 19 (1930).** N^{15}, Naude, **Phys. Rev., 36,333 (1930);** Herzberg, *Z. physik. Chem.,* [B]9, 43 **(1930).** O^{17}, O^{18}, Giauque and **John**ston, THIS JOURNAL, 51, **1436, 3528 (1929).** Ne^{21}, Hogness and Kvalnes, **Nature,** 122, **441 (1928).**

assume an irregular appearance similar to that of the region from A^{36} to Cu^{63} and we are led to expect that more refined methods will add many more points to the latter region.[6]

In searching for a possible regularity of nuclei in the region above A^{36}, we have well-known rules in regard to the relative abundance of nuclei of different types, due mainly to Harkins.[2] The most abundant nuclei of the earth's crust are those with proton numbers divisible by 4. The solid circles of Figs. 1 and 2 are such nuclei. From helium to Ca^{40} there are ten nuclei which are multiples of the helium nucleus in so far as the numbers of protons and electrons are concerned. From A^{40} to Zn^{64} there are seven nuclei which contain two electrons in addition to an integral number of helium nuclei. This region appears fairly complete in so far as this type of nucleus is concerned. Above Zn^{64} more of these "binding" electrons are required in these nuclei with mass numbers divisible by four. These nuclei are labeled as Series 0, 2, 4, ... in the diagram; the figures represent the numbers of binding electrons present in addition to those present in the α-particles or helium nuclei present.

From O^{16} to A^{36}, three nuclei in a vertical or diagonal row is a prominent feature of the diagram. If we draw lines through all such rows of three nuclei, we secure parallelogram figures as shown by the solid lines of Fig. 1. This feature is so prominent that the completion of the figures as indicated by broken lines is the next obvious step. In completing them, the rule that no element of odd atomic number has more than two isotopes has not been violated for no exceptions to this rule are known outside the radioactive elements.[7] The diagram as so drawn predicts the existence of many more nuclei than are now known, but methods used up to the present would probably not detect isotopes whose abundance is one-thousandth of the abundance of that of the most abundant one. The recent discovery of such rare isotopes by the molecular spectra method shows that the existence of more isotopes in this region is not only possible but very probable.

This pattern for existing nuclei in the proton–electron plot was derived as indicated above, but it is really only an expression of well-known rules due to Harkins[2] in regard to the abundance of nuclei in point of numbers in the earth's crust and in meteorites and the varieties of nuclei classified according to atomic number and nuclear electrons. These can be stated as follows.

(1) The most abundant nuclei, in point of numbers, have mass numbers divisible by 4 and are at the acute angles of the parallelograms. (2)

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[6] The points Cr^{50}, Cr^{53} and Cr^{54} have recently been added by Aston, *Nature*, 126, 200 (1930).

[7] An isotope of chlorine of mass 39 has been reported by Becker [*Z. Physik*, 59, 601 (1930)], but not confirmed by Ashley and Jenkins (Washington meeting of the American Physical Society, April 30 to May 2, 1931).

Nuclei of even atomic number and even proton number are very abundant. In addition to the nuclei given under (1), this class includes the nuclei at the obtuse corners of the parallelograms. **(3)** Nuclei of even atomic number and odd numbers of nuclear electrons are less abundant. These occupy the midpoints on the diagonal sides. (4) Nuclei of odd atomic number and even number of nuclear electrons are less abundant and only two for each element are known. These occupy the midpoints of the vertical sides. (5) Finally, nuclei of odd atomic number and odd number of nuclear electrons are very rare, Li^6, B^{10} and N^{14} being the only known examples among non-radioactive nuclei. Such nuclei would occupy the centers of the parallelograms. In drawing in these parallelogram figures, then, we have only indicated the regions of the proton-electron diagram where it is most probable on the basis of the relative abundance of known nuclear types that other nuclei exist, with the additional assumption that these additional nuclear types will fall near the known nuclei having mass numbers divisible by 4.

The Structure **of** Nuclei.—This proton–electron plot with its parallelogram patterns suggests certain points in regard to nuclear structure. **A** nucleus may be considered as composed of (1) helium nuclei, (2) internal binding electrons, **(3)** additional protons and electrons. A chemical formula for a nucleus might be written $\alpha_n E_m p_k e_l$, where n gives the number of a-particles, m (always even) the number of binding electrons, k and l the numbers of additional nuclear protons and electrons, respectively. There is considerable evidence that the maximum possible number of helium nuclei is not present in all nuclei. Assuming that the protons alone contribute to the nuclear spin, it would be impossible to have nuclear spins greater than $^3/_2$, if the maximum possible number of protons and electrons were combined into helium nuclei having no spins. On the other hand, in the case of nuclei of low atomic number, either the maximum possible numbers of helium nuclei or other combinations of four protons and two electrons having about the same stability as helium nuclei are present. This is shown by the packing fraction curve, which shows a marked periodicity with atoms with mass numbers divisible by four having minimum packing fractions.[8]

Nuclei with mass numbers divisible by four may have additional binding electrons, 0, 2, 4, . . . , as indicated by the numbers of the series defined above. Latimer[9] has constructed a model of this type of nucleus in which extra pairs of electrons are bound in the interior of the nucleus in a regular way. Finally, the additional protons and electrons give the approximate parallelogram pattern of Fig. 1. Having a nucleus containing an integral number of helium nuclei, additional probable nuclei can be secured by

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[8] H. Olson, *Phys. Rev.*, 35,213 (1930).

[9] **W. M.** Latimer, THIS JOURNAL, 53,981 (1931).

adding a proton + a proton + a neutron + a neutron or a neutron + a neutron + a proton + a proton. (A "neutron" is used here as a convenient way of referring to a proton + an electron.) In the region where the series overlap, it is possible to have nuclei occupying the common obtuse corners of the overlapping series. There is the possibility that these two nuclei are not identical, for their formulas as written above differ in the number of internal binding electrons, E, and the number of external electrons, e. The internal electrons occupy some deep-lying position of the nucleus such as suggested by Latimer, while the outer electrons with the addition of two protons may form another a-particle within the nucleus. These formulas would be $\alpha_n E_m p_k e_l$ and $\alpha_n E_{m+2} p_k e_{l-2}$. Such a case is known, for Io^{230} and UY occupy the same position in the plot, which is one of these obtuse corners as can be seen in Fig. 2. UX_2 and UZ also occupy the same position but not such an obtuse corner position.

The nuclei of elements with odd atomic numbers lie toward the middle of the occupied band of this plot. In most cases no attempt is made to predict additional nuclei of odd atomic number and what predictions are attempted are based on this regularity only.

Barton's clusters seem to be due to the overlapping of these series of approximate parallelograms in certain regions. Wherever this occurs it will be possible to select some point in such a region that the rotation of half the figure through 180° will result in the many coincidences of points just as observed by Barton. The best illustration of this is given by his cluster whose center was located by him at $P = 80$, $E = 45$. Because of the discovery of additional germanium isotopes, this is no longer a very good center but the point $P = 78$, $E = 44$ is. This is due to the overlapping of Series 4 and Series 6 and the diagram as sketched in (without any thought of the cluster by the way) is completely symmetrical from $P = 68$, $E = 38$ to $P = 88$, $E = 50$. The isotopes of Mo and Ru recently reported by Aston[10] do not destroy this symmetry within these limits. It may be that nuclei will be found which will fill in the diagram and so destroy the symmetry. Another cluster may be postulated with center at $P = 38$, $E = 20$ (A^{38}) due to the overlapping of Series 0 and Series 2. The cluster with center at $P = 124$, $E = 72$, may be regarded as due to the overlapping of Series 8, 10 and 12.[11]

The cluster with center at $P = 38$, $E = 20$ is imperfect partly because there are fewer known nuclei above this point than postulated by the

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[10] Aston, *Nature*, 126,348 (1930); *Proc. Roy. Soc.*, (London), **A130**, 302 *(1931)*.

[11] It may be said that the cluster at $P = 124$, $E = 72$ is only a symmetry of the isotopes of xenon and tin. In point of numbers this is true but from Cd^{110} to Ce^{140} it is possible to assume isotopes of elements of odd atomic number so that the symmetry in these nuclei is perfect and yet so that there are only two isotopes of odd atomic number differing in mass numbers by two. It would be necessary to add I^{125} to secure complete symmetry in the odd-numbered elements in this region.

parallelogram pattern of Series 2, and partly because the pattern below this point obviously consists of only half parallelograms. If these parallelograms were completed, the additional nuclei required would violate the rule that the number of nuclear electrons can never be less than half the number of protons except in the case of the proton itself. The pattern as drawn for Series 2 does not violate this rule.

The Relation of the Clusters to Nuclear Stability.—It is well known that the elements which occur with greatest abundance in nature have comparatively few isotopes. Thus the most abundant elements, oxygen, silicon and iron, have 3, 3 and 2 known isotopes, respectively, while the rarer elements may have many more. Moreover, the minimum of Aston's packing fraction curve comes near iron and, as mentioned above, the region from Ca^{40} to Cu^{63} evidently has comparatively few nuclear species. Moreover, radioactivity outside the characteristically radioactive group of elements appears to be confined to K, Rb and Cs and though these elements have only 2, 2 and 1 known isotopes, respectively, the elements of even atomic number near the latter two have many isotopes. Thus krypton and xenon have 6, and 9 known isotopes, respectively. Even if the positions outlined in Fig. 1 were completely filled in, there would still be a relatively large number of nuclear varieties in the neighborhood of K, Rb and Cs.

It seems possible to relate the clusters of nuclei to the regions of nuclear instability. This relationship can be illustrated most readily by means of the imperfect cluster at argon. Series 0 breaks off at Ca^{40} and if we assume that higher members of the series are too unstable to exist in detectable amounts, it may be expected that the last members of the series are relatively unstable as compared to the preceding members. On the other hand, Series 2 begins only with Cl^{37}, Cl^{39}(?) and A^{40}, which may mean that the series below this point is unstable and that the first members of the series are relatively so compared to members of the series with larger numbers of protons and electrons. Thus the overlapping parts of the two series will be relatively unstable, but nuclei of both series may occur. Many varieties of nuclei will be found, though due to the instability of these they will be comparatively few in actual numbers as compared to nuclei of elements outside these regions. In the region where the series do not overlap, the one series appears to be very much more stable than the two neighboring series, so that nuclei of only one series are present (referring now to the region of Series 0 and 2) and due to high stability these are present in large numbers. Thus the clusters in agreement with general and well-known facts should lie in regions of comparatively low nuclear stability.

By making the assumption that the relative abundance of nuclei is a measure of their relative stability, we can secure a partial confirmation of the suggestion made in this paper that the clusters should occur in regions of comparatively low stability. The relative abundance of different atomic nuclei should be a test for relative stability if a sample of matter could be studied which conformed to the following conditions: (1) the nuclei of the sample were synthesized from protons and electrons under such conditions that a close approach to thermodynamic equilibrium was attained; (2) since that synthesis, no changes in relative abundance occurred due to the synthesis or disintegration of some nuclei and not of others so as to cause deviations from the equilibrium mixture; (3) no fractionation of the elements has occurred. All available samples do not conform to the third condition certainly regardless of the first two conditions. Thus meteorites consist of three "phases," the stone, iron and troilite phases, of which the first approximates to the crust of the earth.[12] We may be very cautious in accepting the reality of any regularities in abundances which follow the periodic system of the elements, for this may be due only to the well-known chemical similarities. An excellent example is the extreme rarity of the inert gases in the earth's crust, due possibly to their inability to form high-boiling compounds with the other elements.

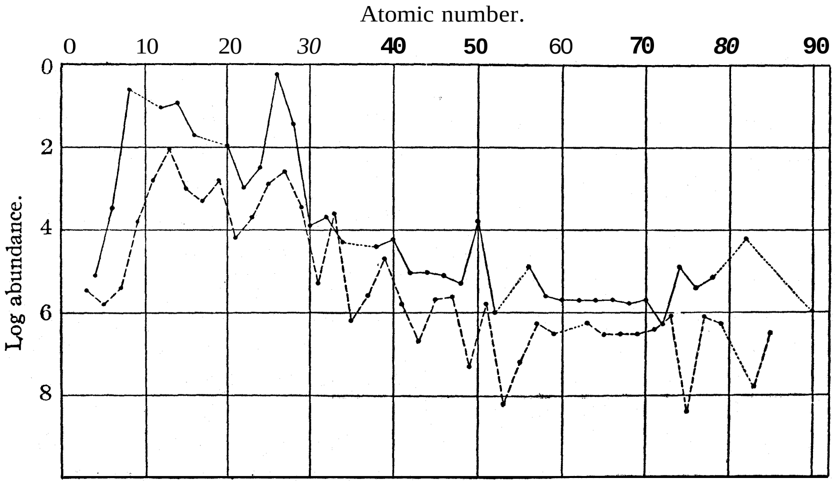

Fig. 3.—The logarithm of the atomic abundances in meteorites plotted against the atomic number. The abundances are expressed as fractions by mass taken from the data by Noddack and Noddack.

Figure 3 is a plot of the logarithm of the fraction of the meteorites by mass contributed by an element against its atomic number as given by the Noddacks. The solid line connects the points of the even-numbered elements and a broken line (long dashes) those of the odd-numbered ones. The short dark lines indicate that an intermediate element has not been

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[12] See Noddack and Noddack, *Naturwissenschaften*, 18, 757 (1930).

detected in meteorites. The method of estimating the amounts of elements not directly determined is described in the legend of the figure.

The well-known Harkins rule that elements of even atomic number are more abundant than those of odd number is evident from the figure and there are at least two well-defined maxima in the even-numbered curve at oxygen and at iron and two in the odd-numbered curve at aluminum and cobalt. The minima between these come at titanium and at scandium. These minima do not coincide exactly with the suggested region of instability at chlorine, argon, potassium and calcium. The abundances of elements in the sun as given by Russell[13] follow a very similar curve. Titanium is relatively more abundant in the sun than in the meteorites, but potassium and calcium have rather high abundances. It seems impossible to decide definitely whether this disagreement in detail is real, especially since we have no assurance that the abundance curve is exactly related to stability anyway. Roughly, however, the abundance curve indicates that the elements of both Series 0 and Series 2 first increase in abundance, reach a maximum and then decrease again, and that there is a minimum near the region where the two series overlap.

Beyond copper the abundance curve is so irregular and the overlapping of the series so continuous that all correlation of the two is uncertain. The present data would indicate a complete contradiction to the assumption of a maximum of stability in each series, for the addition of Mo^{92} and Ru^{g6} would indicate that Series 4 does not follow a regular course.

Whether a minimum occurs at neon is an interesting point. The curves as drawn from the data on meteorites certainly do not suggest the presence of such a minimum. Similar curves for the crust of the earth do, but the crust of the earth approximates the stone phase of meteorites as mentioned so that meteorites probably are the better "sample." An interpolation from the even-numbered curve would indicate that neon should be a very abundant element (between oxygen and magnesium), and the same conclusion is reached on the basis of Russell's curve for the elements in the sun. Yet the spectrum of neon has not been detected in the sun or stars.[14] Since Na^{23} has a nuclear spin greater than $^5/_2$, it may be that Ne^{20} does not consist of five helium nuclei and the rarity of neon may be due to a less stable arrangement of protons and electrons, an instability, however, which must be compensated in Na^{23}.

The system of nuclei suggested by Johnston[15] is very nearly identical

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[13] H. N. Russell, "Contributions from the Mt. Wilson Observatory," No. 383,1929.

[14] Latimer [THIS JOURNAL, **53**, 981 (1931)] has suggested a very interesting model for nuclei which would indicate that Ne^{20} should be less abundant than 0^{16} and Si^{28}. However, the model is not able to satisfy the writer in regard to the striking rarity of Ne^{m}, Ne^{21} and Ne^{22} with respect to F^{19} and Na^{23}, both of which are known to occur in the sun's atmosphere.

[15] Johnston, *ibid.*, **53**, 2866 (1931).

with that suggested here and all conclusions in regard to the relative abundances of the nuclei apply equally well to his system. He does not postulate the existence of so many additional nuclear species, but all those postulated here can be fitted into his scheme. In fact, his classification of nuclei and that of this paper appear to be only different presentations of the same scheme. Beck's[16] classification of nuclei is formally more like that presented by Johnston.

Harkins[2] has given a number of classifications of nuclei emphasizing particularly the use of his isotopic number. The writer believes that the simple proton–electron plot is simpler and more direct than these methods of classification, since it emphasizes the number of ultimate particles in nuclei of different types.[17] In view of the many systems of classification proposed, it would be difficult to originate another system which did not overlap previous ones in many points. This paper is written to emphasize the prominent parallelogram feature of these diagrams and the indication that additional stable nuclei are secured from those having most numbers divisible by four by adding protons and neutrons as indicated by these figures. In this way, it fits in very well with the recent interesting suggestions of Latimer.[9]

Summary

1. By using the proton–electron plot for atomic nuclei, predictions are made in regard to unknown nuclei between A^{36} and Cu^{63}.

2. The formula of a nucleus as consisting of helium nuclei, internal binding electrons, external protons and external electrons is proposed. It is shown that the isotopic isobars Io^{230} and UY may be expected.

3. It is suggested that Barton's clusters may be related to nuclear stability.

4. The system of nuclei proposed is compared to those proposed by other authors.

NEW YORK, N. Y.

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[16] Guido Beck, *Z. Physik,* 47, 407 (1928).

[17] The writer is aware that Harkins has used the proton–electron plot, but the essential regularities brought out in Barton's paper and in this one are not at all evident from his papers [see *Chem. Rev.,* 5, 387, 388 (1928) in particular].

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

ACTIVITY COEFFICIENTS OF SULFURIC ACID IN **ANHYDROUS** ACETIC ACID

BY A. WITT HUTCHISON AND G. C. CHANDLEE

RECEIVED MAY 8, 1931 PUBLISHED AUGUST 5, 1931

In a recent series of papers entitled "Superacid Solutions"[1] acid–base relationships in glacial acetic acid solutions have been studied. These authors reached the conclusion that acids dissolved in this solvent possess a high acidity when compared with similar aqueous solutions. The explanation of this relationship is based on the modern conception of acids and bases expressed by Brönsted.[2]

The conclusions of Hall and co-workers[1] are based in part on the nature of titration curves for anhydro bases with acids in glacial acetic acid solution. The potential difference between a saturated chloranil electrode in the solution of the base and an aqueous saturated potassium chloride calomel half-cell joined to the acetic acid solution by means of a stoppered salt bridge containing a saturated solution of lithium chloride in acetic acid was measured. This potential changed with the addition of acid solutions to the base and a plot of the potentials measured against the quantity of acid added showed clearly the course of the neutralization and its end-point.

Since the reference potential of the saturated chloranil electrode is independent of the solvent, a knowledge of the liquid junction potentials involved would allow such a cell to be used as a measure of the familiar P_H of the solution. The authors have considered the sum of these potentials to be constant in the various solutions measured and have estimated it. From these values they have calculated values of the acidities of the various solutions in terms of a quantity $P_H^{(HAc)}$ comparable to the usual P_H. These values for acid solutions were generally negative, indicating a greater acidity than is possessed for aqueous solutions of the same acids.

This work suggested the desirability of obtaining further information regarding the activity of acids in a solvent of the high acid character possessed by acetic acid.

The measurement of cells without transference furnishes at once a method of obtaining values for the activity or the mean ionic activity coefficients for a solute with no uncertainty beyond the accuracy with which the measurements are made. The activities so obtained are expressed in terms of a standard reference state for the solvent concerned and are not directly comparable to activities in water solution.

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[1] Hall and Conant, THIS JOURNAL, **49**, 3047 (1927); Conant and Hall, *ibid.*, **49**, 3062 (1927); Hall and Werner, ibid., 50, 2367 (1928); Conant and Werner, *ibid.*, 52, **4436** (1930).

[2] Bronsted, *Rec. trav. chim.*, **42**, 718 (1923).

In the present work the potential differences between a hydrogen electrode and a mercury–mercurous sulfate electrode in solutions of sulfuric acid in anhydrous acetic acid from 0.0025 to 0.9 molal in strength have been measured. The reference potential for this cell in acetic acid has been obtained by an extrapolation method based on the Debye–Hückel theory of strong electrolytes and the applicability of this theory to a solvent of a very low dielectric constant has been demonstrated.

Experimental

Preparation of Materials.--Glacial acetic acid of U. S. P. grade was purified by refluxing for ten hours with an excess of chromium trioxide to remove any easily oxidizable material. The acid was distilled from the solid residue and then carefully fractionated in a packed column rectifying still similar to that described by Marshall.[3] A reflux ratio of one to ten was used. The packing of the column was of glass tubing of small diameter cut in such lengths as to give cylinders of equal height and diameter. The packing in the column extended five feet. All of the operations were conducted in all-glass apparatus and at all times the acid was protected from atmospheric moisture by calcium chloride tubes. The main fraction melted at 16.55°, corresponding to an acid of 99.975% purity on the reasonable assumption that the freezing point lowering was due to water.[4]

Anhydrous sulfuric acid was made by mixing concentrated acid with fuming acid, both of Baker's analyzed grade, as described by Kendall and Carpenter.[5] It froze at 10.3°.

The mercurous sulfate was of the best grade obtainable. Mercury of a C. P. grade was further purified by washing in dilute nitric acid and distilling in a current of air as recommended by Hulett and Minchin.[6] Electrolytic hydrogen, dried with phosphorus pentoxide, was used for the hydrogen electrodes.

The solutions were made by adding to a weighed amount of the pure acetic acid the desired amount of sulfuric acid from a weight buret. In the calculations of the molalities of the solutions the necessary corrections for vacuum weights were made. The densities of five of these solutions were determined and the equation $d_4^{25} = 1.043 + 0.062m$ was found to express the relationship between density and molality up to 0.87 molal. This equation was used in calculating the concentrations from the molalities.

The potentials listed are the average of readings taken on two cells prepared at different times, Three pairs of platinum electrodes were used in each cell, thus giving a total of twelve readings at each concentration. When the cell solution was saturated with hydrogen equilibrium was reached almost immediately. The reproducibility of these measurements was about 2 millivolts. In the case of solutions 1 and 9 hydrogen was allowed to bubble slowly for five hours through the cell with no change in potential greater than 4 millivolts. In the case of other cells the constancy of potential for one hour was assumed sufficient test that equilibrium had been reached. The potentials were independent of the rate of hydrogen flow after the solution had been thoroughly saturated with hydrogen

All electromotive force measurements were made with a Leeds and Northrup type K potentiometer by the null method. The potentiometer calibrations were checked in this Laboratory and were found to be as indicated within the limits demanded by the experiments. A saturated Weston standard cell was used as a reference e. m. f. It was

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[3] Marshall, Ind. *Eng. Chem.*, *20*, 1379 (1928).

[4] De Visser, *Rec. trav. chim.*, 12, 101 (1893).

[5] Kendall and Carpenter, THIS JOURNAL, 36, 2498 (1914).

[6] Hulett and Minchin, *Phys. Rev.*, 21,388 (1905).

checked from time to time during the course of the experiments against two other cells of the same type recently calibrated at the Bureau of Standards. In place of the usual galvanometer a Compton quadrant electrometer was used as an indicating instrument. The instrument was used with negative electrostatic control as described by Compton and Compton.[7] Its sensitivity was 3000 mm. per volt. All of the apparatus was completely shielded, the lead wires by lead pipe, and the potentiometer, standard cells, and working battery in specially constructed metal boxes. The electrometer was suspended in a Julius suspension so as to free it from possible mechanical disturbances and the shielding completely eliminated accidental electrical effects. Switches were placed near the potentiometer so that the electrical stirring device as well as the heating system of the thermostat could be disconnected at the time readings were being taken. The lead wires were of No. 18 copper wire. Platinum wires were fused to the ends of the wires used to make connections by means of dipping into mercury. This prevented the possible contamination of the mercury.

The thermostat was maintained at a temperature of 25 ± 0.01°. The cells were placed in a copper tank, filled with oil, suspended in the thermostat water.

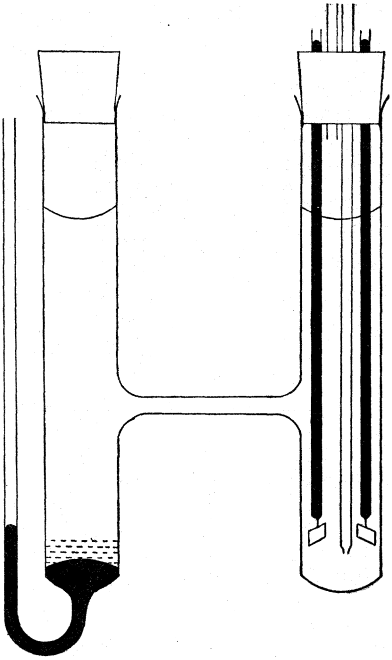
Fig. 1.—The cell.

The cells were of the H type, Fig. 1, similar to that described by Noyes and Ellis[8] and were made by connecting two Pyrex test-tubes by means of a short, about 8-cm., piece of tubing of 7-mm. diameter. A piece of the same tubing was sealed to the bottom of one of the tubes and bent so that it became parallel to the tube. This tube then became the mercury–mercurous sulfate half-cell, and connection was made to it by means of a platinum wire dipping into the mercury. In the second tube was placed a stopper through which were inserted two hydrogen electrodes with mercury contacts and tubes for the inlet and outlet of hydrogen. In some of the preliminary experiments cells of different types were used, some with a stopcock on the cross arm. No difference in potential was noted, so that the simple type described was used in all of the final work. Hydrogen was saturated with acetic acid before entering the cell by bubbling it through a wash bottle, immersed in the thermostat, containing the solution being measured. The outlet tube was protected from the atmosphere by an acetic acid seal.

Data and Calculations

In order to evaluate the activity of the mean ionic activity coefficient of sulfuric acid in the solutions, we may use the equations of Lewis and Randall[9]

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[7] Compton and Compton. Phys. *Rev.*, **14**, 85 (1919).

[8] Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917).

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. *355*.

$$E = E^\circ - \frac{RT}{2F} \ln a_2 \tag{1}$$

$$E = E^\circ - \frac{3RT}{2F} \ln (\gamma m 4^{1/3}) \tag{2}$$

Before a_2 or γ can be evaluated, a value for E° must be determined. Transforming (2) and introducing common logarithms

$$2.303 \times \frac{3RT}{2F} \log \gamma = E^\circ - \left(E + 2.303 \times \frac{3RT}{2F} \log m4^{1/3}\right) \tag{3}$$

If the quantity in the parentheses, $E^{\circ\prime}$, is plotted against some function of m, extrapolation of the curve to $m = 0$ gives at once the value of E°. The data are given in Table 1 and in Fig. 2 values of $E^{\circ\prime}$ have been plotted against $(m)^{1/3}$. Inspection of the graph shows that the curve is approaching a straight line with, however, such a steep slope that a slight error in the choice of its slope would make a large one in the value of E° obtained by simple extrapolation. Solutions less concentrated than 0.0025 molal gave erratic potentials, so that no significance could be attached to them.

TABLE I

EXPERIMENTAL DATA

Solution	m	$(m)^{1/3}$	E	$E^{\circ\prime}$
1	0 002461	0.1350	0 537	0 323
2	.006053	.1823	.525	.346
3	.007730	.1977	.521	351
4	01377	.2397	.512	365
5	.02662	.2986	.5035	.382
6	,03796	.3361	.498	.390
7	.1437	.5238	.480	.423
8	.5014	.7944	.460	.451
9	.8715	.9552	.452	.465

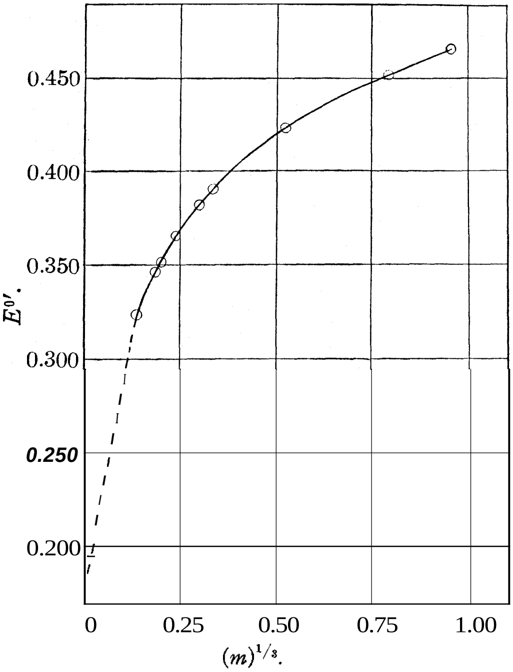

Fig. 2.

The Debye–Hückel[10] theory, however, allows an evaluation with reasonable security of activity coefficients in very dilute solutions. The fundamental equation may be written

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

$$-\ln f = \frac{A\epsilon^2 z_1 z_2 K}{2DRT(1 + Kb)} \quad (4)$$

$$K^2 = \frac{8\pi\epsilon^2 A^2 \mu}{1000\ DRT} \quad (5)$$

The values for the universal constants were taken from the "International Critical Tables," that of the dielectric constant. $D = 6.165$, from the recent work of Smyth.[11] Substituting the numerical values for the constants

$$K = 1.1734 \times 10^8 \sqrt{\mu} \quad (6)$$

Transforming to common logarithms and noting that in the very dilute solutions $f = \gamma$ where γ is the mean ionic activity coefficient based on molality

$$-\log\gamma = \frac{23.033\ z_1 z_2 \sqrt{\mu}}{1 + 1.1734 \times 10^8 b \sqrt{\mu}} \quad (7)$$

which for an electrolyte of the 2–1 type in acetic acid can be written

$$-\log\gamma = \frac{79.79\sqrt{c}}{1 + 2.0325 \times 10^8 b \sqrt{c}} \quad (8)$$

This equation has been modified by Hückel[12] for use in more concentrated solutions by the introduction of a third term to allow for consideration of the changing dielectric constant of the pure solvent brought about by the introduction of solute. For sulfuric acid solutions in acetic acid the equation may be written

$$-\log\gamma = \frac{79.79\sqrt{c}}{1 + 2.0325 \times 10^8 b \sqrt{c}} - \beta c + \log(1 + 0.18m) \quad (9)$$

The last term is necessary in concentrated solutions because of the transformation from an activity coefficient based on mole fraction to one based on molality.

Equation (2) may be written

$$E = E^\circ - 0.08872 \log(\gamma m 4^{1/3}) \quad (10)$$

$$\log\gamma = -\frac{E}{0.08872} - \log m + \left(\frac{E^\circ}{0.08872} - \log 4^{1/3}\right) \quad (11)$$

and denoting the quantity in parentheses by K

$$-\log\gamma + K = \frac{E}{0.08872} + \log m \quad (12)$$

The constants b and β of equation (9) were evaluated by the method proposed by Hückel[12] on page 123 of his article. Such modification of the equations given as was necessary for a 2–1 type electrolyte was made. The values found were $b = 1.5 \times 10^{-7}$ and $\beta = -0.35$.

If the data of Table II are substituted in equation (12) and values of $-\log\gamma + K$ are plotted against the half-power of the concentration, the

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[11] **Smyth,** THIS *JOURNAL*, 52, 1825 (1930).

[12] Hückel, *Physik.* Z., 26, 93 (1925).

TABLE II

EXPERIMENTAL DATA

Solution	m	c	$(c)^{1/2}$	E	$-\text{Log}\,\gamma + K$	$(-\text{Log}\,\gamma + K) - K$
1	0.002461	0.002567	0.05067	0.537	3.44	1.60
2	.006053	.006315	.07947	.525	3.71	1.87
3	.007730	.008063	.08980	.521	3.76	1.92
4	.01377	.01436	.1198	.512	3.91	2.07
5	.02662	.02773	.1665	.5035	4.10	2.26
6	.03796	.03954	.1989	.498	4.19	2.35
7	.1437	.1490	.3860	.480	4.57	2.73
8	.5014	.5133	.7165	.459	4.89	3.05
9	.8715	.8770	.9370	.452	5.04	3.20

curve should be of the same nature as that of equation (9). In Fig. **3** the full curve is that of equation (9). The circles represent values of (– log y + K) – K, taking K as 1.84.

It is of interest to see just how much influence the various terms of equation (9) have on values of $-\log\gamma$. In the extremely dilute solutions the slope of the curve should be 79.79, represented by the straight line of Fig. **3.** It is not surprising that even at the very low concentrations measured this slope is not reached since the dielectric constant of acetic acid has such a small value. Introduction of the ion diameter term, however, gives a coincidence of the four experimental points with the curve up to 0.014 molal. The addition of the second term includes three additional points up to 0.15 molal. The more concentrated solutions depart from the theoretical curve. In Table III are listed the values for the terms of the Huckel equation, – log γ calculated from this equation and – log γ experimentally determined from the value of (– log γ + K) – K taking K as 1.84.

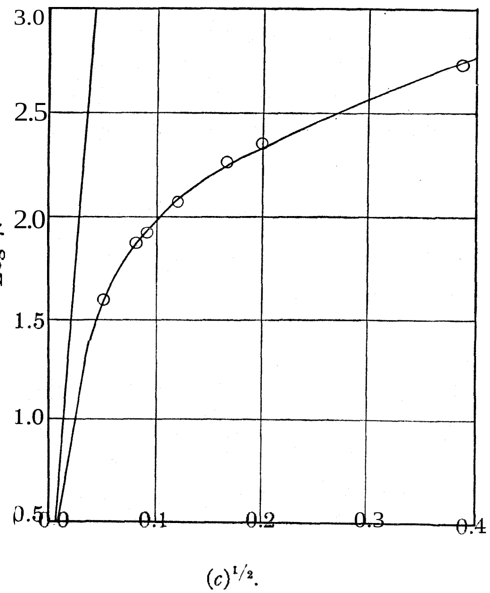

Fig. 3.

A comparison of the values used for the arbitrary constants with those chosen by other workers may be of interest. The value chosen for b, the average ion diameter in the solution, is somewhat larger than is generally used in aqueous solutions but is of the same order as values used by other

TABLE III

EXPERIMENTAL DATA

Solution	(1st term)	$-B6c$	Log $(1 + 0.18m)$	$-\text{Log }\gamma$ (calcd.)	$-\text{Log }\gamma$(exp.)
1	1 59	0 01		1.60	1.60
2	1.86	.01		1.87	1.87
3	1.92	.02		1.94	1.92
4	2.06	.03		2.09	2.07
5	2.19	.06		2.25	2.26
6	2.25	.08		2.33	2.35
7	2.42	.31	0 01	2.74	2.73
8	2.51	1.08	.04	3.63	3.05
9	2.53	1 84	.06	4.43	3.20

workers in acetic acid solutions. Conant and Werner,' in applying the Debye–Hückel equation to data for sulfuric acid–anhydro base buffer solutions in acetic acid used values of 1.3×10^{-7} and 1.24×10^{-7} for b, with, however, a slightly different limiting slope because of a different value for the dielectric constant. Webb[13] in studying the freezing points of acetic acid solutions of salts used for b, in the case of lithium bromide, 7.1×10^{-8}, for sodium bromide, 6.8×10^{-8}, and for sodium acetate, 6.2×10^{-8}. He apparently used a still different value for the dielectric constant.

The large values for b in acetic acid solutions might be accounted for by considering the ions solvated in all solvents, and since the acetic acid molecules are probably larger than water molecules, an increased diameter would be expected. In general the ion diameter b is larger than the diameter of ions in the crystal lattice.

The value of B in aqueous solutions is ordinarily a small positive number. However, Webb[13] found that his data were in accord with an equation of the type of (9) only when B was a negative number. Thus for lithium iodide b is taken as 6.75×10^{-8} and B as -1.38. The sign of the constant could be explained on the assumption that the dielectric constants of the solutions are greater than that of the pure solvent. Walden and Ulich[14] and Walden, Ulich and Werner[15] have found that with many organic solvents the dielectric constant is increased on the addition of electrolytes.

From the value of 1.84 assigned to K a value for E^0 of 0.181 volt can be calculated. Then for solutions of sulfuric acid in acetic acid at 25.0° may be written the equation

$$E = 0.181 - 0.08872 \log (\gamma m 4^{1/3}) \qquad (13)$$

from which activity coefficients can be calculated at any molality measured.

Summary

A convenient method for the preparation of large quantities of anhydrous acetic acid of a high grade has been found.

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[13] Webb, THIS JOURNAL, 48, 2266 (1926).

[14] Walden and Ulich, Z. *physik. Chem.*, 110, 43 (1924).

[15] Walden, Ulich and Werner, *ibid.*, 116, 261 (1925).

A general equation for the calculation of activity coefficients of sulfuric acid in glacial acetic acid solutions has been developed.

It has been shown that an equation of the type proposed by Huckel as a modification of the Debye–Hückel theory of strong electrolytes is applicable in a solvent of very low dielectric constant.

STATE COLLEGE. PENNSYLVANIA

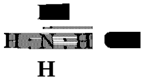
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE DIPOLE MOMENT OF SEMI-POLAR BONDS

BY JOHN DEVRIES AND WORTH H. RODEBUSH

RECEIVED MAY 8, 1931 PUBLISHED AUGUST 5, 1931

The term semi-polar bond has been used to designate a shared electron bond in which both electrons are contributed by one atom. This term has been used in the absence of a more suitable designation without much idea as to its fitness since it has not been known with certainty whether any considerable degree of polarity is characteristic of this bond. Two common examples of this bond are ammonium chloride and perchloric acid.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$$\underset{H}{H:N:H}$$

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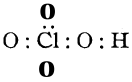
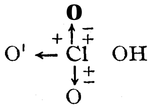


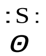
$$\begin{matrix} & & O & & \\ O & : & \ddot{Cl} & : & O:H \\ & & O & & \end{matrix}$$

In the case of the ammonium chloride the identity of the semi-polar bond is completely lost. In the perchloric acid the strength of the acid may be explained by assuming a considerable degree of polarity in the semi-polar bonds thus

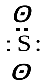


Any other explanation of the strength of perchloric acid seems to be barred, since double bonds are out of the question.

It is impossible to determine the dipole moment of the semi-polar bonds in the above-mentioned molecules for obvious reasons. Recently, however, Professor Shriner[1] of this Laboratory has synthesized some organic sulfur compounds which contain semi-polar bonds. Professor Shriner has kindly furnished us with samples of these compounds for measurement of the electrostatic moment. The compounds were diphenyl sulfoxide, diphenyl sulfones and homologs. The electronic structures of the sulfoxide and sulfone arc



$$\underset{O}{:S:}$$



$$\overset{O}{\underset{O}{:\ddot{S}:}}$$

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[1] Shriner, Struck and Jorison, THIS JOURNAL, 52,2060 (1930).

It is impossible to assign any other electronic structure which seems at all probable. In both compounds the electrons linking the oxygen to the sulfur are both furnished by the oxygen. These compounds are stable and sufficiently soluble in benzene for satisfactory determinations. For purposes of comparison measurements were made upon diphenyl sulfide.[2]

Experimental

The method used to measure the dielectric constants of the liquids under consideration was essentially the same as that developed by Nernst[3] and his students The apparatus consisted of a Type 216 capacity bridge manufactured by the General Radio Company in which capacities as well as resistance are balanced. The bridge consists of two resistance arms, R_1 and R_2, of 5000 ohms each and two capacity arms In one arm of the bridge was placed a balancing condenser, and in the other arm two standard variable air condensers made by the General Radio Company and having capacities of 1500$\mu\mu$ farads. Only one of these was accurately calibrated, the other being used so that there would be a larger capacitance in each arm of the bridge, this giving a sharper minimum point in the phones. Connected in parallel with these two condensers was the comparison condenser (modeled after that of Hartshorn and Oliver)' built of brass plates and mounted in a shielded Pyrex tube with a ground glass top. The capacity of this condenser was 403.1$\mu\mu$ farads. This was measured by submerging the plates in purified benzene, the dielectric constant of which has been accurately determined by Hartshorn and Oliver[4] as 2.282 ± 0.002 at 20". The capacity of this cell was frequently checked throughout the course of the work. All of the work was carried out at 25°.

The entire apparatus was placed on a metal topped table and carefully grounded. All possible precautions were taken to prevent stray capacities The frequency used in measuring the dielectric constant was 1000 cycles, which was produced by a General Radio Audio oscillator Power was brought from the oscillator to the bridge by a pair of twisted wires, heaviiy insulated.

Experimental Procedure

The method of operation was to vary the capacity of the standard condenser and the balancing resistance of the bridge until a sharp minimum was received on the phones. This reading was noted and then the comparison cell containing the binary mixtures under investigation was connected in parallel and readings again were taken. The difference between the two readings represents the capacity of the cell plus the liquid. In filling the comparison condenser, care was taken to prevent the formation of bubbles between the plates by tilting the cell and allowing the liquid to flow slowly down the side of the tube.

It must be noted that the capacity of this cell is made up of two parts, the capacity due to the leads and insulation and the capacity between the plates. In the neighborhood of dilute solutions, when the dielectric con-

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[2] Since this research was started, Bergmann, Engel and Sandor [Z. *physik. Chem.*, [B] 10, 397 (1930)] have published results for diphenyl sulfide and diphenyl sulfoxide. The agreement between their values and ours is satisfactory.

[3] Nernst, *ibid.*, 14, 622 (1894).

[4] Hartshorn and Oliver, *Proc.* Royal *Soc.* (London), April, 1929

stant is nearly the same as that of benzene, the error due to the leads capacity cancels out, as the capacity of the cell as obtained by us is really that of the cell plus the leads. In the neighborhood of the dilute solution where the highest accuracy is desired, this accuracy is also obtained.

To make certain, however, that this error due to the leads capacity might also be safely neglected in the range of the more concentrated solutions, where we measured dielectric constants in the neighborhood of four, it was decided to check the apparatus by measuring the moment of a compound already known. *p*-Nitrotoluene was selected, having an electric moment of 4.50×10^{-18} e. s. u. as reported by Williams.[5] The value as determined by our method is within the limits of the precision of any method to measure electric moments. The capacity of these leads as calculated from the law of infinite cylinders was $1\mu\mu$ farad, a value small in comparison with the $1000–1500\mu\mu$ farads measured.

The method used to calculate the moment of a molecule was to make a saturated solution of the compound in benzene, the latter being a non-polar solvent. The dielectric constant was measured at each dilution five to seven readings being taken on each dilution and at various balanced capacities to check the readings. Variation here in capacity was as a maximum about $1.5\mu\mu$ farads, although in the diluted solutions the readings checked within $0.5\mu\mu$ farad. This represents an error of approximately 0.15% in the concentrated solutions. Densities were accurately determined by means of a specific gravity bottle, giving values accurate through the fourth decimal place.

The polarization of the solution was calculated by the method pointed out by Debye,[6] using the equation

$$P_{1,2} = P_1f_1 + P_2f_2 = \frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{f_1M_1 + f_2M_2}{\rho}$$

where $P_{1,2}$ is molar polarization of the mixture; P_1, molar polarization of the solvent; P_2, molar polarization of the solute; f_1, mole fraction of the solvent; f_2, mole fraction of the solute; ρ, density of the solution; ϵ, dielectric constant of the solution. The values of P_2 were then obtained by plotting $P_{1,2}$ values as abscissas and F_2 values as ordinates. From this curve P_2 values were calculated, which were then plotted against f_2 and again extrapolated to infinite dilution, giving the value for the polarization of a single molecule between the plates of the condenser.

To obtain the values for the optical polarization (the polarization due to the deformation of the molecule) the individual atomic refractivities were added, proper allowances being made for the different types of linkages. This method was used as the refractive indices of the compounds under investigation have not as yet been determined. The difficulty we

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[5] Williams, *Chem. Rev.*, **6**, 589 (1929).

[6] Debye, "Polar Molecules," Chemical Catalog Co., Inc., New York, 1929.

encountered in calculating this P_0 (optical polarization) is that no value is known for sulfur in the type of linkage we were interested in. The assumption was made that the values of sulfur from known compounds, e. g., sulfides, disulfides, could be used, where the atomic refractivity has a value of eight. Debye justifies an assumption of this kind, considering the possible precision of the value obtainable for the optical polarization.

From the values of the molar polarization P_2 of the polar molecule itself and the value P_0 for the optical polarization, the electric moment μ can be calculated as Debye shows by

$$\frac{4\pi}{3} N \frac{\mu^2}{3kT}$$

Substituting $N = 6.06 \times 10^{23}$ and $k = 1.372 \times 10^{-16}$, the equation becomes

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_2 - P_0)T}$$

where T is the absolute temperature.

The values obtained are shown in Table I together with the values for some related compounds which have been determined by other investigations.

TABLE I

DIPHENYL SULFIDE (Temp., 25°)

f_2	ϵ	ρ	$P_{1,2}$, cc.
0.23120	3.064	0.9658	43.49
.09605	2 641	.9195	34.00
.04626	2.458	.8973	29.91
.03670	2 418	.8940	29.45
.02814	2 389	.8904	28 82
.01790	2 354	.8870	28.04
00890	2 323	.8814	27.44
.00620	2 310	.8791	27.22
.00270	2 292	.8774	26.84

Diphenyl Sulfoxide (T, 25°)

f_2	ϵ	ρ	$P_{1,2}$, cc.
0.051	3.807	0.908	44.92
.0481	3.679	.906	43.75
.04595	3 497	.904	42.08
,04265	3 46	.9022	41.62
.0396	3.307	.9002	40 08
.0367	3 214	.8987	39.03
0339	3.132	.8970	38.1
.0312	3 037	.8952	37.04
.0283	2.968	.8935	36.16
02465	2 8597	.8912	34.83
,02085	2.764	.8889	33.59
.01805	2.693	.8866	32.67
01340	2 600	.8843	31.35
0098	2.510	882	30.09
.0062	2 426	8799	28 87

TABLE I (Concluded)

Diphenyl Sulfone (T, 25")

f_2	ϵ	ρ	$P_{1,2}$, cc.
0.0262	3 187	0 890	38.70
.0229	3 069	888	37.33
.0201	2 958	.8865	36.01
.0173	2 872	885	34.92
.0144	2 766	8837	33.55
.0115	2 702	882	32.67
.0088	2 606	880	31.39

POLARIZATION IN BENZENE

	P_2, cc.	P_0, cc.	$P_2 - P_0$	$\mu \times 10^{-18}$
Diphenyl sulfide	111	59	52	1 565
Diphenyl sulfoxide	423	60 5	362 5	4 17
Diphenyl sulfone	593 5	63 3	530 2	5 05

TABLE II

VALUES FOR COMPOUNDS

	$\mu \times 10^{-18}$
Diphenyl ether	1.0
Sulfur dioxide	1 8
Benzophenone	2.5
Acetone	2 7

Attempts were also made to measure μ for $C_6H_5SO_2CH_2C_6H_5$, and C_6H_5-$CH_2SOC_6H_5$, but their insolubility prevents an accurate determination of their electric moment by this method. All we can say is that they have a high moment, comparable to the simple sulfoxide and sulfone.

Discussion.—The results obtained indicate a surprisingly high value for the dipole moment of the semi-polar bond. This result seems to be established with certainty since the largest errors that may reasonably be assumed would not affect the results seriously. The value of 8.0 that was assumed for the atomic refraction of sulfur is a maximum; the correct value may be less. If this is the case the moments obtained are even larger.

It is to be expected of course that if the molecule has an approximately tetrahedral arrangement, the moment of the sulfone would not be much greater than that of the sulfoxide.

In Table II are given the accepted values for the electrostatic moments[7] of some compounds for comparison purposes. It will be noted that oxygen doubly bound to carbon has a moment much smaller than the semi-polar bond with sulfur.

One might be tempted to assume an even smaller moment for oxygen doubly bound to sulfur. If we assume a linear form for the sulfur dioxide molecule and that it contains one double bond and one semi-polar bond, then the moment of sulfur dioxide is about what would be expected. Great caution must be used, however, in drawing conclusions in this way

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[7] "Ergebnisse der exakten Naturwissenschaften," 1929, Vol VIII, p. 288.

Summary

The dipole moments have been determined in benzene solution for diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone. The sulfoxide and sulfone have a very large moment.

URBANA, ILLINOIS

[COMMUNICATION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE REACTION BETWEEN NITRITE AND IODIDE AND ITS APPLICATION TO THE IODIMETRIC TITRATION OF THESE ANIONS

BY CARLOS A. ABELEDO AND I. M. KOLTHOFF

RECEIVED MAY 11, 1931 PUBLISHED AUGUST 5, 1931

The reaction between nitrous acid and iodide

$$HNO_2 + I^- + H^+ \longrightarrow H_2O + NO + 1/2\ I_2$$

occurs only in acid medium. In the presence of oxygen the nitric oxide is oxidized to nitrogen dioxide which partly reacts with water, forming nitrous and nitric acid. With regard to the application of the reaction between nitrite and iodide to the iodimetric determination of these components, it was desirable to know at which hydrogen-ion concentration the reaction between the two takes place with a measurable speed. Moreover, it was of importance to study the reaction between iodide, dissolved oxygen and nitric oxide at various PH values.

To 10 ml. of Clark's buffer solutions, known amounts of potassium iodide and sodium nitrite were added and after definite times of standing the iodine was titrated with thiosulfate. Some results obtained at room temperature are given in Table I.

TABLE I

REACTION BETWEEN NITRITE AND IODIDE AT VARIOUS PH

PH of buffer, 10 cc.	Concn. I^- molatity	Concn. NO_2^- molarity	Time of standing, in minutes	0.1 *N* thiosulfate, cc.
3.4	0.2	0.2	5	2
4.0	.2	.2	5	1.5
4.0	.4	.2	5	2.5
5.0	.2	.2	5	0.4
5.0	.4	.2	5	.7
5.6	.2	.2	5	.05
5.0	.2	.2	30	.20
5.6	.4	.2	5	.10
5.6	.4	.2	30	.40
6.0	.4	.2	5	.04
6.0	.4	.2	240	.09
7.0	.4	.2	30	00

From the results in Table I it may be concluded that under practical conditions at a PH larger than six, the reaction between nitrite and iodide takes place with a negligibly slow speed. This is not true for the reaction between nitric oxide, iodide and oxygen. Solutions of nitric oxide in buffers of various *PH* were treated with iodide in the presence of air. Even at a PH of 9.0 a trace of iodine is liberated very quickly; if the latter is titrated after five minutes no further reaction takes place upon standing. The same is true at *PH* values between 6 and 9, and the amounts of iodine liberated are relatively small even at a PH of 6. It should be mentioned, however, that the amount of iodine formed is not only dependent upon the PH, but also on the type of buffer used; in borate buffers more iodine is formed than in phosphate solutions of the same PH. Further studies for a better understanding of the reaction are in progress. Anyhow, the results obtained at PH values between 6 and 9 show definitely that the reaction between nitric oxide, iodide and oxygen at these low acidities cannot be interpreted by the hydrolysis of the oxidation product, nitrogen dioxide, to give nitrite and nitrate, since traces of nitrite do not react with iodide at a PH larger than 6. Therefore, it must be assumed that the nitrogen dioxide formed by the oxidation of nitric oxide reacts with iodide to liberate iodine. Even in stronger acid medium this kind of reaction must take place as it is impossible to interpret the results of the nitrite–iodide reaction on the sole assumption that the nitrogen dioxide formed by oxidation of the nitric oxide hydrolyzes to give nitrous and nitric acids.

For the analytical application of the reaction between nitrite and iodide it is of importance to know under what conditions nitrous acid and nitric oxide can be removed from the solution by addition of urea. In acetic acid medium the reaction is very incomplete even after a long time of standing. The best conditions are obtained if the solution contains at least 0.2 N hydrochloric or sulfuric acid and a large excess (1–2 g. was generally used) of urea. After fifteen minutes' standing no iodine is liberated on addition of potassium iodide.

On the basis of these preliminary experiments procedures were developed for the iodimetric titrations of iodide and nitrite.

Determination of Iodide.—Pure substances were used and the solutions standardized according to reliable methods of volumetric analysis.

Procedure.—Thc iodide solution is introduced into a 250-cc. glass-stoppered Erlenmeyer flask; about 1 *g*. of urea, 5 cc. of 0.5 molar sodium nitrite and 5 cc. of 4 N sulfuric acid are added. The flask is stoppered and allowed to stand with frequent shaking for about ten minutes, thereupon 1–2 g. of potassium iodide is added and the solution titrated with 0.1 N thiosulfate.

Note: 1. The amount of sodium nitrite given in the procedure is satisfactory for the oxidation of 25 cc. of 0.054.2 N iodide. It was found that in the presence of oxygen the nitrite will oxidize twice the theoretical amount of iodide. A large excess of nitrite is not harmful, provided urea has been added.

2. Since part of the nitric oxide formed is present in the gas phase, frequent shaking

is recommended to allow of all this gas reacting with urea. If at the end of the titration the color quickly comes back, the nitrogen oxide was not completely removed and the procedure must be repeated.

3. For the determination of very dilute solutions (25 cc., 0.01 to 0.001 *N*), 0.5 g. of urea, 1 cc. of 0.2 molar nitrite, 5 cc. of chloroform and 5 cc. of 4 *N* sulfuric acid were used and the liberated iodine titrated (after addition of some iodide) after thirty minutes' standing in the stoppered flask. Even in very dilute solutions accurate results are obtained (see Table II). It may be mentioned here that the iodide–nitrous reaction has already been applied by Grange[1] and later by Fresenius[2] to the determination of traces of iodide. The iodine is shaken out in carbon disulfide. Various authors have examined the method, but it cannot be recommended for the determination of traces of iodide, the chief reason being that the excess of nitrous acid or the nitrogen oxide formed interferes more or less. It was found by the present authors that the procedure is improved if the excess of nitrite and the nitrogen oxide formed are removed by urea. The iodine can be shaken out in chloroform, carbon tetrachloride, carbon disulfide, benzene, etc., and no difficulties are encountered.

4. Chlorides do not interfere with the iodide determination. Too high results are found if more than the equivalent amount of bromide is present. Improvement is obtained if the sulfuric acid is added in portions of 1 cc. at five-minute intervals (compare results in Table II).

5. Recently H. Szancer[3] applied the nitrite–iodide reaction to the determination of iodide. After the liberation of the iodine, the acid solution is neutralized with a slight excess of sodium bicarbonate and the iodine titrated with thiosulfate or arsenious-

TABLE II

TITRATION OF IODIDE ACCORDING TO RECOMMENDED PROCEDURE

Potassium iodide, cc.	Addition, g.	Thiosulfate used, cc.	Thiosulfate, theoretical, cc.	Deviation in. %
25		24.80 0.1 *N*	24.80 0.1 *N*	0.0
25		24.75 0.1 *N*	24.80 0.1 *N*	− .2
25		24.83 0.1 *N*	24.80 0.1 *N*	+ .1
25		24.83 0.1 *N*	24.80 0.1 *N*	+ .1
25	1 NaCl	24.67 0.1 *N*	24.70 0.1 *N*	− .1
25	2 NaCl	24.65 0.1 *N*	24.70 0.1 *N*	− .2
25	0.26 NaBr	25.50 0.1 *N*	24.70 0.1 *N*	+3.2
25	.26 NaBr	25.65 0.1 *N*	24 70 0.1 *N*	+3.8
25″	.26 NaBr	24.85 0.1 *N*	24.70 0.1 *N*	+0.6
25[a]	.26 NaBr	24.75 0.1 *N*	24.70 0.1 *N*	+ .2
25[a]	.26 NaBr	24.75 0.1 *N*	24.70 0.1 *N*	+ .2
25′	.52 NaBr	25.20 0.1 *N*	24.70 0.1 *N*	+2 0
10		9.85 0.01 *N*	9.84 0.01 *N*	+0. 1
10		9.82 0.01 *N*	9.84 0.01 *N*	− .2
10		9.81 0.01 *N*	9.84 0.01 *N*	− .3
10[b]		9.58 0.001 *N*	9.44 0.001 *N*	+1.4
10[b]		9.50 0.001 *N*	9.44 0.001 *N*	+0.6

[a] Sulfuric acid added in fractions of 1 cc.; *cf.* Note 4 in discussion. [b] This solution contained only 1.25 mg. of iodide.

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[1] Grange, *J. prakt. Chem.*, 55, 167 (1852).

[2] Fresenius, "Anleitung zur quantitativen Analyse," 1875, Vol. II, p. 482.

[3] H. Szancer, *Arch. Pharm.*, 268, 263 (1930).

trioside. Under these conditions the nitrite does not react any more with iodide. However, in the slightly alkaline medium the iodine–thiosulfate reaction gives somewhat erratic results owing to a slight oxidation to sulfate. The results obtained by us with Szancer's method for this reason were 2 to 3% low. Probably the As_2O_3 titration will give better results; we have not tried it. Presence of bromide has the same effect in Szancer's method as in the procedure proposed by the authors.

Some results obtained are reported in Table II. The figures have been recalculated on the basis of a normality of the thiosulfate of exactly 0.1 N (0.01 N and 0.001 *N*, respectively).

Determination of Nitrite.—C. P. sodium nitrite was recrystallized twice from water and dried at 110°. Qualitative tests indicated its purity. The nitrite content was determined gravimetrically by treating with silver bromate and weighing as silver bromide.[4] The results indicated that the sodium nitrite contained 99.9–100.3% $NaNO_2$. Previous authors[5] have made use of the reaction between nitrous acid and iodide for the evaluation of nitrites. B. S. Davisson[6] has tested the various methods, but did not find them very satisfactory. He developed a method giving results accurate to within —1.5 and +2.5%. F. Dienert[7] described another elaborate procedure which, however, is no more accurate than to about 2% for 3 mg. of nitrite nitrogen. No experimental figures are given in his paper.

Proposed Procedure.—Ten to twelve grams of sodium bicarbonate, 3 g. of potassium iodide, 0.5 to 1 cc. of amyl alcohol and 25 cc. of water are introduced into a 250-cc. glass-stoppered Erlenmeyer flask, whereupon a measured volume of the nitrite solution is added. The contents of the flask are well mixed by shaking. After most of the sodium bicarbonate has settled, about 4 cc. of glacial acid is added from a pipet in such a way that the acid is well distributed through the solution, without shaking the flask. The latter is loosely stoppered and after the evolution of the carbon dioxide has nearly ceased gently rotated. After the sodium bicarbonate has settled, 6 to 7 cc. of 20 N sulfuric acid is added quickly without shaking the flask. The latter is loosely stoppered again, and after evolution of most of the carbon dioxide has ceased gently rotated to allow thorough mixing. The stopper is rinsed with water and the solution titrated with standard thiosulfate, using starch as an indicator.

After the end-point has been reached the stoppered flask is allowed to stand for ten minutes. If more than 0.1 to 0.2 cc. of 0.1 N iodine is formed (titration with thiosulfate), the procedure should be repeated.

NOTE: 1. A large excess of bicarbonate has to be used in order to remove all nitric oxide with the carbon dioxide during the reaction between nitrite and iodide. Potassium bicarbonate cannot be substituted for the sodium salt since the former is too easily soluble.

2. Since the presence of oxygen is very harmful during the reaction between iodide and nitrous acid, the air has to be removed from the reaction mixture before the strong acid is added. This is done by the addition of glacial acetic acid. At the low hydrogen-ion concentration in the acetate buffer formed no, or a very slight, reaction between nitrite and iodide takes place.

3. The addition of amyl alcohol is not essential, but is strongly recommended as it prevents overfoaming of the liquid during the evolution of carbon dioxide.

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[4] Busvold, *Chem.-Ztg.*, **38**, 28 (1914).

[5] Comp. L. W. Winkler, *ibid.*, **23**, 545 (1899); **25**, 586 (1901); Z. *Unt. Nahr. Gen.*, 29, 107 (1915); Meisenheimer and Heim, *Ber.*, **38**, 3834 (1905); **F.** Raschig, ibid , **38**, 3911 (1905).

[6] B. S. Davisson, THIS JOURNAL, **38**, 1683 (1916).

[7] F. Dienert, *Ann. chim. anal. chim. appl.*, [2] **1**, 4 (1919).

4. If the air is not removed completely the blue color returns after the end-point has been reached. To test the reliability of the result it is necessary to titrate the liquid ten to fifteen minutes after having reached the end-point. If more than **0.1** to 0.2 cc. of thiosulfate is then used, the result should not be accepted and the determination should be repeated.

5. Very dilute nitrite solutions can be titrated according to the recommended procedure. The accuracy is about 0.5%. (See Table III.)

6. Good results are obtained in the presence of no more than 2–3% of ethyl alcohol and of amyl alcohol. Therefore the procedure seems well adapted for the determination of nitrites in the presence of these organic substances (e. g., in amyl nitrite, spirit of ethyl nitrite U. S. P.) where the permanganate method cannot be applied.

TABLE III

IODIMETRIC TITRATION OF NITRITE

Nitrite, cc.	Addition, cc.	Thiosulfate, cc.	Thiosulfate, theoretical, cc.	Deviation in, %
10		9.82 0.1 *N*	9.82 0.1 *N*	0
10		9.80 0.1 *N*	9.82 0.1 *N*	− .2
10		9.81 0.1 *N*	9.82 0.1 *N*	− .1
25		24.55 0.1 *N*	24.55 0.1 *N*	0
25		24.55 0.1 *N*	24.55 0.1 *N*	0
25		24.50 0.1 *N*	24.55 0.1 *N*	− .2
40		39.30 0.1 *N*	39.28 0.1 *N*	+ .05
40		39.30 0.1 *N*	39.28 0.1 *N*	+ .05
25	5 Ethyl alcohol	24.10 0.1 *N*	24.55 0.1 *N*	−1.8
25	5 Ethyl alcohol	24.20 0.1 *N*	24.55 0.1 *N*	−1.4
25	5 Ethyl alcohol	24.20 0.1 *N*	24.55 0.1 *N*	−1.4
25	2 Ethyl alcohol	23.50 0.1 *N*	23.55 0.1 *N*	−0.2
25	1 *Sec.*-amyl alcohol	23.60 0.1 *N*	23.55 0.1 *N*	+0.2
25	1 *Sec.*-amyl alcohol	23.60 0.1 *N*	23.55 0.1 *N*	+ .2
25		24.65 0.01 *N*	24.55 0.01 *N*	+ .4
25		24.60 0.01 *N*	24.55 0.01 *N*	+ .2
25		24.62 0.01 *N*	24.55 0.01 *N*	+ .3
25		24.60 0.01 *N*	24.55 0.01 *N*	+ .2

Summary

The reaction between iodide and nitrite and nitric oxide, respectively, has been investigated at various PH values.

The optimum condition for the reaction between urea and nitrite and nitric oxide, respectively, has been determined.

Applications have been made to the iodimetric determination of iodide and nitrite, respectively. The Fresenius method for the determination of iodides has been improved.

The procedure described for the determination of nitrite can also be used in the presence of alcohols.

MINNEAPOLIS. MINNESOTA

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

THE EMULSIFYING PROPERTIES OF GELATIN SYSTEMS

BY LEO FRIEDMAN AND DONALD N. EVANS

RECEIVED MAY 11, 1931 PUBLISHED AUGUST 5, 1931

That gelatin will act as an emulsifying agent is generally known, but extensive investigations of this property of gelatin have been very few. Holmes and Child,[1] in the study of emulsifying properties of gelatin, found that the maximum lowering of surface tension should be secured; that an excess of strong acids, bases or liquefying salt should not be added; and that the viscosity should not be greatly increased above that of water in order to obtain good emulsions. Working with kerosene–water emulsions, they did not find any convincing evidence that gelatin particles were withdrawn from the solutions to form adhesion layers about the oil droplets. Their conclusion was that the leading factor in an oil–water emulsion with the aid of gelatin is viscosity, not maximum, but the most favorable viscosity.

In this investigation it was desired to determine (a) how the emulsifying properties vary with the gelatin content, (b) the effect of PH on the emulsifying properties of gelatin, and (c) the extent of the adsorption of gelatin in the interface of the emulsion.

Experimental Procedure

The gelatin used (U. S Gelatin Company) was purified by first soaking in 1/128 molar acetic acid, then in distilled water, and finally electrodialyzing until a minimum current flowed. The solutions were made more acid or basic as required with hydrochloric acid or sodium hydroxide. The PH of the resulting solutions was measured electrometrically.

Emulsions were made with 5 cc. of the gelatin solution and 10 cc. of the immiscible liquid in a test-tube. Tubes with a diameter of 2 cm. were used for the study of the influence of *PH*, whereas tubes with a diameter of 3.5 cm. were used in the study of the influence of concentration of the gelatin. Because of the influence of the vessel on the emulsion process, this accounts for the fact that values from Table I do not coincide with those given in Table II. The tubes were stoppered and placed in a shaking machine for one hour, at the end of which time they were removed, given 100 shakes by hand, and set aside. Readings were taken from time to time showing the amount of stable emulsion remaining.

Experimental Results

Effect of Concentration of Gelatin.—The concentrations of the gelatin used varied from 0.25 to 1.5%. Experiments were carried out by mixing these gelatin solutions with eight different liquids in the manner described above. These liquids were ethyl acetate, n-butyl alcohol, ether, benzene, nitrobenzene, chloroform, carbon tetrachloride and cottonseed oil. The first three did not form emulsions.

Emulsions were also made using gelatin adjusted to PH 3, and to PH 6

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[1] Holmes and Child, THIS JOURNAL, 42, 1049 (1920).

with the same concentration range of gelatin. The results are given in Table I.

TABLE I

PERCENTAGE STABILITY OF EMULSIONS *vs.* CONCENTRATION OP THE GELATIN

Emulsion	*P*H of the gelatin	Concentration of gelatin, % 0 25	 0 5	 0.75	 1	 1.25	 1.5
Benzene-water	3 0	20	87	87	100	93	87
	1 7	87	88	87	93	99	95
	6 0	92	94	92	93	97	97
Carbon tetrachloride-water	3.0	0	85	87	90	94	90
	4.7	88	90	93	100	100	100
	6 0	83	83	83	83	87	82
Chloroform-water	3.0	13	73	73	87	90	87
	4 7	87	88	94	97	87	87
	6.0	24	88	88	90	90	87
Nitrobenzene-water	3.0	0	77	26	80	80	53
	4 7	93	94	94	97	97	94
	6.0	77	80	80	87	97	84
Cottonseed oil-water	3.0	80	83	83	67	97	93
	4.7	60	60	60	60	87	60
	6.0	93	93	93	93	93	93

TABLE II

PERCENTAGE STABILITY OF EMULSIONS *vs.* PH OF GELATIN

Emulsion	% Gel	Time after shaking	*P*H 1 8	 2 2	 3.1	 4.7	 5.8	 6.4	 9.1	 10.9	 11.2
Chloroform-water	1	1 hour	70	73	67	60	54	57	60	17	3
		3 weeks	20	33	47	53	42	53	63	15	0
Carbon tetrachloride-water	1	1 hour	77	80	27	40	50	60	67	73	14
		3 weeks	33	60	0	26	40	46	53	60	10
Benzene-water	1	1 hour	13	15	17	93	93	43	86	80	74
		3 weeks	3	3	7	80	80	34	74	70	53
Nitrobenzene-water	1	1 hour	0	87	17	24	22	4	20	92	6
		3 weeks	0	80	10	20	18	0	17	87	3
Cottonseed oil-water	1	1 hour	90	93	93	93	93	92	93	93	100
		3 weeks	0	0	0	21	20	24	27	30	100

			*P*H 1.8	 2.2	 3.1	 4.7	 5.7	 6.3	 8.1	 9.9	 11.7
Chloroform-water	0.5	1 hour	10	30	15	93	87	88	7	87	90
		3 weeks	3	14	5	53	30	50	0	47	60
Carbon tetrachloride-water	0.5	1 hour	3	5	17	100	10	17	13	93	30
		3 weeks	0	0	13	96	2	10	7	80	25
Benzene-water	0.5	1 hour	73	73	44	90	90	23	37	84	93
	.	3 weeks	33	47	20	87	87	17	33	53	80
Nitrobenzene-water	0.5	1 hour	0	0	8	10	7	10	10	8	7
		3 weeks	0	0	3	3	3	5	5	3	5
Cottonseed oil-water	0.5	1 hour	77	80	94	94	94	94	94	94	97
		3 weeks	0	0	0	7	10	10	14	14	12

Effect of P_H.—The results obtained for the influence of P_H on the emulsifying properties of gelatin are given in Table II. It is to be noted that practically all the experiments show a good stability near the P_H of the dialyzed gelatin, with a minimum and a maximum on each side. Near a P_H of 1 or of 12 there is a second drop in emulsifying properties and beyond this the gelatin loses its emulsifying properties. This effect is not shown in all of the experiments but is shown for at least one concentration of gelatin with each substance.

Cottonseed oil did not give a good emulsion in the 0.5% solutions, even with the most basic solution. In the 1% solution the emulsions were poorest at the most acid and the best at the most basic points.

The Adsorption of Gelatin at the Interface.—In order to determine the extent of adsorption of gelatin at the interface of the emulsions, analyses of the aqueous phase before emulsification were compared with analyses of the first few cc. of aqueous phase that separated from the emulsion as it started to break down. The micro-Kjeldahl method for nitrogen in proteins was used to determine the gelatin content. The results are shown in Table III. It is to be observed that gelatin had been removed from the aqueous phase and concentrated at the interface in the emulsions of carbon tetrachloride, chloroform and benzene with gelatin solutions at P_H 4.72. These emulsions were stable at the end of one hour after shaking. The chloroform emulsion with gelatin solution at P_H 8.13, and the carbon tetrachloride emulsion with gelatin solution at P_H 2.25 were not stable, and Table III shows that there was no adsorption of gelatin at the interface of these emulsions. Apparently gelatin will serve as an emulsifying agent only when conditions are such as favor adsorption at the interface.

TABLE III

REMOVAL OF GELATIN FROM 0.5% SOLUTIONS TO INTERFACE OF EMULSIONS

Solutions analyzed	P_H	% Stability at 1 hour	N in 1 cc of solution mg.	Gelatin removed, %
Original	4.72	..	0.8370	..
From carbon tetrachloride	4.72	100	.7786	6.9
From chloroform	4.72	93	.6470	22.6
From benzene	4.72	90	.7299	12.8
Original	8.13	..	.9231	..
From chloroform	8.13	7	.9399	−1.7
Original	2.25	..	.8803	..
From carbon tetrachloride	2.25	0.5	.9058	−2.8

Discussion of Results

In the use of gelatin as an emulsifying agent for oil–water systems, it was found that the concentration of the gelatin between 0.25 and 1.5% at P_H 3, 4.7 and 6 was of little influence on the stability of the emulsion. The outstanding exception to this generalization was found in the case of

0.25% gelatin at PH 3, where the stability of four of the five emulsions was greatly decreased.

Examination of Table II showing the influence of PH on emulsifying properties of gelatin solutions shows that if PH of the gelatin solution is near the isoelectric point stable emulsions are formed. Addition of acid results in less stable emulsions at PH of about 3, another point of increased stability near 2.5 with a sharp drop when the PH is further decreased. Addition of alkali results in a sharp decrease in stability near PH of 6 with a maximum near PH of 10, and another decrease when PH rises above 11.

The factors which are generally considered important in the process of emulsification are: (1) mechanical treatment, (2) volume composition, (3) relative densities, (4) character of the walls of the container, (5) viscosity of the components and (6) the interfacial tension. In the experiments carried out the first four of these were kept as constant as possible, so that differences in stability of emulsions formed were probably due to changes in viscosity and interfacial tension. That such is the case can be seen from a comparison of the results obtained with curves showing the relation between viscosity of gelatin solutions and PH[2] and surface tension vs. PH.[3]

It is not to be expected that the maximum and minimum stabilities for one combination should exactly coincide with any other, for the nature of the interface is different in each case.

Summary

1. The emulsifying properties of gelatin for oil--water emulsions have been studied with reference to concentration of gelatin, PH of gelatin solution, and the possible adsorption of gelatin at the interface.

2. It has been found that variation of concentration between 0.25 and 1.5% has little effect at PH 3, 4.7, 6.

3. Changing the PH of the gelatin solution affects the emulsifying properties of the gelatin in a manner closely related to the changes of surface tension and viscosity of gelatin solutions with PH.

4. It has been found that whenever stable emulsions were formed, gelatin was concentrated at the interface.

EUGENE, OREGON

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[2] Elmer O. Kraemer, "Colloid Symposium Monograph," 1926, Vol. IV, 102.

[3] J. H. St. Johnston and G. T. Peard, Biochem J., 19, 281 (1925).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

DIPHENYLAMINE SULFONIC ACID AS A NEW OXIDATION–REDUCTION INDICATOR

BY L. A. SARVER AND I. M. KOLTHOFF

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Introduction

It was shown in a recent paper[1] that the first product of the oxidation of diphenylamine is the very insoluble white diphenylbenzidine, and that all but a trace of the indicator precipitates out with the completion of this stage of the reaction. The precipitate remains suspended in a finely divided condition, however, and is oxidized somewhat slowly by excess oxidant to the highly colored holoquinoid compound, diphenylbenzidine violet; but when the attempt is made to start with a solution of diphenylbenzidine, instead of producing it by the oxidation of diphenylamine, practically all of the indicator precipitates and settles out in large flocks. This suspension yields the violet color only after contact with a considerable excess of oxidant for several minutes. Therefore, while diphenylbenzidine is very satisfactory for reverse titrations, it does not work so well in direct titrations.

Furthermore, diphenylbenzidine violet reacts quickly with any unchanged diphenylbenzidine to form the very insoluble greenish-black meriquinoid compound, diphenylbenzidine green, which under certain circumstances imparts a muddy appearance to the solution, due to a mixture of considerable white and greenish-black precipitate with the violet solution. In addition, neither diphenylamine nor diphenylbenzidine give their color changes in the presence of even traces of tungstate,[2] a property which greatly limits their usefulness in the analysis of alloy steels. The present authors have ascertained that tungstate forms blue insoluble compounds with the colored oxidation products of diphenylamine, thus removing them from the solution. Hence, it was thought that some of the objectionable features might be corrected by introducing a strongly polar group like —SO_3H into the molecule, thereby increasing its solubility and that of its oxidation products.

I. Preparation of Barium Diphenylamine **Sulfonate.**—Equimolecular quantities of diphenylamine and acetic anhydride were treated with a few cubic centimeters of concentrated sulfuric acid and refluxed for one hour, after which the excess acetic acid was removed by washing with cold water and the acetyldiphenylamine recrystallized from ether and dried at 100°.[3] Then 200 g. of 20% fuming sulfuric acid was cooled to 5°, and

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[1] I. M. Kolthoff and L. A. Sarver, THIS JOURNAL, 52, 4179 (1930).

[2] H. H. Willard and Philena Young, *Ind. Eng. Chem.*, 20, 764 (1928).

[3] A. Claus, *Ber.*, 14, 2365 (1881).

100 g. of the pulverized acetyldiphenylamine added in small portions, with constant stirring. The mixture was warmed to 45° on a water-bath for two hours, with continued stirring, then poured into 250 cc. of water and boiled for three hours to hydrolyze the acetyl compound, after which it was poured into a large volume of water and the unchanged diphenylamine filtered off. The filtrate was neutralized with barium carbonate, the barium sulfate filtered off[4] and the white barium diphenylamine sulfonate removed from barium acetate by fractional crystallization. The barium salt of diphenylamine sulfonic acid is sufficiently soluble for the preparation of indicator solutions, and has been used for subsequent work.

An analysis of the salt showed 21.88% barium, whereas the theoretical value for the anhydrous salt of the monosulfonic acid is 21.64%. Being primarily interested in the purity of the product, no attempt was made to secure a quantitative yield, though it may be mentioned that Gnehm and Werdenburg[4] obtained 80% of the theoretical amount of the monosulfonic acid, with 17% of the diphenylamine recovered unchanged.

II. Indicator Properties.—All the experimental evidence confirms the assumption that the mechanism of the oxidation of diphenylamine sulfonic acid is similar to that of diphenylamine; that it is first oxidized to diphenylbenzidine sulfonic acid, and then to diphenylbenzidine sulfonic acid violet, which forms a meriquinoid compound, diphenylbenzidine sulfonic acid green, with unoxidized diphenylbenzidine sulfonic acid.

Potentiometric titrations of diphenylamine sulfonic acid with potassium dichromate (similar to those of diphenylamine and diphenylbenzidine described in a previous paper[1]) were not very satisfactory from the stoichiometric point of view; nevertheless, it has been possible to determine the potential at which the color change takes place. Since the oxidation by dichromate is very slow in the absence of ferrous iron, it was more advantageous to add an excess of the dichromate to the acidified solution of diphenylamine sulfonic acid, and then titrate back with ferrous solution. For the details of the performance of these experiments the reader is referred to the previous paper. Further addition of ferrous solution after the reduction of the reddish-violet to diphenylbenzidine sulfonic acid green changes the color to a pale yellow, whereas diphenylbenzidine green was not affected by an excess of ferrous ions. The color change green to reddish-violet, and the reverse, takes place at a potential of about 0.59–0.60 v. (against the saturated calomel electrode, or 0.83–0.84 v., against the normal hydrogen electrode) in sulfuric acid solutions between 0.5 and 2.0 normal, whereas the color change for diphenylbenzidine occurs at about 0.51 v. (against the saturated calomel electrode, or 0.76 v., against the normal hydrogen electrode) under the same conditions. This difference of

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[4] R. Gnehm and H. Werdenburg, Z. *angew. Chem*, **43**, 1027 (1899); V. Merz and W. Weith, *Ber.*, 5, *283* (1872), communicated by O. Meister.

oxidation potential was confirmed by the following experiment. A portion of a ferrous solution in normal sulfuric acid, but without any phosphoric acid, was titrated potentiometrically in one case, 20.23 cc. of 0.1 N dichromate being required; a similar sample showed a faint trace of color with 20.20 cc., and a good color with 20.25 cc., when diphenylamine sulfonic acid was used as indicator; but when diphenylamine was used as indicator in another similar sample, a muddy green precipitate appeared when about 19.00 cc. had been added, with more and more violet from 19.50 cc. on.

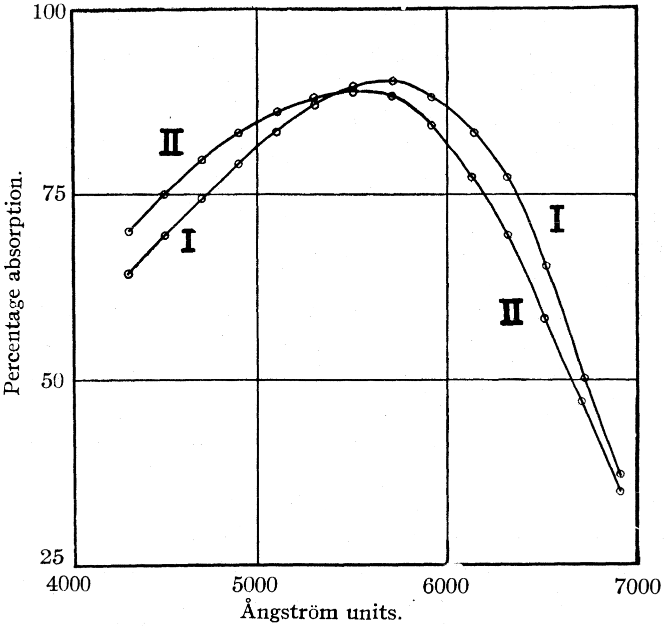

Fig. 1.—Absorption spectra of diphenylbenzidine violet and diphenylbenzidine sulfonic acid violet. I, diphenylbenzidine violet; II, diphenylbenzidine sulfonic acid violet.

The diphenylbenzidine sulfonic acid violet has a reddish-violet color resembling that of a dilute permanganate solution, and its absorption spectrum in the visible region resembles that of diphenylbenzidine violet (cf. Fig. 1), except that the former absorbs more in the red.

The speed of formation of the diphenylbenzidine sulfonic acid violet depends upon the oxidation potential of the solution, as is the case with diphenylamine and diphenylbenzidine. With permanganate or vanadate an acidified solution of the diphenylamine sulfonic acid is colored almost instantly; but with dichromate the coloration is very slow, even at high hydrogen-ion concentrations and with a relatively large excess of oxidant;

with this reagent the speed of oxidation is much less than in the case of diphenylamine or diphenylbenzidine. The presence of ferrous iron (see also the previous paper[1]) accelerates the oxidation of diphenylamine sulfonic acid tremendously; for example, with 0.1 cc. of 0.005 M indicator and 0.2 cc. of 0.01 N dichromate in 50 cc. of 2 N hydrochloric acid the violet color appeared within fifteen to twenty seconds in the case of diphenylaniine, and after two to three minutes in the case of diphenylamine sulfonic acid; but if 0.2 cc. of 0.01 *N* ferrous solution are first added to the acid solution of the latter indicator, and then 0.4 cc. of 0.01 N dichromate, the color appears after about one second with diphenylamine, and instantly with diphenylamine sulfonic acid.

The color change in the titration of ferrous iron by dichromate is very brilliant and sharply reversible; indeed, the coloring power of the substance is so great that titrations may be made in highly colored solutions where diphenylamine and diphenylbenzidine are not satisfactory. The presence of mercuric chloride has no influence upon the speed of formation of the reddish-violet oxidation product, whereas it retards the oxidation of diphenylamine and diphenylbenzidine very markedly. Finally—and this is the main advantage of the new indicator—its indicator properties are not affected by the presence of tungstate, whereas diphenylamine and diphenylbenzidine are useless in the presence of even traces of this substance.

The indicator corrections for diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid in dilute solutions will be considered in a future paper.

Summary

Diphenylamine sulfonic acid has indicator properties similar to those of diphenylamine, but its color change is more sharp and brilliant. It can be used in the presence of tungstate, whereas diphenylarnine and diphenylbenzidine cannot. Ferrous iron has an enormous accelerating effect upon the speed of its oxidation, while mercuric chloride has no harmful effect. The absorption spectrum has been determined, and the electrochemical properties investigated.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

INDICATOR CORRECTIONS FOR DIPHENYLAMINE, DIPHENYLBENZIDINE AND DIPHENYLAMINE SULFONIC ACID

BY L. A. SARVER AND I. M. KOLTHOFF

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Introduction

The reaction mechanisms of the oxidation of diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid have been discussed in previous papers,[1] and it may be predicted from these that in the titration of reducing agents with potassium dichromate, diphenylbenzidine will require a negligible correction, whereas diphenylamine or diphenylamine sulfonic acid ought to consume an equivalent amount of reagent for their oxidation to the diphenylbenzidine state. In the titration of oxidizing agents with ferrous iron, however, it is hard to predict the size of the corrections, because of the instability of the colored holoquinoid compounds. Therefore an extensive study has been made of the analytical conditions and indicator corrections necessary for diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid in the various titrations.

I. Indicator Solutions.—Each indicator was made up so as to be 0.005 molar (1.69 g. of diphenylamine per liter of concentrated sulfuric acid; 1.68 g. of diphenylbenzidine per liter of nine parts glacial acetic acid and one part concentrated sulfuric acid; 3.17 g. of anhydrous barium salt of diphenylamine sulfonic acid per liter of water), and to require theoretically an equal volume of 0.01 N oxidizing or reducing solution for each stage of the oxidation of the indicator.

II. Standard Solutions.—The dichromate solution was prepared by dissolving a given weight of pure potassium dichromate in water, and making up to a known volume. The ferrous and vanadate solutions were then standardized potentiometrically.

III. Titration of Ferrous Iron with Potassium Dichromate. 1. Recommended Conditions.—The solutions should be about 1.0 N with sulfuric or hydrochloric acid (the former being somewhat preferable), but they may vary between 0.5–2.0 N when diphenylamine or diphenylbenzidine is used as indicator, or between 0.25–3.0 N when diphenylamine sulfonic acid is used. About 10 cc. of 25% phosphoric acid should be present for each 50 cc. of volume, but considerable variation is permissible. Mercuric chloride renders color development slower with diphenylamine or diphenylbenzidine, but does not otherwise affect the accuracy of the titration; it has no appreciable effect upon the behavior of diphenylamine sul-

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[1] I. M. Kolthoff and L. A. Sarver, THIS JOURNAL, 52, 4179 (1930); L. A. Sarver and I. M. Kolthoff, *ibid.*, 53, 2902 (1931).

fonic acid. In those cases where color development is slow, the oxidation of the indicator can be speeded up by warming to 50°, but the colors are then less permanent; diphenylbenzidine is generally less satisfactory than the other two for titrations of ferrous iron by dichromate, on account of the slowness of color development. No unnecessary excess of stannous chloride should be used in the reduction of the iron, because of the large amount of mercurous chloride precipitate obtained later. Stannic and manganous salts have no effect upon any of the three indicators, but only diphenylamine sulfonic acid can be used in presence of tungstate. Titrations can be made with 0.1, 0.01 or 0.001 N dichromate, but diphenylbenzidine is not recommended for the weaker solutions. Diphenylamine sulfonic acid is recommended for the micro-titration of ferrous iron, it being possible to determine 0.5 mg. of iron in a small volume within an accuracy of 1%. Especially when titrating with the weaker solutions, the volumes should not greatly exceed 50 cc., although they may be 100–250 *cc.* for 0.1 N dichromate.

2. Recommended Amounts of Indicators.—For titrations with 0.1 N dichromate in 100–250 cc. volumes, 5–6 drops of 0.005 molar indicator (7–10 drops of 0.1% diphenylamine or diphenylbenzidine or of 0.2% diphenylamine sulfonic acid barium salt) should be used. With 0.01 or 0.001 N dichromate in 10–50 cc. volumes, 0.02–0.05 cc. of 0.005 molar diphenylamine or diphenylamine sulfonic acid (0.03–0.06 cc. of 0.1% diphenylamine or 0.2% diphenylamine sulfonic acid barium salt) will give sharp distinct color changes.

3. Indicator Corrections.—Indicator corrections for titrations with 0.01 and 0.001*N* dichromate solutions, respectively, are given in Table I. It is seen that the excess of dichromate required for obtaining an end-point increases with increasing amounts of indicator; with diphenylamine, the corrections were found to be approximately the theoretical for amounts up to 0.3 cc. of 0.005 molar indicator, and 0.1 cc. of 0.01 *N* dichromate (or 1.0 cc. of 0.001 N dichromate) should be deducted for each 0.1 cc. of

TABLE I

INDICATOR CORRECTIONS FOR TITRATIONS OF FERROUS IRON WITH **0.01** OR **0.001** *N* POTASSIUM DICHROMATE SOLUTION

For each titration, 10 cc. of 0.01 or 0.001 N ferrous solution was added to a mixture of 10 cc. of 25% phosphoric acid, 1.2 cc. of concentrated sulfuric acid, 15 cc. of water and the stated volume of indicator.

Volume of 0.005 *M* indicator, cc.	Diphenylamine Excess of $K_2Cr_2O_7$ required, cc. 0.01 N	Diphenylamine Excess of $K_2Cr_2O_7$ required, cc. 0.001 *N*	Diphenylamine sulfonic acid Excess of $K_2Cr_2O_7$ required, cc. 001 N	Diphenylamine sulfonic acid Excess of $K_2Cr_2O_7$ required, cc. 0 001 *N*
0.02	0.01	0.21	0.02	0.21
.04	.04	.41	.05	.44
.10	.10	.95	.18	.93
.20	.21	1.90	.34	1.85
.30	.39	..	.51	3.48
.50	.63	..	0.75–0.90	..

indicator used (0.06 cc. and 0.6 cc., respectively, for each 0.1 cc. of 0.1% diphenylamine). With larger amounts of indicator, the presence of much diphenylbenzidine green interferes with the observation of the color. With diphenylamine sulfonic acid also, the corrections (expressed in terms of 0.01 N oxidizing solution) were found to be equal to the volume of 0.005 molar indicator (0.06 cc. of 0.01 *N* solution for each 0.1 cc. of 0.2% diphenylamine sulfonic acid barium salt) when less than 0.3 cc. was used and the titration made with 0.001 N dichromate solution; but when the titrations were made with 0.01 *N* dichromate solution, the corrections were somewhat larger than the theoretical.

IV. Titration of Dichromate or Vanadate Solutions with Ferrous Iron.—The same considerations as to titration volume, quantity of indicator and concentrations of phosphoric acid and sulfuric or hydrochloric acid, apply to the titration of 0.01 *N* dichromate or vanadate by 0.01 N ferrous iron. The presence of sodium acetate in the vanadate titration, as recommended by Willard and Young,[2] does not seem to be necessary, although the neutralization of the strong mineral acid does take away a disturbing color when much ferric iron is present. The violet color develops very slowly in acid dichromate solutions, especially when diphenylamine sulfonic acid is used as indicator, but a brilliant color appears instantly when the titration with ferrous iron is begun. In an acid vanadate solution the color develops rapidly without the addition of ferrous iron, so the titration can be started almost immediately after the addition of any of the three indicators.

TABLE II

INDICATOR CORRECTIONS FOR TITRATIONS OF DICHROMATE OR VANADATE SOLUTIONS WITH 0.01 N FERROUS IRON SOLUTION

For each titration, 10 cc. of 0.01 N dichromate or vanadate solution was added to a mixture of 10 cc. of 25% phosphoric acid, 1.2 cc. of concentrated sulfuric acid, 15 cc of water and the stated volume of indicator; the whole was then titrated at once with 0 01 *N* ferrous solution. The volumes given below should be added to the volume of 0.01 N ferrous solution used in any given titration.

Volume of 0 005 *M* indicator, cc.	Diphenylamine		Diphenylbenzidine		Diphenylamine sulfonic acid	
	Dichromate, cc.	Vanadate, cc.	Dichromate, cc.	Vanadate, cc.	Dichromate, cc.	Vanadate, cc.
0.02	0 04	0 03	0.02	0.03	0 05	0.03
.04			04	05	.13	.12
.10	.24	20	.10	.11	.31	.30
.20	..	.40	.17	.20	.58	.60
.30	.63	.63	.24	.29	.95	.95
50	..	..	.36		..	..

From the data in Table II it is seen that the indicator corrections are approximately the same in the dichromate and the vanadate titrations. If the titration is started immediately after the addition of the indicator

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[2] H. H. Willard and Philena Young, *Ind. Eng. Chem.*, 20, 764 (1928).

0.1 cc. should be added to the volume of 0.01 *N* ferrous solution required for each 0.1 cc. of 0.005 *M* diphenylbenzidine (0.06 cc. for each 0.1 cc. of 0.1% diphenylbenzidine), 0.2 cc. for each 0.1 cc. of 0.005 *M* diphenylamine (0.12 cc. for each 0.1 cc. of 0.1% diphenylamine) and 0.3 cc. for each 0.1 cc. of 0.005 M diphenylamine sulfonic acid (0.18 cc. for each 0.1 cc. of 0.2% diphenylamine sulfonic acid barium salt). The correction is smaller for diphenylbenzidine than for diphenylamine, as could be expected. Diphenylamine sulfonic acid has the largest correction, but it is still recommended because it gives a sharp, brilliant color change, and can be used in the presence of tungstate. If the titration is not started immediately after the addition of the indicator, the corrections will be larger, on account of the decomposition of the holoquinoid compounds. This increase in the correction with time is negligible in the case of diphenylbenzidine when the titration is completed within fifteen minutes after the addition of the indicator, but it is appreciable in the case of diphenylamine sulfonic acid. For example, when a mixture of 10 cc. of 0.01 N vanadate solution, 10 cc. of 25% phosphoric acid, 1.2 cc. of concentrated sulfuric acid, 15 cc. of water and 0.2 cc. of 0.005 *M* diphenylamine sulfonic acid, was titrated with 0.01 N ferrous solution as quickly as possible, the correction was 0.55 cc. of 0.01 *N* solution; but after five, ten, fifteen and thirty minutes' standing, the corrections were 0.62, 0.68, 0.74 and 0.76 cc., respectively.

Summary

Analytical conditions (acidity, volume, amount of indicator, etc.) and indicator corrections have been given for the titration of 0.1, 0.01 and 0.001 N ferrous solutions with 0.1, 0.01 and 0.001 N potassium dichromate solutions, respectively, as well as similar information on the titration of 0.01 N dichromate or vanadate solutions with 0.01 N ferrous iron solution, using diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid as indicators. Diphenylamine sulfonic acid is recommended because of its rapid brilliant completely reversible color changes, and its usefulness in the presence of tungstate.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE KINETICS OF GAS EXPLOSIONS: THE THERMAL DECOMPOSITION OF OZONE SENSITIZED BY BROMINE VAPOR[1]

BY BERNARD LEWIS[2] AND W. FEITKNECHT[3]

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The kinetics of the thermal reaction between ozone and bromine below 13° was studied by Lewis and Schumacher.[4] It was found that bromine reacts with ozone quantitatively, forming a white crystalline oxide of bromine having the composition Br_3O_8 which is slowly deposited on the walls of the vessel. Following the complete disappearance of free bromine, the ozone decomposes into oxygen at a constant rate which is independent of the size and the kind of reaction vessel, ozone concentration (above a certain limit) and inert gases, but which depends on the quantity of oxide formed and on the temperature. Thus it was found that the rate of decomposition of ozone is directly proportional to the original concentration of bromine, namely

$$+\frac{dp}{dt} = k[Br_2]$$

and that the temperature coefficient has a value of **3.15** for 10° between 0 and 10°.

These investigators observed that if the temperature is raised to 20° no oxide of bromine is deposited. Instead there is a period of quiescence (lag period) during which no change in pressure occurs, followed by a sudden explosion which is accompanied with the evolution of light. This phenomenon, which involves only the decomposition of ozone into oxygen in the presence of the catalyst bromine, seemed to present a medium by which some light might be thrown on the concept of chain reactions.

The experiments in the transition range between temperatures at which solid oxide is formed and explosions occur are described elsewhere.[5] They are interpreted on the basis of the formation of an unstable adsorption compound of bromine and ozone at the wall which becomes increasingly more stable with decreasing temperature. The unstable compound, on decomposing, forms an active product which is ejected into the gas phase and starts reaction chains. By lowering the temperature the product of

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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 the Indianapolis, Indiana, meeting, April, 1931.

[2] Physical chemist, U. S. Bureau of Mines. Pittsburgh Experiment Station. Pittsburgh, Pa.

[3] Foreign exchange fellow, University of Pittsburgh.

[4] Lewis and Schumacher, (a) *Z. physik. Chem.*, 138A, *462* (1928); 6B, 423 (1930); *(b) Z. Elektrochem.*, 35, *651* (1929); (c) *Z. anorg. Chem.*, *182*, 182 (1929); (d) *Nature*, 125, 129 (1930).

[5] Lewis and Feitknecht, Z. *physik. Chem.*, (in press).

this decomposition becomes less active as far as its ability to start reaction chains is concerned. This is shown by the gradually changing character of the reaction from a predominantly gas phase to a wall reaction.

Preliminary Experiments

In some early experiments, on mixing ozone and bromine in certain proportions, we were struck by the remarkably long lag periods which preceded explosions. Their duration was, in some instances, as long as one hour. The time was not easily reproducible.

It was soon discovered that these exceptionally long lag periods were caused by arsenous bromide. Due to the nature of the experimental technique, which involved repeated evaporation and freezing out of bromine on one side of a brass needle valve, arsenic in the latter was attacked and accumulated in the bromine reservoir as a white crystalline arsenous bromide ($AsBr_3$, melting point 31°). This compound was carried with the bromine into the reaction vessel and was adsorbed on the walls. Upon replacing the brass needle valve by a specially constructed stainless-steel diaphragm valve, the arsenic compound was eliminated completely and the lag periods were shortened to the order of one minute.

The length of the lag period is influenced by such factors as the ozone and bromine concentrations, the temperature and the activity of the vessel. As far as the lag period was concerned it made considerable difference whether ozone or bromine was admitted to the reaction vessel first. The lag times were shortened from minutes for the order bromine + ozone to several seconds for the order ozone + bromine.

The pressure of ozone just necessary to develop an explosion will be used as a measure of the explosion limit.[6] It was found to be influenced principally by temperature and the presence of inert gases. Moreover, the slow decomposition (in the event that the ozone pressure was below the explosion limit) was similarly affected.

These experiments led us to the belief that the wall of the vessel is of considerable importance for the development of explosions in this reaction, namely, that it is the seat of the initiation of chain reactions. Other investigators working with quite different systems have recently arrived at the same conclusion.[7,8]

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[6] The term explosion limit in a two-component system at a definite total pressure. say atmospheric, is usually applied to the percentage combustible necessary to develop an explosion. In a one-component system, as in the present case, pressure is used as a measure of the explosion limit

[7] See experiments on the inflammation of hydrogen and oxygen by Alyea and Haber, *Naturwiss.*, 18, 443 (1930); *Z. physik. Chem.*, **10B**, 193 (1930); Farkas, Haber and Harteck, *Naturwiss.*, 18,443 (1930); *Z. Elektrochem.*, *36*, *722* (1930).

[8] Thompson, *Z. physik. Chem.*, **10B**, 273 (1930); Alyea, THIS JOURNAL, 53, 1324 (1931).

Apparatus

The apparatus used in this investigation was described in its essential details in an earlier work.[4b] Certain additional features will be mentioned. In order to obtain pure and stable ozone, all greased stopcocks had to be eliminated and metal needle valves used in their stead. The needle valves used here are similar to those used previously with a slight modification to prevent the needle from sticking in the seat of the valve. The cone of the needle was made of a specially hard non-corrosive chrome–nickel–vanadium–tungsten steel. A stainless-steel diaphragm valve separated the bromine reservoir from the rest of the apparatus. It is similar in principle to that of Bodenstein and Dux,[9] but its principal parts consist of only two pieces, thus limiting the number of soldered joints to one. This joint is on the outside of the lapped-over rim of the diaphragm. The chief advantages of the valve are its simplicity of construction and freedom of exposure of corrosive gases to soldered joints.

The manometer system consisted of a Bodenstein quartz spiral manometer as a null instrument, backed by a mercury manometer and bromonaphthalene manometer (1 mm. Hg = 9.15 mm. bromonaphthalene). By means of a graduated scale in the telescope used for observing movements of the quartz spiral manometer pointer, a change of 0.02 mm. of mercury was observable.

Inert gases were stored in liter flasks. Before being used they were passed very slowly through a liquid-air trap (ether–carbon dioxide mixture for carbon dioxide gas) and a fine porous-plate Pyrex glass filter sealed into the Pyrex tubing to remove any possible suspended material. The filter is similar to the Jena porous-plate filter but is not obtainable commercially in Pyrex glass. Since the Jena filter could not be sealed into Pyrex tubing, a simple method[10] of making them of Pyrex glass was developed by one of us (B. L.) and they have been in use in this Laboratory for a year and a half with excellent results.

The reaction vessels used were two Pyrex glass bulbs (hereafter called vessels I and II) and a quartz bulb, each of 250 cc. capacity, and a number of cylindrical Pyrex glass tubes of various diameters. The experiments were conducted in a temperature-controlled water-bath. The reaction vessel was protected from light exposure.

Materials

The purest Kahlbaum bromine was used. It was distilled at a low temperature under high vacuum through anhydrous magnesium perchlorate and a Pyrex glass porous-plate filter directly into the bromine reservoir and sealed under vacuum.

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[9] Bodenstein and Dux, Z. *physik. Chem.*, 85,297 (1913).

[10] Recently a similar filter and method was described by W. F. Bruce and H. E. Bent, THIS JOURNAL, 53, 990 (1931). Scrap Pyrex glass is ground to a fine powder. For a moderate-size grained filter, glass which passes a 60 mesh but not an 80 mesh sieve may be used. For finer filters, small particles should be ground to pass an 80 but not a 100 mesh sieve, etc. A layer of glass about 1.5 mm. deep is placed in a cylindrical mold such as described by Bruce and Bent or a mold made of platinum foil bent into shape as was used here. The procedure which was found satisfactory is to place the mold in a furnace at 890°. It is removed after twenty seconds and allowed to cool, after which the disk of glass separates easily from the mold. The disk is then placed on a small nickel or iron plate and once again heated in the furnace for forty seconds. The times will vary depending on the kind and size of mold. The technique is soon acquired after a little experimentation. The disk is smoothed with a file, placed in a tapered glass tube of the proper size and sealed in with a fine flame in the usual manner. Filters from 1 to 2.5 cm. in diameter have been made in this way.

Ozone was made and concentrated by the method of Riesenfeld and Schwab.[11] Pure dry electrolytic oxygen was passed through a Pyrex glass filter and a Siemens ozonizer into an evacuated flask containing a liquid-air trap. The oxygen in the mixture of liquid oxygen and ozone was pumped off and the ozone which remained had a purity of 99 to 100%. This was tested by noting the increase in pressure on exploding some of the pure ozone. The ozone was very stable in the temperature range of these experiments. At ordinary temperatures no increase in pressure could be observed over a period of several hours.

The inert gases used, namely, oxygen, nitrogen, helium, argon and carbon dioxide, were the purest obtainable in tanks. The helium and argon contained a little nitrogen and were 97% and 95.5% pure, respectively. Carbon dioxide was condensed in liquid air and the non-condensable gases were pumped off. It was then stored in the gas form.

Experimental Procedure

The principle of the measurements was to admit bromine and ozone separately into the reaction vessel at a definite temperature and to measure the increase in pressure with time caused by the reaction $2O_3 = 3O_2$. During the reaction the pressure of bromine remains unchanged. Before starting an experiment, all the ozone was allowed to evaporate in its reservoir and was then very carefully admitted to the reaction vessel by cracking the needle valve.[12] Unless otherwise stated, the order of entering the reaction vessel was bromine, inert gas (when used), ozone. Occasionally bromine was added last. The ozone was admitted rather rapidly and the time was taken when 10% was already in the vessel. When not in use both the ozone and bromine were maintained in liquid air in their respective reservoirs. Before each experiment the reaction vessel and also the ozone reservoir were pumped out with a diffusion pump to about 10^{-5} mm. For reasons which will become apparent later most experiments were conducted with 5 mm. of bromine.

In order to show the characteristic way in which bromine sensitizes the decomposition of ozone a number of experiments at 35° are plotted in Fig. 1 for different initial ozone pressures for the first three minutes of reaction. The experiments were made in the quartz vessel.

At low pressures of ozone the reaction commences slowly after the lag period. It then accelerates, goes through a maximum, after which it slows down. The form of the curve cannot be represented by a simple relationship. At higher ozone pressures the velocity is correspondingly greater. Above a definite pressure, in this case 32 mm. of ozone, the velocity rises so rapidly that an explosion results. Thirty-two mm. of ozone is therefore the explosion limit for these conditions. The curve for 30 mm. illustrates a mixture on the verge of explosion, the drop in pressure after the sudden rise being due to the dissipation of heat. The curve for 34 mm. represents an explosion. It will be observed that the lag period varies

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[11] Riesenfeld and Schwab, *Ber.*, 55, 2088 (1922).

[12] Violent explosions take place if the needle valve is opened suddenly and too wide.

inversely as the ozone pressure and the rate of decomposition increases with the initial ozone concentration.

Activity of Vessel

Whilst the lag period, limit of explosion and rate of the slow reaction could vary in a given vessel to a considerable degree, they proved to be related to each other, namely, a short lag period corresponds to a low explosion limit and a high reaction rate.[13] It will be evident that these factors are really a measure of the activity of the wall of the vessel. The nature of this activity will be discussed later.

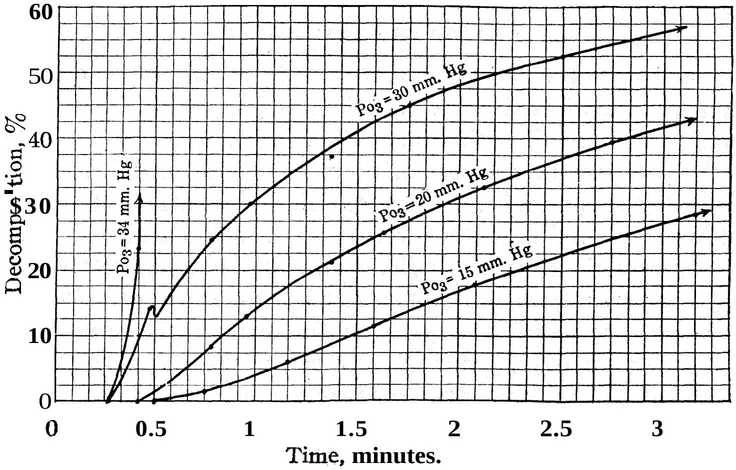

Fig. 1.—Typical curves showing decomposition of ozone: T, 35°; Br_2 pressure, 5 mm.

An inactive vessel could be made active by carrying out a reaction near the explosion limit or more effectively by admitting enough ozone to bring about an explosion. Extreme activity was never realized except by a succession of explosions. It therefore made some little difference from which side the explosion limit was approached, it being 1 to 2 mm. lower approached from the explosion or high ozone pressure side than from the slow reaction or low ozone pressure side. In all experiments the explosion limit was determined from the explosion side.

Deactivation of a vessel became more and more pronounced the longer it remained in disuse. For a moderate reversion to inactivity three or four days were required. It also became increasingly more difficult to reactivate. This is illustrated in Table I, in which are given data for different vessels which had remained unused for different periods of time.

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[13] No such relationship was evident between the lag period and explosion limit when different vessels were compared. A vessel showing a long lag period could have quite a low explosion limit and vice versa (see Table II).

After each experiment the vessel was pumped out thoroughly and a fresh mixture admitted.

TABLE I

REACTIVATION OF VESSELS UNUSED FOR DIFFERENT PERIODS OF TIME

Vessel	Time unused	Temp., °C.	Mixture of gases	Expt.	Remarks
Glass bulb	17 days	25	5 mm. Br_2 16 mm. O_3	1	No change in 20 minutes
			(2 mm. above explosion limit)	2	Lag period 10 minutes; slow reaction
				3	Lag period 2 minutes; explosion
				4	Lag period 30 seconds: explosion (vessel very active)
Quartz bulb	I night	25	5 mm. Br_2 **23** mm. O_3	1	Lag period 1 minute, 15 seconds; slow reaction
			(2 mm. above explosion limit)	2	Lag period **32** seconds; explosion

A decrease in activity was also observed when air or inert gases which were not very carefully purified were admitted to the vessel. A much more marked but similar effect is observed with water vapor. **A** 0.1 mm. pressure of water vapor is sufficient to inhibit completely an explosion and to reduce the reaction velocity considerably. Even when the vessel was activated each day by the same method, it often showed slight differences in activity which affected not so much the explosion limit as the lag period and particularly the slow reaction at low ozone pressures. Thus for apparently the same conditions many experiments showed the same rate of decomposition whilst others differed considerably. Therefore it was necessary to make frequent tests of the activity of the vessel and to compare only those experiments which had been performed under similar conditions.

The differences in the activities observed may be due mainly to two causes: (1) active products formed during the decomposition or explosion of ozone remain adsorbed on the walls, thereby imparting more active properties to the latter (compare Farkas, Haber and Harteck).[7] *(2)* The activity is a property of the wall itself—that is, the surface consists of more or less active spots, according to the views of Taylor.

The experiments indicate, particularly when the activities of different vessels are compared (see Table 11), that it is the second factor which is of greater importance while the first exerts, if any, only a small influence. In this connection a highly active vessel which was heated to *ca.* 300° under high vacuum showed only a small decrease in activity. The inactivity of a new vessel or the deactivation of an active vessel by an impurity (such as $AsBr_3$ or unpurified air) may therefore be due to the adsorption of an impurity on the most active centers. The extreme activity which is observed to follow a number of intensive explosions seems to be due to a temporary change in the nature of the surface.

TABLE II

A COMPARISON OF THE ACTIVITY OF DIFFERENT VESSELS HAVING THE SAME SHAPE AND VOLUME

Vessel	State of activity	Lag period	Explosion limit
Glass I	New (moderate activity)	1'30"	14
Glass I	Very active	30"	12.5
Glass II	New (moderate activity)	1'10"	16
Quartz	New	35"	22
Quartz	Very active	30"	19.5

The experiments to be described and the data to be given in the following sections will be divided into two main parts: those dealing with the explosion limit and those concerning the slow decomposition below the limit.

Experiments on the Explosion Limit

1. Influence of Bromine on the Explosion Limit at **Different Temperatures.**—The main results are given in Fig. 2. The influence of bromine on the explosion limit varies with the temperature. Above 35° the limit is uninfluenced by the bromine concentration, even for a 100-fold variation. Below 35° a small influence is observed which becomes more pronounced as the temperature decreases. The limits were determined with an accuracy of ±0.5 mm. ozone pressure. At about 5 mm. of bromine the explosion limit curve goes through a minimum. For this reason this bromine pressure was used in nearly all subsequent experiments. Below 25° the change in the explosion limits with bromine concentration becomes still more marked, and the deposition of solid oxide becomes increasingly more probable. The phenomena are very different from those at higher temperatures and rather complex. Experiments in this range form the subject of a paper which is published elsewhere.[5]

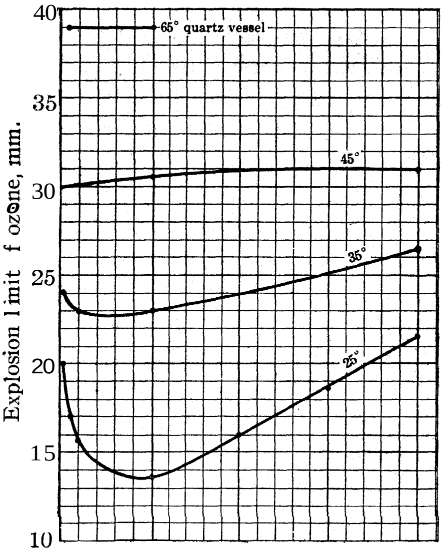

Fig. 2.—Influence of bromine on explosion limit.

2. Influence of **Temperature.** (a) Effect of Temperature on the **Lag** Period and the Decomposition Preceding Explosion.—The influence of temperature on the lag period and on the decomposition preceding an

explosion was studied for ozone pressures just above. the explosion limits and for a constant bromine pressure of 5 mm. The lag period and the length of time during which decomposition takes place before the explosion sets in decreases with increasing temperature (Fig. 3). Of special interest is the character of the curves. Above 25° the decomposition accelerates rapidly and continuously up to the explosion point, whereas below 25° the transition to the explosion is abrupt and increasingly so as the temperature is lowered.

Confining ourselves to temperatures above 25° the amount of ozone decomposed before explosion sets in depends on the temperature. It is greatest between the temperatures of 35 and 55°.

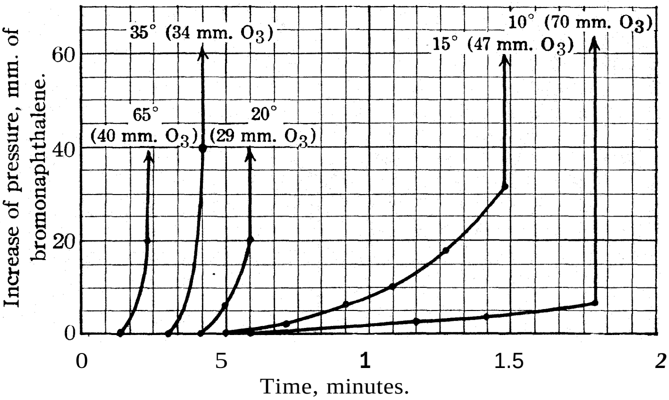

Fig. 3.—Influence of temperature on the reaction preceding explosion.

(b) **Effect of Temperature on Explosion** Limit.—Figure **4** shows that the explosion limit undergoes considerable change with temperature. It goes through a maximum at about 55° and a minimum at about 25°. Usually below 15° no explosions occur except when the vessel is in an exceptionally high state of activity.

A very active vessel may be rendered ineffective for developing an explosion below 15° by carrying out several experiments at an ozone pressure below the explosion limit. Solid oxide of bromine is gradually deposited on the wall, "conditioning" the vessel against explosions. In a vessel conditioned in this way, no explosions occur at 15° far above the normal explosion limit for an active vessel. However, the lag period is still short, indicating that the "conditioning" process does not affect the wall in the same way as the different kinds of deactivation described in a previous section.

3. Effect of Increasing the Surface on the Explosion Limit.—A new glass vessel (No. II) was completely filled with pieces of Pyrex glass tubing about 1 cm. long, 5 mm. outside and 3.6 mm. inside diameter. The actual change in surface was from 163 sq. cm. to 2067 sq. cm. and in volume from 195 cc. to 134 cc. for the empty and packed vessels, respectively. The increase in the ratio of surface to volume was 19 times. The greatest distance between any two surfaces was approximately 3.6 mm. The explosion limit in the empty vessel was about 16 mm. of ozone at 25°, but in the packed vessel no explosion was possible even up to 100 mm. of ozone. Anticipating our discussion later it is evident that although a large number of chains are started from the walls they are terminated by collisions with the surface before they can develop into an explosion.

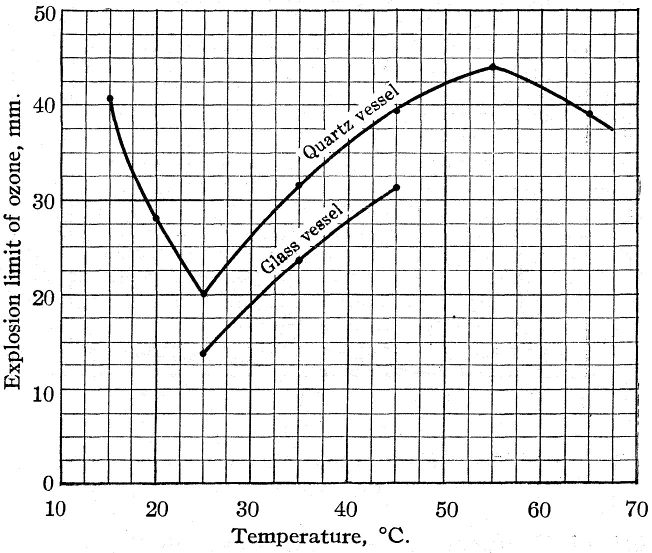

Fig. 4.—Effect of temperature on the explosion limit.

Half the number of glass pieces were now removed, so that half the volume was free. Here the explosion limit was about 29 mm. of ozone, some 13 mm. higher than in the empty vessel. It was found that 100% of the ozone had decomposed during the explosion, indicating that once the latter is started in a free space it travels unhindered through small openings. On several previous occasions the ozone reservoir was blown up due to the propagation of the explosion from the reaction vessel through a slightly opened needle-valve and capillary tubing about 0.1 mm. in diameter.[14] It was estimated that the speed of propagation was of the order of magnitude commonly found for a detonation in gases. From these facts it must be concluded that one is dealing here with detonations rather than

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[14] Obviously the explosion will not travel through very small openings such as are encountered in a fine porous glass filter. (See also Riesenfeld and Wassmuth, *Z physik. Chem.*, **8B**, 314 (1930).)

slow inflammations. This explains the ineffectiveness of the packed half of the vessel in stopping the propagation. It is evident therefore that once the explosion is started the number of chains which terminate at the walls (even when the latter are close together) is insufficient to prevent practically infinite branching of chains.

In view of these results it was considered of importance to study the influence of the size of the vessel on the explosion limit.

4. Influence of Diameter of Vessel on the Explosion Limit.—From the above experiments it appears that under a given set of conditions reaction chains must travel uninterrupted (by walls) for some distance before a sufficient concentration of "reaction carriers"[15] can be developed by chain branching to lead to an explosion. To gain a more distinct idea of this distance the explosion limit was investigated in cylindrical vessels having the same length (12 cm.) but different diameters. Cylindrical instead of spherical vessels were chosen to obtain a greater volume.

Since the explosion limit is affected by the activity, all the vessels were first activated by a number of explosions. Their degrees of activity were similar, judging from the lag period and the rate of decomposition below the explosion limit. Therefore, the explosion limits in these vessels were comparable.

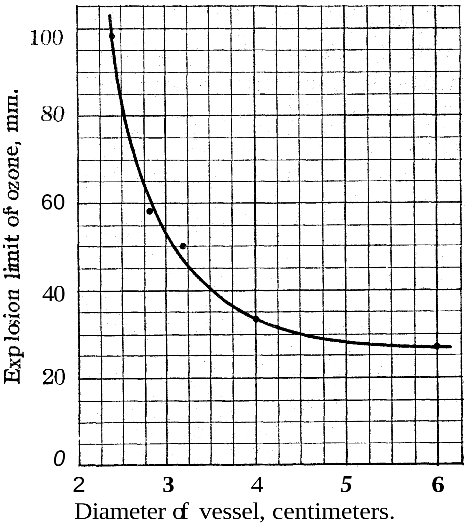

Fig. 5.—Relation between explosion limit at 25° and diameter of vessel.

In Fig. 5 the observed explosion limits at 25° are plotted against the diameter of the vessels. The curve so obtained corresponds to a rectangular hyperbola and is represented by the equation

$$(d - a)(p - b) = K$$

where d is the diameter of the vessel in mm. and p the explosion limit; a and b are constants which depend on the activity of the vessel. Deviations from this law are of the order that may be expected from the differences in activity from vessel to vessel. The curve is asymptotic to two lines parallel to the x and y axes whose coordinate values are represented by the constants b and a in the equation. Thus the value of b represents the

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[15] By "reaction carrier" is meant one of the intermediate active products generated during the reaction through the medium of which the chains are carried on.

rxplosion limit for infinite diameter of vessels of this type which under these conditions is 20 mm. of ozone. The value of a represents the limiting diameter below which no explosion will take place, which under these conditions is found to be 20 mm.

Explosions of ozone alone by direct heating are also prevented in a similar way by proximity of the walls. Thus no explosion occurred in a 4-mtr. Pyrex glass tube containing 40 mm. of ozone when it was heated to 400°. (See also Ref. 14.)

Attention is directed to the existence of a similar hyperbolic law between the gas pressure and the condenser voltage when certain explosive mixtures such as $CO + O_2$, $H_2 + O_2$, $CS_2 + O_2$, are ignited by means of a discharge.[16] Although the method of ignition is quite different from that in our experiments the similarity in the results is striking.

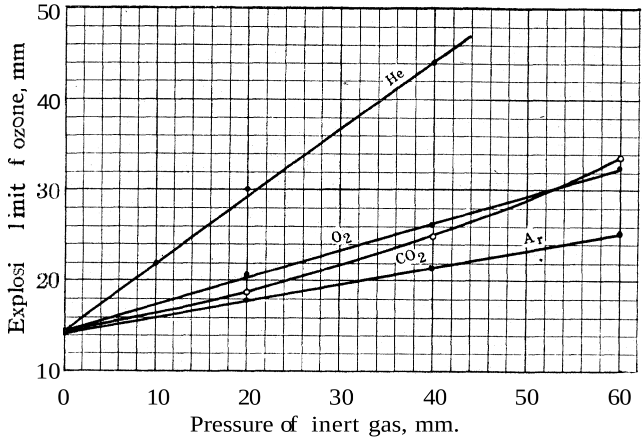

Fig. 6.—Effect of inert gases on the explosion limit at 25° (5 mm. of bromine).

5. Influence of Inert Gases on the Explosion Limit.—The experiments were carried out in the glass vessel I and the quartz vessel at 25°. Preliminary tests showed that the ozone was very stable in the presence of tho inert gases alone. The order in which the gases were admitted was: 5 mm. of bromine, varying amounts of inert gases, ozone.

In all cases the inert gas raises the explosion limit. Within the range of these experiments the limit increases directly proportional to the pressure of helium, argon, oxygen and nitrogen. With carbon dioxide the limit increases somewhat faster than by direct proportionality (see Fig. 6). The curve for nitrogen is not shown as it lies very close to and just above that for oxygen. All the curves meet in a common point, 14 mm. of ozone

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[16] A. K. Brewer, *Proc. Nat. Acad. Sci.*, **13**, 689 (1927); THIS JOURNAL, 52, 4225 (1930); Finch and Cowen, *Proc. Roy. Soc.* (London), **A116**, 529 (1927).

at zero pressure inert gas. This is the explosion limit of pure ozone with 5 mm. of bromine at 25° in this glass vessel.

The effectiveness of inert gases in raising the explosion limit increases in the order, argon, carbon dioxide, oxygen, nitrogen, helium.[17] In the quartz vessel the effect is also in the same order but with helium the increase in the limit is now less than corresponds to direct proportionality.

The effectiveness in increasing the explosion limit is in the order of decreasing molecular weight. It is apparent that bromine should have little influence, which is in agreement with experiments described earlier.

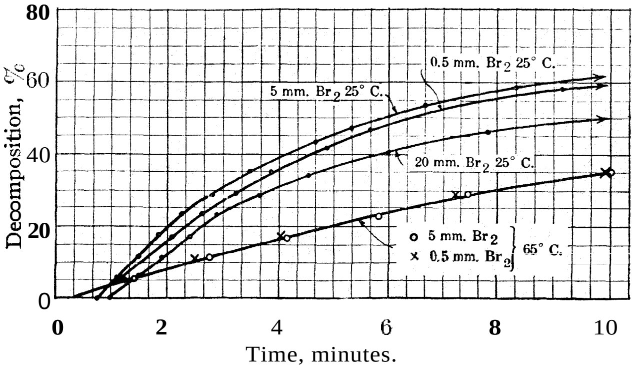

Fig. 7.—Influence of bromine on the rate of decomposition of ozone: pressure of ozone **15** mm.; quartz vessel (explosion limit 20 mm. of ozone).

The Decomposition of Ozone below the Explosion Limit

1. The Influence of Bromine on the Rate of Decomposition.—The influence of bromine on the decomposition of ozone below the explosion limit varies with the temperature. At 65° there is no difference in the rate between 0.5 and 5 mm. of bromine (see Fig. 7). At 35° a small effect can be observed. At 25° the reaction is fastest with 5 mm. of bromine, slower with 0.5 mm. of bromine, and still slower with 20 mm. of bromine. The parallelism between these experiments and those on the effect of bromine on the explosion limit is evident (refer to Fig. 2). For a given temperature the fastest rate corresponds to the lowest explosion limit. These facts indicate that the reaction is the same in principle for the slow decomposition as for the reaction leading to explosion.

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[17] Experiments on the effect of inert gases on the inflammation limits of mixtures of methane–air, and carbon monoxide–oxygen have been conducted by Coward and Hartwell, *J. Chem. Soc.*, **1522 (1926)**; F. W. Stevens, This Journal, 50, **3244 (1928)**; and Jorissen, Booy and Van Heiningen, *Rec. trav. chim.*, *49*, *876* **(1930)**. A different order of effectiveness in raising the limit than in the present experiments was found. This is probably due to the entirely different chemical reactions and experimental conditions.

Below 25° the influence of bromine becomes very marked. The experiments are described fully elsewhere.[5]

2. The Effect of Temperature on the Rate of Decomposition.—The rate of decomposition of ozone was studied at different temperatures and at pressures below the explosion limit. One set of experiments is shown in Fig. 8 for 15 mm. of ozone and 5 mm. of bromine. To avoid crowding, only the temperature interval 25–70' is recorded. The results show that the rate of decomposition decreases as the temperature is raised from 25 to 55° and then increases above this temperature. From 15 to 25° the rate increases once more. Thus there are three distinct regions of temperature coefficients. The temperature coefficients for the first stages of the reaction for different temperature ranges are given in Table III.

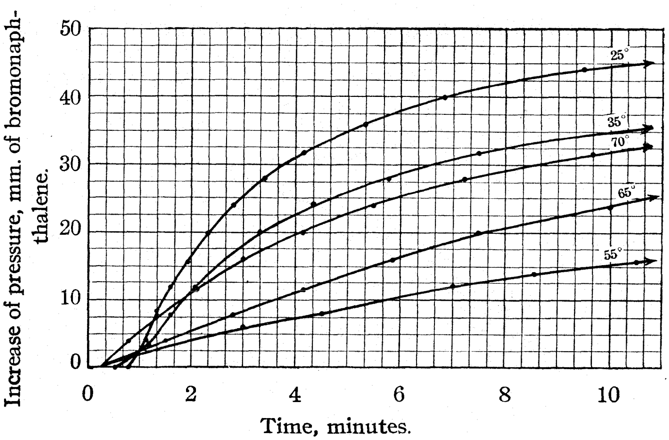

Fig. 8.—Decomposition of ozone at different temperatures: pressure of ozone, 1.5 mm.; bromine, 5 mm.

TABLE III

TEMPERATURE COEFFICIENTS IN DIFFERENT TEMPERATURE RANGES (15 MM. O_3; 5 MM. Br_2, QUARTZ VESSEL)

Temperature interval, °C.	Temperature coefficient[18]
65–55	1.7
55–45	0.6
45–35	.5
35–25	.7
25–15	1.5

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[18] It has been customary to call temperature coefficients positive if they are greater than one, and negative if they are less than one. The term negative temperature coefficient is, we feel, a misnomer and confusing. We therefore suggest with Prof. A. F. Benton (statement at American Chemical Society Meeting, Indianapolis, March 30–April 3) that it be referred to as a temperature coefficient less than one.

The temperature coefficients are derived by dividing the rates of decomposition for short corresponding time intervals at different temperatures separated by 10°. At higher temperatures these temperature coefficients remain fairly constant during a reaction over a moderately long time.

These results show that the rates follow exactly the explosion limits. For different temperatures the lower the explosion limit the faster the rate of the slow reaction here considered (compare Fig. 4).

It is to be anticipated that the percentage decomposition in a given time will become more nearly the same at all temperatures as the initial pressure of ozone approaches the explosion limit. Table IV shows this clearly.

TABLE IV

COMPARISON OF AMOUNT OF OZONE DECOMPOSED AT DIFFERENT TEMPERATURES NEAR THE EXPLOSION LIMIT. QUARTZ VESSEL USED

Temp., °C.	Initial pressure, mm. of ozone	Explosion limit, mm. of ozone	Percentage ozone decomposed in 10 minutes
15	40	41	77
20	27	28	77
25	20	21	71
35	30	32.5	73
45	36.5	39	70
55	42.4	44	61
65	38	39	66

The somewhat greater decomposition below 25° is to be ascribed to a gradually changing type of wall reaction with decreasing temperature.[5]

Since no reaction constant can be calculated to which any significance can be attached, another means of comparing the rates at different temperatures and initial pressures is given. This is $\Delta p/\Delta t$ maximum, the change in pressure for an interval of ten seconds at the steepest portion[19] of each curve. For a given initial ozone pressure the steepest portion occurs soon after the reaction has set in (compare Fig. 1). In Fig. 9, therefore, $\Delta p/\Delta t$ maximum is plotted against the initial ozone pressure for different temperatures. Vertical lines represent the explosion limits at the various temperatures. As long as the pressure of ozone is far below the explosion limit, $\Delta p/\Delta t$ changes only slightly. On approaching the explosion limit it increases rapidly up to the explosion point, where it becomes practically infinite. These curves show graphically the suddenness with which the explosion sets in below 20° (see also reference 5).

3. Effect of Increased Surface on the Decomposition.—The decomposition was studied in the vessel packed with glass tubing used in previous experiments. It was mentioned above that no explosions are possible in the fully packed vessel. It is observed (Fig. 10) that regardless

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[19] Here there is a minimum retarding effect due to oxygen set free in the decomposition.

of the initial ozone pressure the reaction proceeds to about 90% of completion in a comparatively short period of time, namely, about ten minutes. Furthermore, for a given set of conditions (temperature and ozone and bromine pressures) the decomposition in a certain time interval is greater in the packed than in the empty vessel (Fig. 11). However, this increase in the rate in the packed vessel in no way compares with the large increase in the ratio of surface to volume (19:1). This is shown in Fig. 11. The ratio of the reaction rates in the packed and empty vessels at 25°, 15 mm. of ozone, 5 mm. of bromine is calculated to be 1.3 and remains constant over the entire range of the reaction.

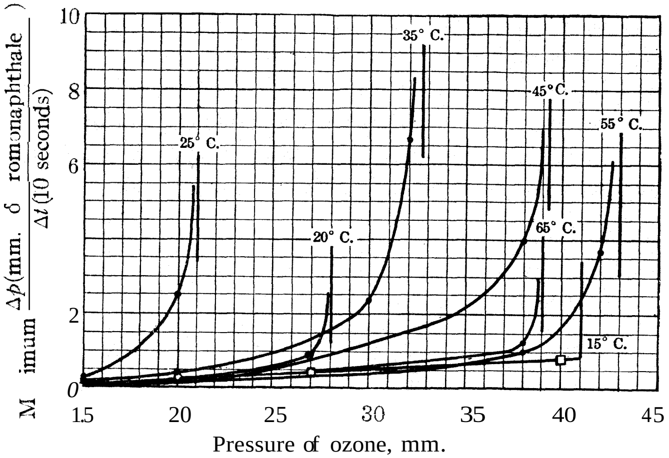

Fig. 9.—Maximum $\Delta p/\Delta t$ for different temperatures.

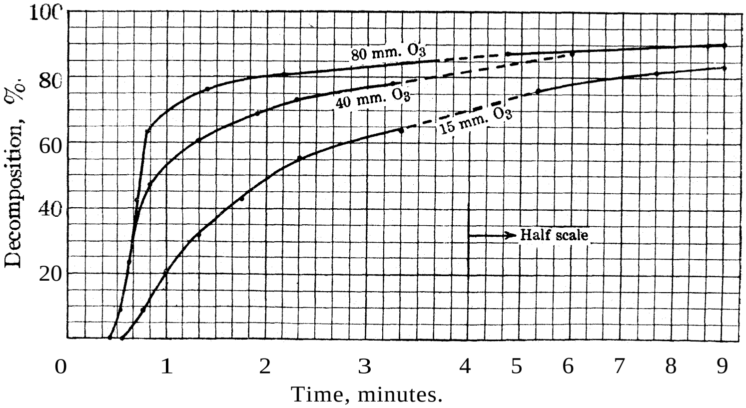

Fig. 10.—Decomposition of ozone in packed vessel at 25° and different ozone pressures.

The small increase in the rate of decomposition in the packed vessel over that in the empty vessel indicates that at 25° and above the larger part of the reaction takes place in the gas phase.

4. Temperature Coefficient in the Vessel Filled with Glass Tubing.—In Table V values for the temperature coefficients in the glass-filled vessel for different temperature intervals are given. Comparing these with the temperature coefficients in the empty vessel, it is a striking fact that whereas the value for the interval 15 to 25° in the empty vessel is 1.5 it is only **0.33** in the packed vessel. This means that the decomposition at the lower temperature is much faster in the packed vessel than in the empty vessel. The ratio of the rates in the packed and empty vessels can be calculated to be 5.25 at 15°. This can easily be understood when it is remembered that at lower temperatures the decomposition becomes more and more a wall reaction, whilst decomposition in the gas phase becomes smaller.[5] Owing to the greater rate of formation of the intermediate adsorption compound at 15° than at 25° the amount of ozone decomposed at the wall is greater at the former temperature; but as the number of active carriers shot out into the gas phase diminishes with decreasing temperature, the rate of decomposition at 15° in the empty vessel is smaller than in the packed vessel where the surface has been increased 19-fold. In fact the increase in surface is so great that the decrease of the reaction in the gas phase is more than overbalanced by the increase in the wall reaction. This is one of the first instances[20] to be recorded of a heterogeneous reaction possessing a temperature coefficient less than one.

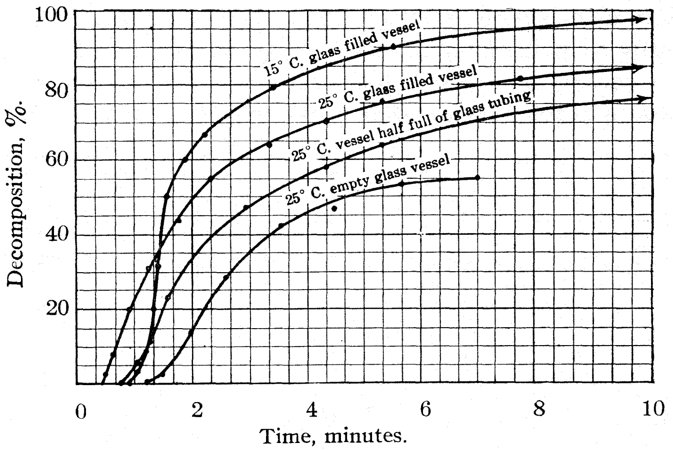

Fig. 11.—Decomposition of ozone: pressure of ozone, 15 mm.; bromine, 5 mm.

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[20] Professor H. S. Taylor reported the discovery of another heterogeneous reaction with a temperature coefficient less than one in the catalytic surface conversion of ortho- and para-hydrogen (Meeting American Chemical Society, Indianapolis, March 30–April 3).

TABLE V

TEMPERATURE COEFFICIENTS IN PACKED VESSEL BETWEEN 15 AND 45°

$\Delta p_{t_2}/\Delta p_{t_1}$[21]	Temperature coefficient for initial pressure, 15 mm. of O_3
$\Delta p_{25}/\Delta p_{15}$	0.33
$\Delta p_{35}/\Delta p_{25}$	.72
$\Delta p_{45}/\Delta p_{35}$	1.05

As the temperature rises the temperature coefficient also rises until above 45° it is greater than one. This is due to the fact that the intermediate adsorption compound emits active carriers at the higher temperatures and gives rise to chains in the gas phase which multiply rapidly with increasing temperature. On the other hand the wall reaction rate decreases with increasing temperature owing to the decreased adsorption and consequently a smaller number of active carriers is emitted. It is obvious that due to these two factors the temperature coefficient should increase and will eventually reach a temperature at which it is greater than one.

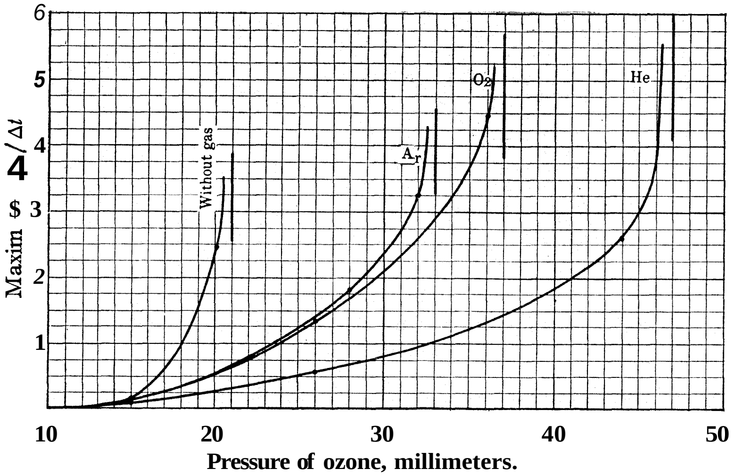

Fig. 12.—Comparison of the effects of inert gases on the maximum rate of decomposition of ozone: pressure of inert gas, 40 mm; bromine, 5 mm.; temperature, 25°.

5. The Effect of Inert Gases on the Decomposition.—The influence of inert gases on the explosion limit was shown to be greatest for those gases which have small atomic weights and high heat conductivities. To learn more about the mechanism of this influence, the decomposition of ozone below the explosion limit in the presence of like quantities of inert gases was studied. The following results were obtained in the quartz vessel at 25° with 5 mm. of bromine. They are shown graphically in Fig. 12, in

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[21] The rise in pressure for an interval of ten seconds over the steepest portion of the curve was taken for comparing the rate.

which $\Delta p/\Delta t$ for the maximum speed is plotted against ozone pressure for 40 mm. of the inert gases, argon, oxygen and helium. A curve for pure ozone is also shown.

If the pressure of ozone is low, 15 mm.,[22] the inert gases exert very little influence on the rate of decomposition. As the ozone pressure is increased the influence of the inert gases becomes marked to a more or less degree depending on the gas. The rate is slowest for helium, faster for oxygen and fastest for argon. Since for like quantities of inert gases the explosion limit is lowest for argon, the rates become even more widely different as the explosion limit for argon is approached. For argon the rate approaches infinity, for oxygen it is slower and for helium very much slower. In the same way on approaching the explosion limit for oxygen the rate is very fast for the latter gas but still very slow for helium. Finally, if the rates of decomposition near the limits of explosion of all the inert gases (for different ozone pressures) are compared they are found to be nearly the same.

Mechanism and Discussion

This rather complex reaction can now be explained satisfactorily from the results of the experiments which have been described. In proposing the following mechanism, no unreasonable assumptions have been made but each step in the process is supported by or deduced from experimental facts.

The whole reaction may be divided into two distinct processes, one which takes place on the walls and the other in the gas phase. In point of view of time the wall reaction precedes the gas phase reaction.

(1) Before any increase in pressure can be observed some process must occur at the wall. The proof for this lies in the numerous observations made of the deactivation of the vessel by impurities such as $AsBr_3$ and impure air, the long lag periods occasioned by the latter, the gradual stepwise activation of a vessel by previous reactions and explosions, the marked differences in activity in different vessels and the effect of such activity on the slow decomposition and the explosion limit.

(2) This wall process is divided into three distinct phases.

(a) Both ozone and bromine are adsorbed on the walls. As far as the adsorption of ozone is concerned, this is shown very clearly by the marked shortening of the lag period when bromine is admitted to the vessel after the ozone. It will be recalled that here the lag period amounts only to some seconds whereas, when ozone is added after the bromine, the lag period involves minutes. The difference in these times is interpreted as the time taken by the ozone to displace part of the bromine adsorbed on the wall and to become adsorbed itself. Taylor[23] has pointed out that certain adsorp-

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[22] This pressure is 5 to 6 mm. below the explosion limit of ozone in the absence of inert gases.

[23] H. S. Taylor, THIS JOURNAL, 53,578 (1931).

tion processes may be very slow. In the present case it is not possible to decide whether it is the replacement of bromine by ozone or the slow adsorption of ozone which accounts for this difference in the lag period. It would indeed be very difficult to account for the fact that the temperature coefficient between 25 and 55° is less than one were adsorption of ozone and bromine unnecessary.

(b) An intermediate unstable compound of ozone and bromine is formed at the walls. From general considerations, as both ozone and bromine are necessary for the decomposition or explosion and both constituents are adsorbed, it follows that some type of compound between ozone and bromine must be formed at the walls, apart from all considerations concerning its nature, stability or life-time as an entity. There is no clue to the chemical structure and composition of this oxide. It is not to be confounded with the solid crystalline oxide of bromine Br_3O_8 observed by Lewis and Schumacher,[4] nor with a volatile oxide of bromine, presumably Br_2O, recently described by Zintl and Reinäcker.[24] At 25° and above, the experimental results indicate that this oxide is very unstable. As the temperature is decreased below 25° a continuous increase in stability takes place. Already at a temperature of 15° under favorable conditions the once unstable oxide is observed to go over into the solid crystalline compound.[5]

(c) The unstable oxide decomposes immediately and expels or ejects into the gas phase energy-rich groups, most probably oxygen atoms or active oxygen molecules. The more stable adsorption compound at lower temperatures appears to eject groups which are too inactive to initiate further reactions in the gas phase. In support of this are the results showing that at lower temperatures the wall reaction increases and the gas phase reaction decreases and disappears (see also Reference 5).

(3) The active groups, which will be referred to as reaction carriers, on colliding with appropriate ozone molecules in the gas phase cause the latter to decompose and at the same time give rise to new active reaction carriers. In this way reaction chains build up and undergo branching or multiplication, the rate of which is dependent on the temperature, the ozone concentration, and the presence of inert gases. They spread out and propagate through the gas phase until they are broken up by collisions with the walls of the vessel. Individual links in the chain are also destroyed by unfavorable collisions with ozone or inert gas molecules. If the concentration of reaction carriers in an element of volume of the gas exceeds a critical value, the chains undergo practically unlimited branching and the reaction goes over into an explosion which leads to the complete decomposition of the ozone in the vessel. If the number of original reaction carriers shot out from the wall is too small (which is affected by tempera-

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[24] E. Zintl and G. Reinacker, Ber., 63, 1098 (1930).

ture, ozone pressure and bromine pressure), the ozone concentration too low, or if a sufficient concentration of an inert gas is present, so that the critical concentration of reaction carriers is not attained, the reaction velocity after reaching a maximum slows down again long before all the ozone has decomposed.

(4) The actual reactions which occur in the chains are unknown. One probable mechanism may be suggested. It is supported to a certain extent by calculations of the velocity of propagation of a detonation wave in ozone. If the chain reaction theory of Lewis,[25] and the mechanism suggested by him are considered—namely

$$\begin{array}{l} O + O_3 = 2O_2^* \\ O_2^* + O_3 = 2O_2 + O \\ O + O_3 = 2O_2^* \\ \text{etc.} \\ \downarrow \\ O_2^* \end{array}$$

where O_2^* is an active molecule, the reaction carrier turns out to be an excited oxygen molecule with a total energy of 47.2 Kcal. of which 17.7 Kcal. is available as translational energy. (Heat of formation of $O_3 = 32$ Kcal. and heat of dissociation of $O_2 = 117$ Kcal.) The velocity of propagation is calculated to be 2150 meters/sec. Using the theory of Chapman and Jouguet,[26] which is strictly hydrodynamical and thermodynamical in character and does not consider the individual reactions at all, the velocity is calculated to be 2123 meters/sec. The speed of detonation of ozone has never been determined experimentally, but both theories have been able to account very closely for the velocities of detonations in other gas mixtures for which good experimental values are available. It may therefore be expected that the experimental value for the speed of detonation in pure ozone will be close to the value calculated above. It has been shown that the explosion of ozone in these experiments is in reality a detonation, which furnishes evidence for the probability of the above reaction mechanism.

The way in which branching occurs can be represented in the following scheme. We shall assume that the initial reaction carrier shot off from the wall is an active oxygen molecule. An oxygen atom might do just as well. As mentioned above, any one of the links in the branches may be terminated by unfavorable collisions with other molecules or with the wall. Chains may also terminate by a collision between two oxygen atoms and a third body to form an oxygen molecule. In a spherical vessel this may be a real factor due to the fact that chains start from all points on the wall, spread out spherically in all directions and overlap each other. The overlapping of the chains tends to accumulate reaction carriers and oxygen atoms, the

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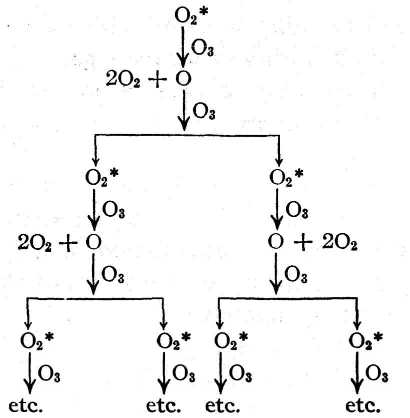
[25] Bernard Lewis, THIS JOURNAL, 52, 3120 (1930).

[26] Bernard Lewis and James B. Friauf, *ibid.*, 52, 3905 (1930), and references contained therein to papers by Chapman, Jouguet and others.



concentrations of which increase on approaching the center of the vessel. Obviously the formation of oxygen molecules from oxygen atoms is a slow process compared with the accumulation of reaction carriers. Referring to the experiments with different sizes of cylindrical vessels, it is obvious that the walls must be far enough apart to prevent the interruption of chains before a sufficient concentration of reaction carriers is built up. It is astonishing how far the carriers have to penetrate into the gas phase before this concentration necessary for explosion is reached.

(5) One may conclude from the results of studies on the photochemical decomposition of ozone that the chains are negligible or very short in the red region of the spectrum,[27] while in the ultraviolet[28] chains exist but they too are very short. The mechanism given by Schumacher[27] involves the formation of active oxygen molecules. These active molecules do not react further and start chains. It is believed that the chains in the present reaction are also propagated through the medium of active oxygen molecules. It is possible that the difference in behavior of the active oxygen molecules in both cases lies in the fact that the energy resides in the molecule in different forms. In this investigation a large amount of the energy is probably in the form of energy of translation which is in a more suitable form to react with ozone. In the photochemical reaction it may be that only a small amount of energy is available as energy of translation and that the efficiency of favorable collisions with ozone is much smaller. The writers realize the difficulties in the way of arriving at precise conclusions in this matter. Although the experiments do not indicate it, it may still be possible that bromine takes part in the chain mechanism in some unknown way. Further experiments are in progress.

(6) From these views, the reason for the influence of bromine on the

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[27] G. B. Kistiakowsky, *Z. physik. Chem.*, **117,** 337 (1925). (For more complete list of references see H. J. Schumacher, THIS JOURNAL, 52, 2377 (1930).

[28] E. Warburg, *Sitzb. preuss. Akad. Wiss.*, 644 (1913).

explosion limit and the slow decomposition below the explosion limit becomes clear. At the lower temperature, say 25°, if too little bromine is present, not enough bromine is adsorbed and too few reaction carriers are emitted from the wall. If too much bromine is present it displaces ozone from the walls and again too few carriers are formed. Somewhere there is an optimum bromine pressure at which a maximum number of carriers is formed. At higher temperatures the bromine has no effect because the surface is covered only partially and does not influence appreciably the ozone adsorbed. The number of carriers formed is therefore constant.

(7) The temperature coefficient of the reaction is divided into three parts. It is greater than one below 25°, less than one between 25 and 55°, and again greater than one above 55". These may now be explained on the basis of the mechanism given above. There are two main parts of the reaction which are affected by temperature, namely, the wall effect and the gas phase reaction. These gross effects are due to a number of separate causes.

A. Wall effect.
  1. Speed of adsorption with temperature.
  2. Amount of adsorption with temperature.
  3. Speed of formation of unstable intermediate adsorption compound.
  4. Speed of decomposition of unstable intermediate adsorption compound.
  5. Change of type of intermediate adsorption compound with temperature.

B. Gas phase reaction.
  1. Increase in chain length with temperature (speed of chain branching).
  2. Diffusivity of the carrier to the wall with temperature.

The temperature coefficients above 25° are explained as follows. (a) The amount of adsorption decreases with increasing temperature. We shall neglect the speed of adsorption, although this probably increases with increasing temperature. (b) Therefore, on the basis of mass effect alone, the speed of formation of the intermediate adsorption compound decreases with increasing temperature. (c) It is assumed that the intermediate compound decomposes fast enough so that the rate of emission of carriers is governed by (a). (d) The length of the chains of branching increases exponentially with the temperature. (e) The diffusivity of the active carriers to the wall increases as some power of the temperature, T^x, where $x = ca.\ 1.7$–2.

The effect of (a) and (e) is to slow down the rate as the temperature rises by decreasing the number of carriers emitted from the wall and by deactivating them (or others formed in the chains) on the wall. The effect of (d) is to speed up the rate as the temperature rises; (d) increases rather rapidly with temperature, faster than (e). It is possible, however, for the curves of the combined effect of (a) and (e) and that for (d) to possess such a character that they intersect at some temperature in the neighborhood of

55°. Thus between 25 and 55" the effects of (a) and (e) outweigh the effect of (d) and the temperature coefficient is less than one. Above 55° the effect of (d) outweighs the effect of (a) and *(e)* and the temperature coefficient is greater than one. In other words, when the gas phase reaction (branching of chains) becomes more extensive than the combined wall effects, the temperature coefficient is greater than one and ***vice versa.***

Concerning the temperature coefficient of less than one below 25°, it has been shown6 that as the temperature decreases below 25° the unstable intermediate compound goes over to a more stable form whose decomposition products are incapable of propagating chains in the gas phase. Therefore, as the temperature decreases the wall reaction becomes more pronounced and the gas phase reaction less. The combination of both effects result in a smaller total reaction occurring at the lower temperature. If the temperature and other conditions are such that solid bromine oxide is formed, the gas phase reaction disappears entirely.[4] The influence of temperature in the glass-filled vessel has been discussed above.

(8) It remains now to explain the effects of inert gases. At low ozone pressures where the reaction is normally very slow and the branching and spreading of chains is a minimum, the addition of moderate amounts of inert gases (10 to 60 mm.) will have very little effect on the already small branching. However, when the ozone pressure is raised to a point approaching the explosion limit (without inert gas), the branching of chains goes on to a marked degree and the addition of inert gases should produce a greater or smaller effect depending on the gas used. Moreover, whatever the inert gases used, the rate should be the same close to the explosion limit since here the branching becomes practically infinite. These limits are given in Fig. 6.

The manner in which the inert gases effect the branching of the chains may be understood as follows. Three different effects should be considered. These are: (1) the effectiveness of the inert gas in deactivating the reaction carrier. This is (for translational energy) a function of the mass of the inert gas. It is greatest for a mass similar to the carrier itself. (2) The number of collisions the inert gas makes with the carrier. Everything else being equal this is inversely proportional to the square root of the mass of the inert gas. The larger the number of collisions the greater the chance for deactivation. *(3)* The speed with which the heat energy liberated in the decomposition is transported to the wall—that is, heat conductivity. The heat conductivity of the inert gases used decreases in the order of increasing molecular weight. The greater the heat conductivity, the higher the explosion limit.

It is not possible to calculate quantitatively the exact influence of each inert gas. The combination of these three effects, however, checks well the order of the influence of the inert gases realized in the experiments.

The reason for the relatively small effect of bromine on the explosion follows from these considerations.

(9) It may be worth while to point out what new light this research throws on the general concept of chain reactions. First of all the experiments show that the conditions in the system ozone--bromine-surface are very complicated. The results, therefore, cannot be used for a precise formulation of the chain reaction mechanism, nor for the measurement of the length of the chains.

However, the reaction provides another example of chains starting and ending at the walls, that the chains are initiated by a wall adsorption compound. The results indicate that in this particular case the branching of chains in the gas phase occurs slowly and that it can become practically infinite only after the carriers and chains have penetrated a relatively great distance into the gas phase. Considerable decomposition as a result of branching of reaction chains also takes place under conditions where no explosions occur. The chains may be long or short depending on the conditions of the experiment. It is of interest to point out that as the explosion limit is approached they become gradually longer and longer. This and the fact that inert gases have an identical effect on the decomposition below and above the limit show that the reaction during the slow decomposition is identical with the reaction during explosion and furnishes unequivocal evidence for the chain theory of detonations in gas mixtures.

In contrast to this reaction are a number of other examples like the hydrogen–oxygen and carbon disulfide–oxygen systems.[8] In these latter reactions the transition from the non-explosive to the explosive stage occurs abruptly. Beyond the explosion limit only a slow reaction occurs (little or no branching of chains) which passes over suddenly at the limit to an explosion (practically infinite branching).

The dependence of the propagation of chains on the way in which the energy is distributed in the initial reaction carriers shot off from the wall or formed in the light reaction and the fact that the explosion involves a single molecule only, would seem to make the ozone explosion very suitable for a study of the fundamentals of gas explosions.

Summary

1. The decomposition of ozone sensitized by bromine vapor has been investigated. The reaction begins only after a lag period, following which an acceleration takes place which culminates in an explosion if the pressure of ozone exceeds a certain critical value. Below this explosion limit the reaction rate goes through a maximum and slows down again.

2. The lag period (ranging from a few seconds to an hour), the explosion limit, and the rate of the slow decomposition depend on the activity of the vessel. The activity is a property of the surface of the wall and can be

influenced by several factors which are discussed. Slow decomposition and particularly explosions render a vessel very active. A vessel so activated retains a considerable part of its activity even if unused for several days.

3. The concentration of bromine between rather wide limits has no influence on the explosion limit nor the slow reaction above 35°. Below this temperature an influence appears which becomes more marked with decreasing temperature. The explosion limit goes through a minimum and the slow reaction a corresponding maximum for 5 mm. of bromine.

4. For a definite bromine concentration the explosion limit goes through a minimum at 25° and a maximum at 55°. Corresponding to this the slow reaction has a temperature coefficient greater than one below 25°, less than one between 25 and 55° and greater than one above 55°.

5. No explosion is possible in a vessel filled with pieces of glass tubing. The results show that below 25° the reaction gradually becomes predominantly a wall reaction while above 25° the reaction takes place mainly in the gas phase. It is shown that the explosion is in reality a detonation.

6. The explosion limit increases with decreasing diameter of cylindrical vessels. A hyperbolic law is found to exist between the explosion limit and the diameter. Under certain experimental conditions no explosions are possible in a vessel smaller than 2 cm. in diameter. It is interesting to observe that reaction chains must travel a considerable distance into the gas phase before an explosion results.

7. The explosion limit is increased proportionally to the pressure of inert gases. The effect increases in the order argon, carbon dioxide, oxygen, nitrogen and helium. The slow reaction is affected similarly.

8. A mechanism based on the experimental facts is proposed. Reaction chains start at the wall due to the emission of an active product of a decomposing wall adsorption compound between bromine and ozone. The chains propagate in the gas phase and may terminate there or on the wall.

9. The photochemical decomposition of ozone is discussed in relation to the present investigation.

10. A method of making porous plate filters of Pyrex glass is described.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORIES OF THE MOUNT SINAI HOSPITAL]

DETERMINATION OF SOLUBILITY OF SPARINGLY SOLUBLE LIQUIDS IN WATER

BY HARRY SOBOTKA AND JOS KAHN[1]

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During a biochemical investigation, we found it necessary to ascertain the solubility in water of several simple aliphatic esters, primarily the ethyl esters of the saturated normal monocarbonic and dicarbonic acids. Except for a few of these esters, no data could be found in the reference books of physical and organic chemistry. We therefore proposed to determine the water solubility of a number of these substances.

The quantitative estimation of sparingly soluble liquids in their saturated aqueous solutions sometimes meets with obstacles caused by difficulties in the analytical determination of small amounts of these substances. More often, however, the difficulty arises with the separation of the saturated solution to be analyzed. Depending on the attempted method of separation, losses by evaporation, adsorption to filters or other difficulties of mechanical nature may hamper the effectual and correct separation of a saturated solution from the excess of undissolved substance. The proximity of specific gravity of solvent and solute limits the choice of methods in many instances; in other cases a substance with relatively low refractive index will escape detection by inspection.

Schuncke and Bodtker[2] determined the mutual solubility in the system water-ether by mixing varying amounts of the two fluids and by observing the appearance of a second phase. Herz[3] applied the same principle to the estimation of the water solubility of a few other liquids as chloroform, benzene, etc. An improved method was used by Klobbie.[4] He added ponceau de xylidine, a dye insoluble in ether and soluble in water, to dry ether and then added water. As soon as the ether was saturated with water the formation of water droplets changed the appearance of the hitherto dry ponceau particles.

We were unaware of Klobbie's method when we devised the following procedure to overcome the difficulties mentioned above. It offers a quick and simple method of ascertaining data on solubility with 'an accuracy, satisfactory for various purposes, of ±0.001% (*i. e.*, 0.01 cc. in one liter).

Principle and Description of Method.—A few cc. of purified ester was stained with a minute quantity of Sudan IV, a water-insoluble lipoid-

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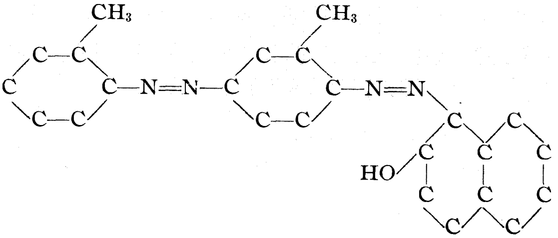
[1] Isidore Hernsheim Research Fellow.

[2] (a) Schuncke, *Z. physik. Chem.*, 14, 331 (1894); (b) Bddtker, *ibid.*, 22, 505, 511 (1897).

[3] Herz, *Ber.*, 31, 2669 (1898).

[4] Klobbie, *Z physik. Chem.*, 24, 615 (1897).



soluble dye. It was then added drop by drop from a micro-buret with a capillary tip to 100, 250, or 500 cc. of distilled water of constant temperature (usually 20°) in a narrow-mouthed stock bottle provided with a well-ground glass stopper. The bottle was thoroughly shaken after each addition of ester. While the added ester was dissolved, the Sudan dye contained in the ester was also wholly or partially dissolved, imparting a pink tinge to the aqueous solution. When Sudan had been added in more liberal quantities a part of it was precipitated and floated on the surface in the form of dark brown solid particles. When the water was saturated with ester, a second liquid phase formed, consisting of transparent droplets of ester. These readily dissolved the solid phase if such had been formed. The last reading of the buret before appearance of the droplets was used for the computation of the solubility.

The end-point of this titration was improved by the following modification. Instead of adding the Sudan IV to the ester, one to five mg. of it is put into the water. The ester is run into the water drop by drop. The dilute solution, shaken frequently, assumes a pink color. When saturation is reached, one additional drop will suffice to convert the floating jagged indicator particles into dark transparent droplets.

In the case of the more soluble esters, a slightly larger amount of Sudan must be added. With less soluble homologs, the accuracy can be enhanced by using larger volumes of water.

The influence of trifling amounts of Sudan is as negligible in regard to the solubility to be measured as that of indicators on the stoichiometric relations in ordinary acidimetric procedures.

Solubility of Ethyl Esters of Mono- and Dicarbonic Acids.—This method was applied to the ethyl esters of the homologous series from propionic to capric acid and from malonic to sebacic acid. Most of these esters were supplied by the Eastman Kodak Laboratories, some were synthesized in our laboratory and all were purified by repeated distillation under reduced pressure. Their purity was checked refractometrically. The specific gravity had to be determined in the monocarbonic series above ethyl caprylate and the refractive indices above ethyl valerate; the refractive indices of the propionate and butyrate were redetermined. Our refractive indices for the dicarbonic esters tallied with those given by

Karvonen;[5] the specific gravities of these esters were taken from this author.

The molecular refractions derived from our observations according to the Lorentz–Lorenz formula agreed throughout with the theoretical values calculated from Eisenlohr's atomic refractions.[6] The theoretical value for ethyl propionate is 27.15, for laurate 68.70, for diethyl malonate 37.83 and for sebacate 70.16. The corresponding experimental figures (Tables I and II) are: 27.0, 68.8, 37.9 and 70.0.

TABLE I

SOLUBILITY OF ETHYL ESTERS OF SATURATED NORMAL MONOCARBONIC ACIDS IN WATER AT 20°

Name	Formula	d^{20}_4	n^{20}_D	M_D	Gram dissolved in 100 cc. H_2O	Normality of satd soln.	−Log₁₀ of normality pS
Propionate	CH_3CH_2COOEt	0 8889"	1 3853[a,b]	27 0	1 75[c]	1 71	0 77
Butyrate	$CH_3(CH_2)_2COOEt$	8784[d]	1 3931[d]	31 6	0 510"	0 044	1 36
Valerate	$CH_3(CH_2)_3COOEt$	8756[e]	1 4016	36 2	.223[f]	0171	1.77
Caproate	$CH_3(CH_2)_4COOEt$	8728"	1 4089	40 9	063	0044	2 36
Oenanthate	$CH_3(CH_2)_5COOEt$	8716[e]	1 4137	45 4	.029	00183	2 74
Caprylate	$CH_3(CH_2)_6COOEt$	,8674	1 4197	50 0	007	.00041	3.4
Pelargonate	$CH_3(CH_2)_7COOEt$	8647[g]	1 4223	54 7	003	00016	3 8
Caprate	$CH_3(CH_2)_8COOEt$	8637	1 4269	59 5	(0015)	(.00008)	(4.1)
Laurate	$CH_3(CH_2)_{10}COOEt$	.8615	1 4323	68 8		....	..
Myristate	$CH_3(CH_2)_{12}COOEt$	8589	1.4381	78 6	..	....	..

[a] *Cf.* Ref. *6.* [b] *Cf.* Auwers and Eisenlohr, *Z. physik. Chem* , 83, 429 (1913); *cf* also[(a)] [c] *Cf.* Traube, *Ber.*, 17, 2294, 2304 (1884) [d] Matthews and Faville, J. *Phys. Chem* , *22,* 1 (1918). [e] Corrected from d^{20}_{20} in Lieben and Rossi, *Ann*, 165, 109 (1872–1873), and Lieben and Janecek, *Ann*, 187, 126 (1877). [f] *Cf.* W. D. Bancroft, *Phys. Rev* , 3,114 (1895–1896). [g] Zincke and Franchimont, *Ann* , 164,333 (1872).

TABLE II

SOLUBILITY OF DIETHYL ESTERS OF DICARBONIC ACIDS

Name	Formula	d^{20}_4	n^{20}_D	M_D	Grams dissolved in 100 cc. Hz0	Normality of satd. soln.	−Log₁₀ of normality pS
Malonate	$COOEtCH_2COOEt$	1.0550	1.4144	37.9	2.08	0.130	0.89
Succinate	$COOEt(CH_2)_2COOEt$	1.0402	1.4200	42.4	1.92	.110	.96
Glutarate	$COOEt(CH_2)_3COOEt$	1.0220	1.4242	46.9	0.882	.047	1.33
Adipate	$COOEt(CH_2)_4COOEt$	1.0086	1.4278	51.6	.423	.0209	1.68
Pimelate	$COOEt(CH_2)_5COOEt$	0.9945	1.4303	56.1	.199	.0092	2.04
Suberate	$COOEt(CH_2)_6COOEt$	.9822	1.4334	60.9	.068	.00296	2.53
Azelate	$COOEt(CH_2)_7COOEt$	.9729	1.4358	65.5	.025	.00102	2.99
Sebacate	$COOEt(CH_2)_8COOEt$	.9646	1.4368	70.0	.008	.00031	3.5

The last column in both tables gives the negative logarithm of the concentration in saturated solution. These logarithms, when plotted against

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[5] Karvonen, *Ann. acad. sci. Fenn., [A]10,* No 5, 12 (1916).

[6] Eisenlohr, *Z. physik. Chem., 75,* 585 (1910).

molecular weights, would yield a straight line if there was a geometric decrease of solubility.

The graph for the dicarbonic esters shows an irregularity between malonate and succinate. Further on, it follows a regular course with a sharper decrease of solubilities above azelate.

The solubility of the monocarbonic esters shows a slightly sharper decrease than that of the dicarbonic ones. A zig-zag in this series is caused by the relatively higher solubility of the esters with an odd number of carbon atoms. This oscillation may be observed up to pelargonate while the figure for the very slightly soluble caprate does not harmonize, probably because of the limitations of accuracy in this range.

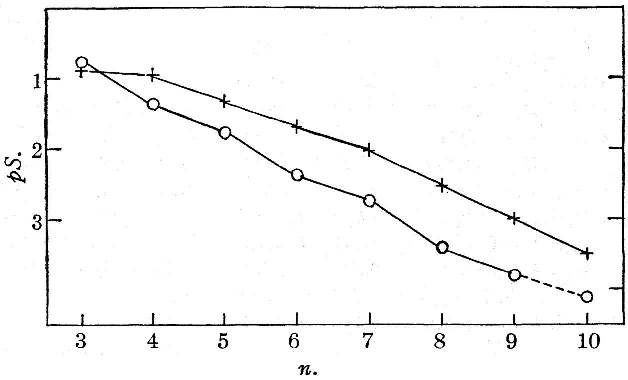

Fig. 1.—Solubility of ethyl esters of monocarbonic acids (○) and of dicarbonic acids (+) in water at 20°: *n*, number of carbon atoms; *pS*, − $\log_{10}$ of normality of saturated solution.

The solubility of the ethyl ester of a monocarbonic acid with *n* carbon atoms is between the solubilities of the diethyl esters of the dicarbonic acid with (n + 1) and that with (n + 2) carbon atoms.

Summary

1. A simple and inexpensive method is presented for the determination of the solubility in water of sparingly soluble liquids.

2. Complete data are given for the solubility at 20° of the ethyl esters in the monocarbonic series below capric (decanoic) acid and in the dicarbonic series below sebacic acid. The refractive indices of the monocarbonic esters were also determined.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE RELATION BETWEEN THE RELATIVE STRENGTHS OF ACIDS IN TWO SOLVENTS

BY J. O. HALFORD[1]

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The expression, the strength of an acid, is frequently used in referring to either of two quantities between which a distinction should be made. In the general sense, the strength of an acid is a measure of its intrinsic tendency to lose protons, independent of the interference of a solvent. This property eludes specific evaluation. More frequently, the expression refers to a measured value in some solvent, expressed quantitatively on an arbitrary scale of proton potential, such as the P_H scale of aqueous solutions. We are concerned here not with acid strength in the general sense, but rather with a procedure by which to express the position of an acid on an arbitrary scale of strengths in one solvent in terms of its position on a similar scale in another.

Several years ago, Brönsted[2] made the statement that "Absolute comparison of the strengths of two acids or two bases is impossible because it requires the absence of any solvent medium." In other words, the three molecular species involved in the characteristic equilibrium of dissociation are affected differently and specifically by transfer from one medium to another, and the measured relative strength of two acids is, in general, dependent upon the solvent as well as the characteristics of the acids. For convenience, we may say that two effects require consideration when we compare the acidities of a series of substances in two solvents. The one, which involves the relation of the P_H scales, or their equivalent, we avoid by selecting these scales arbitrarily; the other is an irregular variation of relative strengths.

The dissociation of the three types of acids most frequently encountered may be represented by the equations

$$HA'' = A^- + H^+ \qquad (1)$$
$$HA^* = A + H^+ \qquad (2)$$
$$HA^- = A^{--} + H^+ \qquad (3)$$

The first includes the substances usually classed as weak acids, the second applies to acids of the type of ammonium ion and the third to the second dissociation of a polybasic acid. We may refer to these classes as different valence types. It is evident that in going from one solvent to another of different dielectric constant, the relative strength of two acids of different valence types will be considerably changed. For example, Reaction 1, in

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[1] Alfred H. Lloyd Fellow in the Graduate School, University of Michigan.

[2] Bronsted, J. *Phys. Chem.*, **30**, 777 (1926).

which the ions appear only on one side of the equation, should be much more sensitive to the dielectric properties of the medium than Reaction 2, in which a singly charged positive ion appears on each side.

In the comparison of reactions of any one type, we find relative strengths fairly concordant, as in the summary by Hall[3] of reactions of type 2 in glacial acetic acid. However, minor variations occur, even within one valence type, and Hall's results indicate that they are usually within one pK unit.

Considering valence type 1, we find, in the measurements of Michaelis and Mizutani[4] in ethyl alcohol, water and their mixtures, that similar variations of relative strength occur, again of the order of one pK unit. The fact that these variations are small is ascribed by Hammett[5] to the circumstance that a solvent which is better for the free acid is also better for its salts. This is equivalent to a statement that the reaction of the ion A^- to forces other than those concerned with the ionic charge and its distribution is not greatly different from that of the free acid HA.

The relation between the ionization equilibria of an acid in two solvents and the distribution coefficients of the acid and its ions has been considered in detail by Bjerrum and Larsson.[6] They have employed solubility measurements in the evaluation of the distribution ratios of the ions. In this way, they have expressed the relation between the dissociation constants in two solvents in terms of the solubilities of the acid and its salts.

If we accept the importance of placing a large number of acid strengths on the same scale, such a relation becomes necessary, for it is improbable that we shall be able to make the required number of measurements in any one solvent. For example, acids which are classed as strong in water show differences in glacial acetic acid, while water is the better solvent for bringing out the differences between the stronger bases. In the selection of a solvent for the study of a given series of acids or bases, two main factors must be considered. The first is that the substances shall be sufficiently soluble to permit accurate measurement, and, if a potentiometric method is to be used, the solubility requirement also applies to the salts of the substances under investigation. The second requirement is that the solvent shall be sufficiently sensitive to variations of strength of the magnitude to be measured. The amphiprotic type of solvent is best suited to measurement, and it is this type which, because of its ability to reduce markedly the apparent strength of strong acids and bases, per-

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[3] Hall, THIS JOURNAL, 52, 5115 (1930).

[4] Michaelis and Mizutani, *Z. physik. Chem.*, 116, 135 (1925); Mizutani, *ibid.*, 116. 350 (1925).

[5] Hammett, THIS JOURNAL, 50, 2666 (1928).

[6] Bjerrum and Larsson, *Z. physik. Chem.*, 127, 358 (1927).

mits the narrowest range of application. In order to place the desired number of measurements on a comparative scale, more than one solvent, probably at least three, will be necessary, if the requirements of solvent power and range of application are to be met. Further, since at present we have no good reason for preferring one scale to another, it becomes desirable to compare results on several scales.

We present here a derivation of the relation between acid strengths in two solvents, in a form which, in our opinion, is more convenient than that of Bjerrum and Larsson. The concept of ion distribution coefficients is not directly involved. The following equations apply to valence type 1. Consider the dissociation constants, K_1 and K_2, of an acid in two solvents, distinguished by the subscripts 1 and 2.

Equation	ΔF	
$HA\text{(standard)} = HA_{(1)}$	$-RT \ln a_1$	(a)
$HA_{(1)} = H^+_{(1)} + A^-_{(1)}$	$-RT \ln K_1$	(b)
$HA_{(2)} = HA\text{(standard)}$	$RT \ln a_2$	(c)
$H^+_{(2)} + A^-_{(2)} = HA_{(2)}$	$RT \ln K_2$	(d)
$H^+_{(1)} = H^+_{(2)}$	B	(e)
$MA(s) = M^+_{(2)} + A^-_{(2)}$	$-RT \ln \sigma_2^2$	(f)
$M^+_{(1)} + A^-_{(1)} = MA(s)$	$RT \ln \sigma_1^2$	(g)
$M^+_{(2)} = M^+_{(1)}$	C	(h)

Since the sum of these equations is zero

$$RT \ln (a_2/a_1 \times K_2/K_1 \times \sigma_1^2/\sigma_2^2) = -(B + C) \qquad (4)$$

$$\frac{a_2\, K_2\, \sigma_1^2}{a_1\, K_1\, \sigma_2^2} = \text{constant} \qquad (5)$$

Here a_1 designates the activity, in solvent 1, referred to the usual standard state at infinite dilution, of the acid HA, when at equilibrium with HA (standard). For moderately soluble solid acids, this is approximately equal to the solubility. MA is the salt of the acid with the positive group M, and Equations f and g imply that the activity methods commonly employed with strong electrolytes are applicable. The quantity a is the mean activity of the ions, M^+ and A^-, in the saturated solution of the salt MA, the activity again so defined as to approach the concentration at infinite dilution. For slightly soluble salts, σ^2 is approximately equal to the solubility product. The quantity $B + C$, by which the constant of Equation 5 may be evaluated, should be the same for all acids of type 1. This is probably best determined by measurement, for at least one acid, of the other quantities in the equation. Also, it is directly related to the difference between the distribution coefficients, expressed logarithmically, of the ions H^+ and M^+.

Similar equations may be developed for each of the other types of dissociation equilibrium. We give here the result for type 2, representing the dissociation of such acids as ammonium ion

$$RT \ln (a_1/a_2 \times K_2/K_1 \times \sigma_2^2/\sigma_1^2) = -(B + D) \qquad (6)$$

$$\frac{a_1 K_2 \sigma_2^2}{a_2 K_1 \sigma_1^2} = \text{constant} \qquad (7)$$

Here *a* refers to the free base A, and a to the salt AHX, so that D applies to the work of transfer of the ion X^-. *C* and D have opposite signs, and the constants of Equations **5** and 7 are different. However, the corresponding equation for type ***3*** contains the same constant term as that for type 1. In order, then, to correlate the scales of two solvents for a number of acids involving all three valence types, it will be necessary to evaluate independently the constant terms of Equations **5** and 7.

These equations impose no restriction on the method of setting up the scale of acidities or *P*H values in any one solvent. Equations b and d imply that the scales are to be developed in the manner in which the PH scale of aqueous solutions has been established, so that the pK of an acid is equal to the negative logarithm of the dissociation constant. However, the appearance of the constant term in Equation ***5*** removes this apparent restriction. This is clearer if we examine the logarithmic form of the equation, employing the symbol pK, as defined above.

$$\log \frac{a_2 \sigma_1^2}{a_1 \sigma_2^2} + pK_1 = pK_2 + \text{constant} \qquad (5')$$

It is evident that either pK_1 or pK_2, or both, may be altered by the addition of an arbitrary constant, without interference with the validity of the equation. Such an alteration is equivalent to the use of an arbitrary PH scale. However, it will probably be most convenient, when circumstances are favorable, to employ the scale similar to that of aqueous solutions, in which the simple relation between pK and the dissociation constant is retained.

The shift of relative strength of two acids, in going from one solvent to another, is entirely a function of the quantities *a* and a. From Equation 5', for two acids, it follows that

$$\Delta pK_2 - \Delta pK_1 = \log \frac{a_2 \sigma_1^2}{a_1 \sigma_2^2}(\mathrm{A}) - \log \frac{a_2 \sigma_1^2}{a_1 \sigma_2^2}(\mathrm{B}) \qquad (8)$$

where A and B refer to the two acids compared, and $\Delta pK = pK(\mathrm{A}) - pK(\mathrm{B})$ in either solvent. In the first approximation, the calculation of the variation of relative strength is independent of the actual values of acid strength in either medium. However, the accurate evaluation of the activity of the undissociated part of the acid may require knowledge of its dissociation constant.

The above equations are exact if a and a are interpreted as activities. However, a useful approximation may be introduced by assuming that solubilities, when sufficiently low, may be employed to replace the activities. We have carried out this approximate calculation for several acids and their silver salts, in water and in 50% alcohol by volume, at 24 ± 1°. The solubility data have been taken from various sources. Where data on the free acids were lacking, we have obtained them by weighing the residue from evaporation of samples of the saturated solutions. The solubility of silver salicylate was determined as residue from evaporation, that of the other silver salts by titration of the saturated solutions with ammonium thiocyanate to a ferric thiocyanate end-point.

The results are summarized in Table I. The first column shows the acid, the second its solubility in water corrected for dissociation, the third its solubility in 50% alcohol, used without correction, the fourth and fifth the solubility of the silver salt in water and in 50% alcohol. Concentrations are expressed as moles per liter. The sixth column shows the quantity on the right side of Equation 8, the shift of acid strength relative to salicylic acid. The last column gives the corresponding measured value, taken from the following paper.[7]

TABLE I

DIFFERENCE OF STRENGTHS, RELATIVE TO SALICYLIC ACID, IN WATER AND IN 50% ALCOHOL BY VOLUME, AT 24 ± 1°

Acid	a_1	a_2	σ_1	σ_2	Diff. of rel. strength Calcd.	Measd.
Acetic	....	...	0.0670	0.0180	−0.20	0
Benzoic	0.0264	0.918	.0115	.00763	+ .56	0.5
Salicylic	.0142	.552	.0069	.0092	*0*	0
o-Nitrobenzoic	.0278	.898	.0291	.0204	.46	.5
α-Naphthoic	.00040	.0388	.00405	.00440	.60	.6

In the calculation for acetic acid, a_2/a_1 was taken arbitrarily as unity. The values in the last column, which were obtained by combining known relative strengths in water with measurements in 50% alcohol with the antimony electrode, may be in error by as much as 0.2 unit.

The writer is grateful to Professor James B. Conant, who suggested this problem and contributed valuable advice.

Summary

Equations which connect the relative strengths of acids in one solvent with those in another by means of solubility data, or their equivalent, have been discussed. Some applications to acids in water and in 50% alcohol are presented.

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[7] Halford, THIS JOURNAL, 53, 2944 (1931).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

SOME EFFECTS OF HYDROCARBON GROUPS ON THE STRENGTH OF CARBOXYLIC ACIDS

BY J. O. HALFORD[1]

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In the preceding paper,[2] the quantitative relation between relative strengths of acids in different solvents has been discussed. The relative strength of two acids has been found, in general, to vary from one medium to another. The magnitude which this variation can attain becomes important, particularly to the organic chemist, for it determines the limits within which measurements of acid strength may be interpreted as truly characteristic of the acids. It has been useful, in correlating the properties of organic compounds, to consider the effect of substittitions and structural modifications on acid strength, to know, for example, how the dissociation varies through an homologous series, or how it is changed by the substitution of one group for another within the molecule. The use, for this purpose, of acid strengths measured by our present methods, involves the assumption that they evaluate a property of the acids. The variation of relative strength with the solvent shows that acid strength, as measured, depends on the solvent as well as the acid. It follows that the variation of acidity through a series of substances cannot be expressed in terms of other measured properties, such as distances between atoms, without taking into account the specific nature of the interaction of substance and solvent.

However, it should not be concluded that acid strengths, measured in one solvent, are entirely without significance in the correlation of the properties of series of related compounds. There can be little doubt that trichloroacetic acid is intrinsically stronger than acetic acid, or that phenol is weaker than benzoic acid. Our problem, then, is to decide what minimum difference of measured acidity may be interpreted as indicating a characteristic difference between the acids compared, or what is the maximum value of the uncertainty introduced by the irregular character of the solvent effect. An idea of the magnitude of this quantity can be obtained by measuring the strength of a sufficient number of acids in several solvents.

As an addition to the available experimental data, we have measured the strength of a number of acids, including some which are not readily studied in water because of low solubility, under conditions which permit the comparison of a relatively large number of substances. Following Michaelis and Mizutani,[3] we have employed 50% ethyl alcohol by volume

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[1] Alfred H. Lloyd, Fellow in the Graduate School, University of Michigan.

[2] Halford, THIS JOURNAL, 53, 2939 (1931).

[3] Michaelis and Mizutani, *Z. physik. Chem.*, 116, 135 (1925); Mizutani, *ibid.*, 116, 350 (192.5).

as solvent in some of the measurements, partly for the purpose of checking our procedure against theirs. However, we have given more attention to a solvent containing 60% by volume of butyl carbitol (diethylene glycol mono-butyl ether) and 40% of water. This solvent was selected because butyl carbitol–water solutions have somewhat more general solvent power than the corresponding alcohol–water solutions. For example, a solution of myristic acid and potassium myristate, each at a concentration of 0.0025 N, shows a precipitation in 50% alcohol, but does not come out of the butyl carbitol–water solution until the butyl carbitol content is reduced below 20%. The butyl carbitol content may be as high as 80% without serious interference with electrometric measurement. The selection of the 60% solution is arbitrary, but this figure is in the neighborhood of the optimum for high solvent power and ease of measurement.

Experimental

Procedure.—All measurements were made at 23 ± 1°. In order to examine the applicability of a titrimetric method, a set of titration curves was obtained, using the antimony or quinhydrone electrode against a saturated aqueous calomel cell. Having demonstrated in this way the greater reliability of the antimony electrode, it was adopted for the determination of acid strength. To obtain a measure of the strength of an acid, two solutions were made up, the one containing acetic acid, the other the unknown, each at a concentration of five millimoles per liter. To provide conductance, and standardize the salt effect, all solutions were 0.1 molal in lithium chloride. Each acid was then half neutralized with potassium hydroxide. The acetate buffer was introduced into the cell with the antimony electrode, and the potential against a saturated aqueous calomel cell determined. The procedure was repeated with the buffer of the unknown acid, followed by a repetition with the acetate buffer. In this way the electrodes were checked against previous measurements, and chance variation of electrode behavior directly following a determination was guarded against. Stirring was employed, but with the antimony electrode this was always gentle enough to prevent mixing large quantities of air through the solution.

Electrodes.—The hydrogen, antimony and quinhydrone electrodes were tested. None of these proved entirely satisfactory, at least by comparison with the precision attainable in aqueous solutions. The hydrogen electrode was too readily poisoned in the solutions containing butyl carbitol, the average life of those tried being about fifteen minutes. The quinhydrone electrode was better, but extraneous effects which cause small variations in water tend to introduce large errors in the mixed solvents, and it was difficult to obtain reproducibility within 20 mv. It was found possible to prepare sets of platinum electrodes by slightly different methods, such that satisfactory agreement within each set could be obtained, but large differences between different sets appeared. When used for the purpose of measuring equivalent weights, which depends on the sharpness of the break at the point of equivalence, the quinhydrone electrode was entirely satisfactory.

The antimony electrode, in the form of sticks of the metal, gave the most reproducible results. Regardless of age or previous treatment, it was exceptional to find two electrodes which differed by more than 2 mv. or failed to reproduce measurements by more than 5 mv. This statement applies to the measurement of acid strength by means of buffered solutions. We have no explanation of the behavior of these electrodes in titrations. The titration curves up to the point of equivalence were entirely satisfactory, but thereafter a drift back toward the initial readings set in, partially masking the break. However, the same electrodes gave good results, before or after such titrations, when used with buffered solutions in either the acid or alkaline range.

The experience of others[4] with the antimony electrode in aqueous solutions indicates that in the form of sticks it does not give the correct reversible potentials. However, it should be satisfactory in comparative work. In changing from water to a water–alcohol system, the potentials of the antimony electrode cannot be expected to follow those of the hydrogen electrode, for the latter is independent of the water activity, except for its influence on the hydrogen-ion activity, while with the former, water enters into the electrode reaction. If a given buffer in water shows a considerable difference of potential against the same buffer in 50% alcohol with hydrogen electrodes, a smaller potential should be observed with antimony electrodes. The difference between two buffers at constant water concentration, however, is practically the same with the two electrode systems.

Cells.—The cells were of the same type as those employed by Conant and Werner,' with a saturated potassium chloride–agar bridge, except that the junction from the bridge to the calomel cell was not stoppered. Antimony electrodes were suspended by copper or platinum wires.

Butyl Carbitol.—Commercial butyl carbitol was allowed to stand over lime for several days, then distilled at a pressure of 30 mm. No difficulty was experienced in obtaining a large fraction boiling within one degree, a 90% recovery from the commercial product being readily attained. This purification was made because the solvent, when mixed with water, was frequently 0.001 to 0.002 molar in an acid of about the strength of acetic acid. Even the purified solvent, when mixed with water and allowed to stand for several days, showed slight acidity. Apparently the acid was formed only in the solutions containing water, for the anhydrous solvent could be kept at least for several weeks without deterioration. Consequently, butyl carbitol–water solutions were made up shortly before use.

Acids.—The acids were mainly Eastman Kodak Co. products. Melting points of most of them are recorded in Table I. Stearic acid, a sample of unknown origin, gave the correct equivalent weight within one per cent. An attempted purification of tridecylic acid, which melts twelve degrees below the value given in "International Critical Tables," produced no increase of the melting point.

Results

Titrations with the Antimony Electrode in 60% Butyl Carbitol.—In order to obtain sufficiently sharp end-points with the antimony electrode it was necessary to employ acid concentrations of 0.05 to 0.1 molal, titrated with 1.0 molal potassium hydroxide. The results of several such titrations are plotted in Fig. 1, with potential as the ordinate against the function $\log(X/1 - X)$ as abscissa, where X represents the fraction of the acid neutralized. The slope of the lines is slightly higher than that obtained in aqueous solutions. Stearic acid was titrated at a smaller concentration, because of its low solubility. The order of the curves is the

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[4] Uhl and Kestranek, *Monatsh.*, 44, 29 (1923); Kolthoff, *Rec. trav. chim.*, 44, 113 (1925); Franke and Willaman, *Ind. Eng. Chem.*, *20,* 87 (1928); Roberts and Fenwick, THIS JOURNAL, 50, 2125 (1928); Britton and Robinson, *J. Chem. Soc.*, 458 (1931).

[5] Conant and Werner, THIS JOURNAL, 52, 4436 (1930).

same as in water, with the exception of benzoic acid, which in the water scale lies half-way between formic and acetic acids.

Titrations with the Quinhydrone Electrode in 60% Butyl **Carbitol.**—In Fig. 2 are shown the results of a number of titrations with the quinhydrone electrode. In this case, to show the character of the end-point, the potential is plotted as a function of the volume of standard alkali. The breaks are sharper, for the weaker acids, than those obtained with water as solvent.

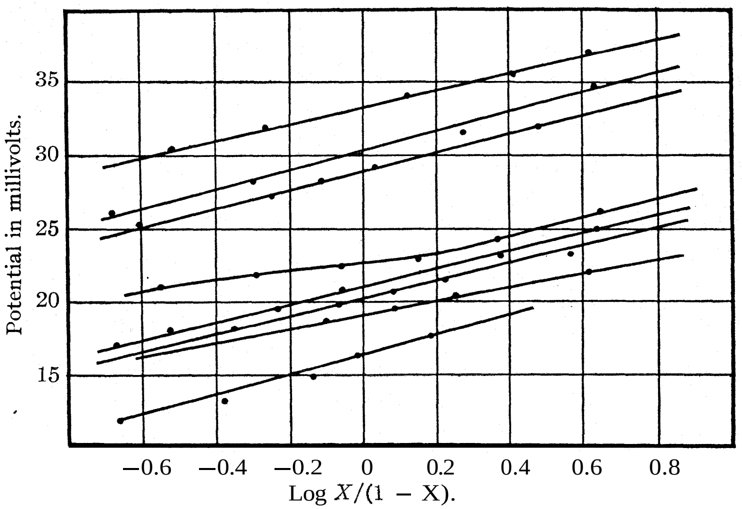

Fig. 1.—Titration curves with the antimony electrode in 60% butyl carbitol. 0.05 M acids titrated with 1.0 M KOH. In order, from the top, stearic, benzoic, acetic, formic, salicylic, chloroacetic, malonic, dichloroacetic (stearic acid at 0.005 M, titrated with 0.1 M KOH).

Strength of Acids.—In Table I the results of the determination of comparative strengths are summarized. The first column shows the acid, the second and third the melting point, measured and taken from "International Critical Tables,"[6] the fourth the *pK* value in water from the same source and the fifth the potential in volts, against a saturated aqueous calomel cell, of the half-neutralized solution of the acid in 60% butyl carbitol, as measured with the antimony electrode. The sixth column shows the strength, in *pK* units, on a scale in which the *pK* of acetic acid is arbitrarily taken as zero. The rate of change of potential with *P*H in water was determined with several electrodes to be 54 mv. per *P*H unit. The values of column six were obtained on the assumption that 54 mv. corresponds to one PH unit in the mixed solvent as well. Columns seven and eight are similar to five and six, for 50% alcohol.

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[6] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. I, p. 176, 1926; Vol. VI, p. 261, 1929.

TABLE I

RESULTS OF DETERMINATIONS

Acid	M p., "I. C T.," °C.	M. p., °C., measd.	pK (aq.)	60% Bu. carbitol E	60% Bu. carbitol ΔpK	50% Alcohol E	50% Alcohol ΔpK
Acetic			4.74	0 298	0	0.285	0
Formic			3.68	.235	−1.2	.215	−1.4
Valeric			4 81	.332	0.6	,302	0.3
Isovaleric			4.78	.333	.6	,302	.3
Methylethylacetic			4 78	.333	.6	.305	.4
Trimethylacetic			5 0 2	.354	1.1	.318	.6
Caproic	− 9 5	−10	4 85	.336	0.7	.305	.4
Isocaproic			4 84	.337	.7	.304	.4
Heptylic	−10	−10.5	4.89	.340	.8	.307	.4
Cyclohexanecarboxylic	31	29.7	4.9	.338	.8	.319	.6
Caprylic	16	14 5	4 85	.343	.8	.309	.4
Pelargonic	12	10 3	4 96	.346	.9	.313	.5
Capric	31	31– 2		.347	.9	,312	.5
Undecylic	20.3	22		.348	.9	.317	.6
Lauric	48	42– 3		.352	1.0	.314	.5
B		129–129 5		.405	2.0	.377	1.7
G		88– 9		.384	1.6	.345	1.1
Campholic				.387	1.6	.358	1.3
Tridecylic	51	39– 40		.342	0.8	.319	0.6
Myristic	58	54		.346	.9		
Pentadecylic	54	48– 49		.351	1.0		
Palmitic	64	62– 63		.350	1.0		
Stearic	69 3	55– 56		.345	0.9		
Benzoic	121 2	122	4.22	.315	.3	.285	0
Hydrocitmamic	48.7	48– 49	4 65	.305	.1	.292	0.1
Diphenylacetic	148	146–147		.305	.1	.275	−0.1
Salicylic	158	158–159	3.00	.220	−1.4	.195	−1.7
o-Nitrobenzoic	148	147–148	2.20	.215	−1.4	.179	−2.0
α-Naphthoic	160	161–162	3.7	.304	0.1	.266	−0.4
p-Nitrophenol	114	113–114	7.2	.412	2.1	.383	1.8
Phenol	42–3	42– 43	9.98	.575	5.1	.566	5.2
Chloroacetic	62–3	62– 63	2.82	.206	−1.6	.185	−1.9
Dichloroacetic			1.2	.173	−2.5	.152	−2.5

Effect of Salt Concentration.—Before attempting to interpret these results, it is desirable to obtain some idea of the effect of total salt concentration on the measurements of acid strength. It is possible that the variation of relative strength between solvents, as measured, might be to some extent the result of irregular variations of the effect of total ionic strength. In the measurements an ionic strength of 0.1025 was maintained by means of lithium chloride. We have measured the relative strength, in 60% butyl carbitol, of acetic, myristic and benzoic acids, at ionic strengths from 0.0025 to 0.1025, with the result that, within the limits of error of the procedure, the total salt concentration introduces no uncertainty if it is constant through the series of measurements. Figure

3 illustrates the effect. For convenience, the curves are drawn to coincide at zero ionic strength. The coordinates are e. m. f. against the square root of the ionic strength. A small differential effect, about 0.1 *pK* unit, is observed, but this may not be real, since the probable error of measurement is of the same order of magnitude- If this quantity was applied as a correction to the relative strength of benzoic acid, its position with respect to acetic acid would deviate still further from that in water. In the working range the curves are nearly horizontal, showing that the potentials are not sensitive to small variations of lithium chloride concentration.

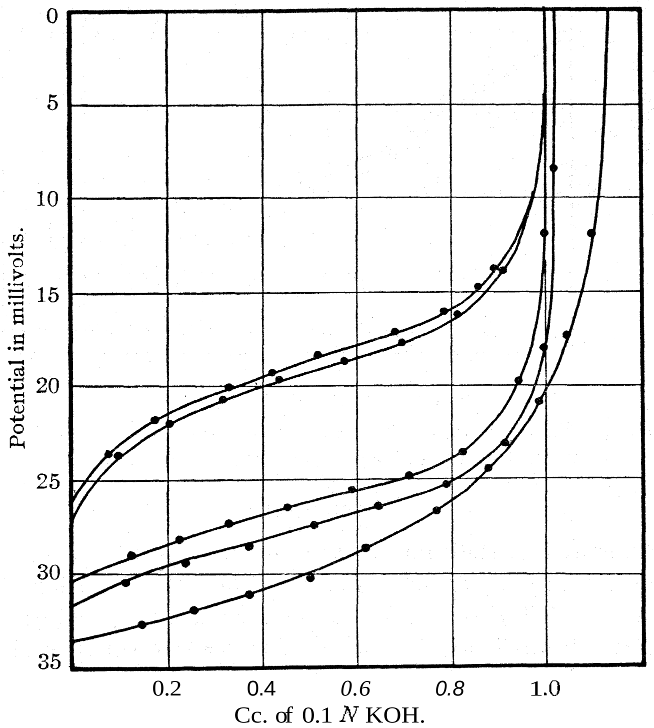

Fig. 2.—Titration curves with the quinhydrone electrode in 60% butyl carbitol. 0.005 M acids titrated with 0.1 M KOH. In order, from the top, acetic, benzoic, o-nitrobenzoic, chloroacetic, dichloroacetic.

Other Sources of Error.—The liquid junction between the aqueous calomel cell and the solution of the half-neutralized acid in the mixed solvent introduces an uncertainty of unknown magnitude. The junction potential should cancel out, in the evaluation of relative strength, if it remains constant in the separate measurements. We have attempted to minimize this error by employing a saturated potassium chloride bridge, and using the same initial acid concentration at all times. The high mole fraction of water in the mixed solvent should produce a tendency toward small junction potentials.

The variation of the potential between successive measurements of the same system is a second source of error. This variation, which is due to the antimony electrode, has been canceled, in part, by frequent measurements of the standard acetic acid system. The total error of measurement should be less than 0.2 *pK* unit.

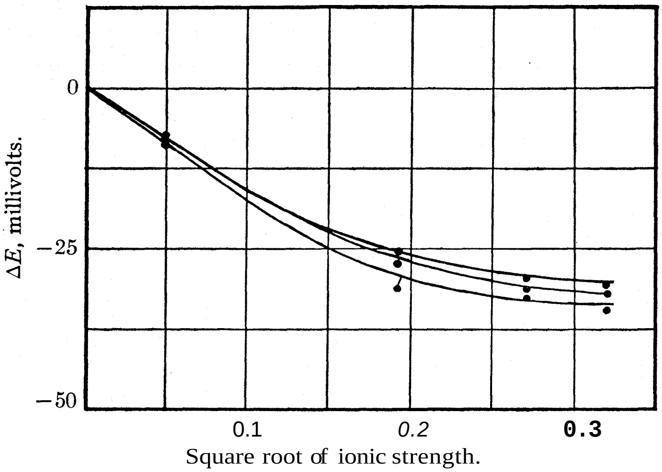

Fig. 3.—Effect of total salt concentration on apparent strength. In order, from the top, acetic, myristic and benzoic acids.

Discussion

We are indebted to Hall[7] for an excellent bibliography of measurements of acid strength in non-aqueous solvents. Since the variations of relative strength, as recorded by others, are of the same order of magnitude as those given here, the discussion will be sufficiently general if it is confined to the data of Table I.

The largest variation is that recorded for a-naphthoic acid, which in water is stronger by one *pK* unit than acetic, but in 60% butyl carbitol is weaker by 0.1 unit. Similarly, benzoic acid in water appears stronger by 0.6 unit than acetic acid, in 50% alcohol their strengths are equal, and in 60% butyl carbitol benzoic acid is the weaker by 0.3 unit. A similar variation is shown by *o*-nitrobenzoic acid. We are therefore unable to decide as to which of the three acids, benzoic, acetic and a-naphthoic, is intrinsically the strongest. Consequently, no specific deduction can be made concerning the relative positive or negative character of the methyl, phenyl and a-naphthyl groups. o-Nitrobenzoic acid appears in every case to be stronger than acetic acid, but we cannot say, within wide limits, how much stronger it is.

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[7] Hall, *Chem. Rev.*, ***8***, **191** (1931).

Any general statement about the uncertainty which variable relative strength introduces into the interpretation of measured acid strengths is based on insufficient data. However, it appears dangerous, at present, to draw conclusions about the intrinsic properties of acids from measured relative strengths which differ by less than one *pK* unit, or a factor of ten in the dissociation constant. This means that the specific nature of the solvent effect introduces an uncertainty of that magnitude. Any deductions which can be made are essentially qualitative. The effect of future data on this conclusion will be, of course, to change the magnitude of the uncertainty. The most probable change is an increase. However, when the rather abnormal properties of water are considered, it is possible that future measurements may show that, by omitting aqueous values from consideration, a more specific set of relations may be deduced.

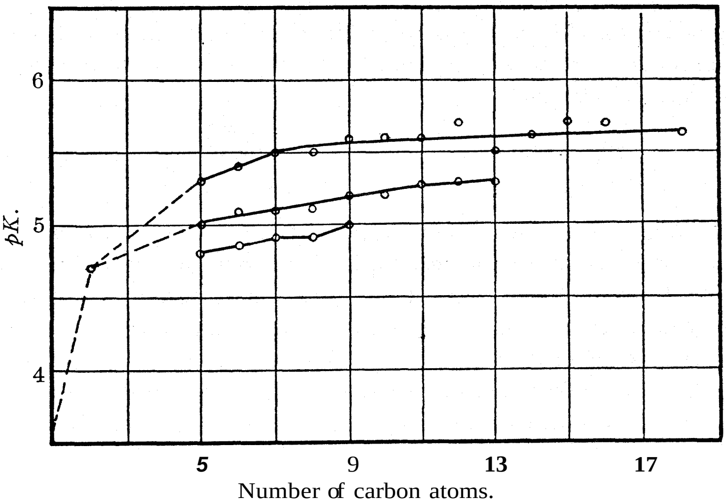


Fig. 4.—Strength (*pK*) of normal aliphatic acids as a function of the number of carbon atoms. Upper curve, 60% butyl carbitol; middle curve, 50% alcohol; lower curve, water.

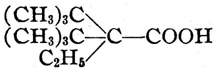
An interesting case arises in the comparison of acetic and chloroacetic acids. Regardless of the magnitude of the measured relative strength, we should feel justified in concluding that chloroacetic acid is the stronger because of the much greater strength of trichloroacetic acid.

Normal Aliphatic Acids.—In Fig. 4 the strength relations of the normal aliphatic acids in water, 50% alcohol and 60% butyl carbitol are plotted as a function of the number of carbon atoms. The curves are drawn to coincide at the point which gives the strength of acetic acid in water. The maximum difference, the relative strength of the higher fatty acids in 60% butyl carbitol, falls just within our limit of interpretation. The conclusion is, therefore, that, within this limit, all the normal aliphatic acids (except formic acid) have the same strength. However, this does not exclude the possibility that stearic acid may be weaker than acetic by one *pK* unit.

If it is assumed that the curve for water is analogous to the others, the *pK* value of stearic acid in water may be estimated as about 5.2. This quantity probably cannot be checked by direct measurement. Any mixture of water, stearic acid and sodium stearate will show much greater alkalinity because of the low solubility of the acid. The mixed solvents appear to increase differences which occur in aqueous solution.

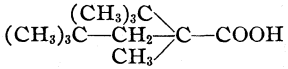
Branched Aliphatic Acids.—The measurements with isovaleric, isocaproic and methylethylacetic acids are inconclusive. However, it is improbable that such closely related substances are very differently affected by the solvent, and the measured values should be significant within rather narrow limits. Trimethylacetic acid is probably weaker than valeric.

The acids B and G, obtained from Mr. G. W. Wheland of this Laboratory, are isomers of lauric acid, and may be represented provisionally by the following structures



$$\left.\begin{matrix}(CH_3)_3C\\ (CH_3)_3C\\ C_2H_5\end{matrix}\right>C-COOH$$

B



$$\left.\begin{matrix}(CH_3)_3C\\ (CH_3)_3C-CH_2\\ CH_3\end{matrix}\right>C-COOH$$

G

The more highly branched B acid appears weaker than lauric acid, in the mixed solvents, by about one *pK* unit. The corresponding figure for the G acid is 0.6 unit. It is interesting to attempt a comparison of the three acids, acetic, lauric and B. Our limit of interpretation makes indefinite the comparison of either of the pairs, lauric and B acid, or lauric and acetic, but permits the conclusion that the B acid is definitely weaker than acetic acid. This means that either lengthening or branching the chain produces a definite weakening effect, but does not decide which of the effects is real. The probable answer is that both are significant.

Aromatic Acids.—The introduction of aromatic hydrocarbon radicals into acetic acid produces no effects large enough to be considered significant. Salicylic and o-nitrobenzoic acids are definitely stronger than benzoic acid.

The writer wishes to express his sincere appreciation of the advice and assistance of Professor James B. Conant, who suggested this problem.

Summary

The relative strength of thirty-one carboxylic acids in a solvent mixture containing, by volume, 60% of butyl carbitol and 40% of water, has been measured with the antimony electrode.

The significance of the variation of measured relative strength with the solvent has been considered, with the conclusion that a measured relative strength less than one *pK* unit, or a factor of ten in the dissociation constant, does not necessarily indicate a difference of intrinsic acidity. Future measurements in solvents other than water may increase this uncertainty.

Aromatic hydrocarbon radicals, when introduced into aliphatic acids, produce no measurable change of acidity.

Either the lengthening or the branching of the hydrocarbon chain in the aliphatic acids produces a definite weakening effect. Probably both effects are real.

CAMBRIDGE, MASSACHUSETTS

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

A POTENTIOMETRIC STUDY OF WURSTER'S RED AND BLUE

BY L. MICHAELIS

RECEIVED JUNE 3, 1931 PUBLISHED AUGUST 5, 1951

In a rather large number of cases there have been found compounds intermediary, with respect to the level of oxidation, between a compound of the quinoid type and one of the hydroquinoid type. In a previous paper[1] it could be shown by a potentiometric method for three organic dyestuffs of the oxyphenazine series, that this intermediary compound is a molecule of the same size as either the holoquinoid form or the hydroquinoid form and differs from the hydroquinoid only by one oxidation equivalent (or hydrogen atom or electron). It must be considered as a radical-like compound with an odd number of electrons. Those three dyes offered a particularly favorable opportunity for the proof of such a statement because the intermediary compounds were very stable and permitted a thorough potentiometric study of the system, there being no drift in the potentials in time. The conclusions were based on observations of systems in a true thermodynamical equilibrium and therefore were scarcely liable to a misinterpretation.

This observation suggested the idea that other examples of half-reduced quinoid substances might be accessible to a similar potentiometric analysis. The difficulty in most of these cases is the fact that these intermediary compounds are as a rule not very stable in aqueous solution but undergo irreversible reactions and so cause a drift of the potentials. An attempt to utilize the potentiometric method for such a purpose was made by Clark, Cohen and Gibbs,[2] who studied the so-called meriquinones formed from aromatic diamines. They took for granted the current idea that these intermediary compounds are meriquinones according to Willstatter's[3]

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[1] Michaelis, J. *Biol.* Chem., in press, July (1931).

[2] W. Mansfield Clark, Barnett Cohen and H. D. Gibbs, *Public* Health *Repts.*, Suppl. No. 54, 1 (1926).

[3] Willstatter and Mayer, Ber., 37, 1494 (1904); Willstatter and Pfannenstiei, *ibid.*, 37,4605 (1905); Willstatter and Piccard, *ibid.*, 41, 1458 *(1908).*

definition as being molecular compounds of the holoquinoid and the hydroquinoid form.

For some years an increasing number of papers has been published advocating the formula of a free radical in such cases in which formerly double molecules were supposed to exist. In some of these cases an equilibrium between the free radical and its polymeric saturated form was assumed. This holds for instance for Gomberg's triphenylmethyl and for Wieland's biphenylnitride. In other cases the existence of the free radical without its polymerized form was assumed. This holds, for instance, for the case of the aromatic diamines, the subject also of this paper. Weitz and Fischer[4] showed by determination of the boiling point in solutions of such compounds that only the formula of a free radical is compatible with the data observed. A thorough compilation of the whole subject has been published by Weitz[5] in which many other examples are enumerated. Yet never has a potentiometric method been applied for the proof of such a contention. Such a method may not be applicable for every case, but in those cases in which it can be used this method is much superior to any other. All those assumptions with respect to incomplete dissociation which have to be considered in order to correct the boiling or freezing point data for electrolytes do not appear in the potentiometric method. This method whenever it is available may be considered as the best method for the determination of a molecular weight for an ionic compound.

The potentiometric analysis presented in this paper was suggested by, and is based on, a set of half-quantitative, preliminary observations which will first be described. These observations hold for asymmetric dimethyl-p-phenylenediamine and tetramethyl-p-phenylenediamine. There is no doubt that the method can be extended to other substances of this type but as we have to deal with very labile systems, each of these cases should be studied separately and may require long experimentation before a definite understanding is attained. Therefore this study will be restricted to the two substances mentioned.

When either of the two mentioned diamines is titrated with an oxidant such as bromine or chlorine, a deep color is developed, called Wurster's red in the case of the dimethyl compound and Wurster's blue for the tetramethyl one. When the titration is performed rather rapidly and farther extended, the color disappears again. When, after reaching the point of color discharge, the solution is allowed to stand, the color gradually turns back, though not to its maximum intensity, at a rate largely dependent on concentration and PH. The spectroscopic analysis shows that it is the same substance which reappears, as recognizable from the characteristic

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[4] Weitz and Fischer, *Ber.*, *59*, 432 (1926).

[5] Weitz, Z. *Elektrochem.*, 34, 538 (1928).

double band, which differs in Wurster's red and blue only by the spectral location of the two bands. It should not be asserted, however, that the return of the color is due only to the reappearance of Wurster's red or blue. According to the conditions other dyes may or may not be developed besides.

The interpretation of this phenomenon is this. Wurster's red or blue differs from the mother substances, the respective diamines, only by one oxidation equivalent (or hydrogen atom, or electron) as Willstatter and his co-workers[3] have shown long ago. The disappearance of the color in the second step of titration indicates that the dye is oxidized to a higher level which has practically no, or very little, color. One might expect this substance to be the second step of oxidation, analogous to diiminoquinone, and very likely it is. But these substances are extremely labile, as Willstatter has shown; in aqueous solution they spontaneously undergo irreversible changes and are converted into substances to which we must attribute a great inclination to still further oxidation. So these secondary substances will reduce those molecules of the diiminoquinone still present in the solution, to Wurster's red (or blue) over again. From these rough observations we may expect that the second half of the titration is characterized by a very labile system which at no point of the titration is in any chemical equilibrium within reasonable time. So we may expect that even in the best case only in the first half of the titration steady potentials might be established.

This is exactly what happens. When during the titration the potential at a blank platinum electrode is read, there are sufficiently constant and reproducible potentials in the first half of the titration. This holds at least for a certain range of PH. The most suitable PH for constant potentials proved to be 4.6 for both substances. In the second part of the titration no constant potentials can be obtained under any condition. The potentials always drift back to the negative side as though the oxidized form (the diiminoquinone) would spontaneously and irreversibly disappear in time. When the second half of the titration is performed rather hastily, the potential will stay within a small, not very well reproducible, range and the end of the titration will sometimes be indicated by a sudden though often not very big jump, which, however, drifts back at a rate depending upon the conditions, such as the time required for the whole titration, the number of steps in which the whole titration had been subdivided and the pause between the successive steps. The color vansihes simultaneously with this potential jump and, on standing, reappears, simultaneously with the back drift. If it happens that no jump of the potential appears, no complete discharge of color will be observed either.

Thus the end-point of the first step of titration can, with a fair approximation, be recognized by the fact that the potentials, which were constant up to this point, begin to drift; and the end of the second step can be recognized, provided the titration in the second step is rapidly performed, by the point of coincidence of potential jump and transient discharge of color, if there is such a point at all. The amount of oxidant used for each of the two steps turns out to be the same, within the limits of error in such a labile system.

A theoretical analysis of the titration curve is, therefore, not difficult for the first half of the titration, but impossible at the present time for the second half. When the titration curve of the first step is analyzed, it turns out to be the curve for a regular reversible oxidation–reduction system, and the difference between the reduced and oxidized form turns out to be only one electron. It is very important to add that the mid-point potentials E_0 of this step of oxidation for different experiments, at the same PH, coincide, independently of the initial concentration of the diamine.[6] Hereby it is proved that Wurster's red or Wurster's blue differs from its particular diamine only by one electron, without any change in molecular size and that it is not a meriquinone according to Willstätter's definition, namely, a compound of one or several molecules of the holoquinoid form with one or several molecules of the completely reduced form. These two dyes, Wurster's red and blue, therefore are of the type of a half-reduced quinone, or semiquinone, a molecule with an odd number of electrons. We may also say that one of the two nitrogen atoms is bivalent as in Wieland's biphenylnitride. In contrast, however, to these biphenylnitrides, or to Gomberg's triphenylmethyl, the unsaturated radical-like compound does not seem to undergo to any measurable extent a polymerization to a double molecule in which the state of unsaturation is abolished. This radical-like compound in aqueous solution of a PH around 4.6, is, though not strictly stable, yet a fairly stable substance, provided there is no excess of oxidant which can oxidize it partly to a higher level. If this is the case, the whole system becomes unstable, and the radical-like compound will partake in the chemical processes which go on with greater or less rapidity. The radicals do not combine with each other to form double molecules or with the original diamine to form quinhydrones, but they undergo condensation or other reactions with the other molecules in the solution, especially with the very unstable substances which are on the oxidation level of diiminoquinones.

In formulating radicals of the described kind one may accept a point of view proposed already by Weitz, which is best presented in this way. In the static Formula I, where R is either a methyl group or hydrogen, it is indicated that one amino group has one electron less than would correspond to an electroneutral state.

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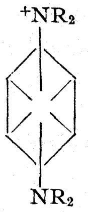
[6] As to significance of the independence of E_0 of the initial concentration, see Ref. 1.



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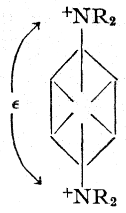

II

This static model should be replaced by a more dynamic one (Formula II). One electron has a circuit around both N atoms, or the two nitrogen atoms share one electron. This, then, is a chemical bond consisting in one shared electron, instead of the two in the ordinary chemical bond of G. N. Lewis.

Experimental

The purest commercial grades of the hydrochlorides of dimethyl-*p*-phenylenediamine and of tetramethyl-p-phenylenediamine (preparations of Eastman) were recrystallized by dissolving in methyl alcohol and precipitating with benzene. A suitable amount of the crystals was dissolved in deaerated water, and *a* suitable portion added to 15 cc. of acetate buffer of PH 4.62 (solution 0.1 normal both with respect to sodium acetate and acetic acid). A freshly prepared solution of bromine was used as oxidant, in such a concentration that 1 to 2 cc. was used to the complete titration of the first step. The titration was performed in a constant temperature chamber at 30° in a stream of nitrogen purified over copper at 450°, though this precaution might not have been imperative in working on such relatively positive potential ranges as we have to deal with here. Three blank platinum electrodes were immersed in the solution. Whenever the potential was steady it was observed for all three electrodes, without there ever being a difference of more than 0.1 millivolt. As soon as the potential began to drift, in the progress of titration, the readings had to be hastened and according to the circumstances only one electrode was used for the potential readings. In the diagrams all potentials, constant over a reasonable time within one or two tenths of a millivolt, are marked with plain circles. For all potentials with a drift the direction of the drift is indicated by an arrow. The short arrows indicate a drift of some tenths of a millivolt per minute; the long arrows indicate a drift of several millivolts per minute. The drawn out curves are those calculated according to

$$E = E_0 + 0.0601 \log \frac{X}{A - X}, \text{ volts}$$

where E_0 is a constant, X the amount of bromine solution in cc., and A that amount of bromine solution used up at the end of the first reversible step of the oxidation. The value of A was determined by the following three methods.

1. The first method is only roughly approximate and cannot be applied in every case; it can only be used when the second step of titration is performed within a few seconds without reading the potentials except for the very last part. This method can only be applied when the end of the second step of titration can be recognized by a transient complete discharge of color and a transient jump of the potential. These two phenomena coincide. On account of the unavoidable secondary reactions during the second half of titration even on rapid titration, the observed end-point, if there is one at all, will always come a little later in the curve than where the theoretical end-point should lie. If such an end-point can be recognized, one may assume that the amount of oxidant at this end-point is approximately equal to, or, more precisely speaking, is somewhat greater than, 2 *A*.

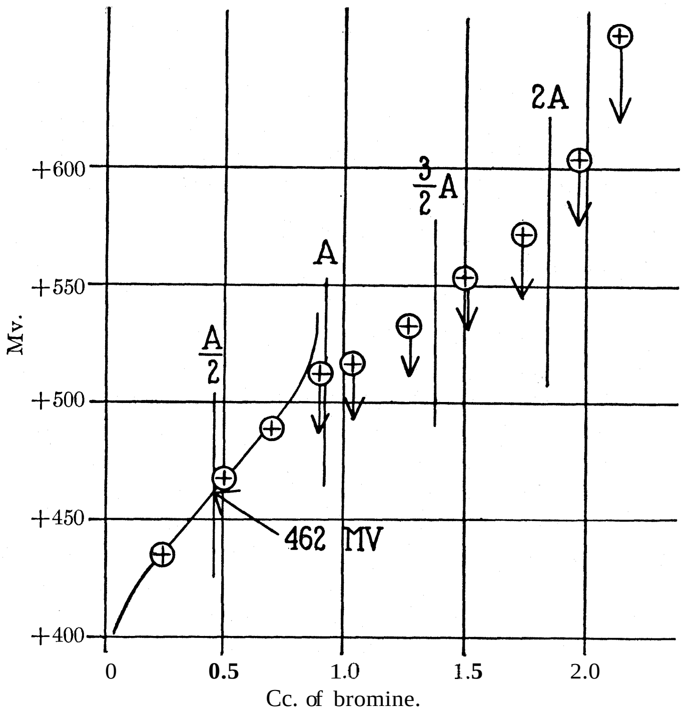

Fig. 1.—2×10^{-4} mole of dimethyl-*p*-phenylenediamine hydrochloride dissolved in 20 cc. of acetate buffer of PH = 4.62 (a solution 0.1 molar both for sodium acetate and for acetic acid) is titrated at 30 °C. with an aqueous solution of bromine. Abscissa, cubic centimeters of bromine. Ordinate, potentials, in millivolts, referred to the normal hydrogen electrode. Arrows signify drift of potential. Potentials without arrow are stable. A is the total theoretical amount of bromine used for the complete oxidation to the level of the semiquinone.

2. That point of titration where the previously steady potentials become inclined to a backward drift, can in the first approximation be taken as the value of A. This method, also, is an approximative one, because a little overlapping of the two steps of titration takes place. The correction of the true value for A lies in such a direction that the first drifting potential must occur somewhat before, but never after, the theoretically required amount, *A*, of the oxidant has been added. The result of this method agreed with that of the first within the limits to be expected, namely, that the first method furnished always a somewhat higher value for *A* than the second. The true value of A may be estimated as lying between those obtained with the first and those obtained with the second method.

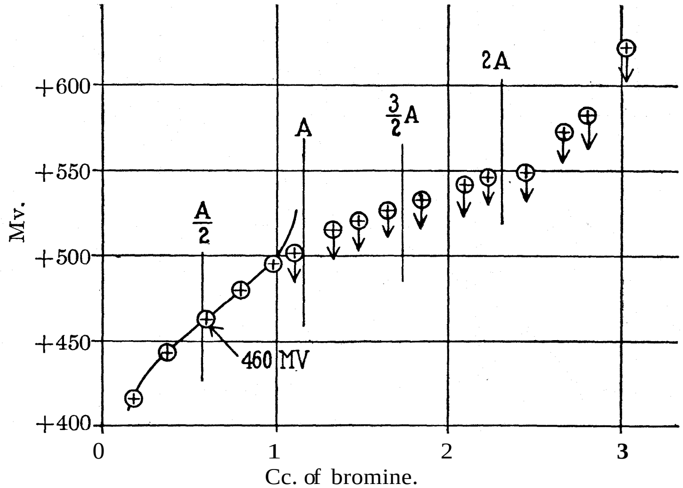

Fig. 2.—4 X 10^{-5} mole of dimethyl-*p*-phenylenediamine hydrochloride dissolved in 20 cc. of acetate buffer titrated with a bromine solution. Designations the same as in Fig. 1.

3. After the value of A had been evaluated approximately by one or both of these two methods, a correction was applied in the following way. By a graphical method of trial and error a value of A was chosen which furnished the best fitting curve for the first half of the titration where the potentials show no drift. It was postulated that there exists some value of *A* that will furnish an entirely fitting curve, and that this value of A should be very close to the one obtained with the two other methods, the deviation lying in the expected direction. This postulate was fulfilled in every case.

So the final and definite method is the third one, and the two others were only used to show that the value, A, obtained with this method can be shown, in suitable cases, to be compatible with those values which might have been approximately determined by the two others.

In any event, the third method furnished a theoretical curve which. except for the very end of this curve, for understandable reasons, fitted perfectly with the observations, and which furnished E_0 values agreeing satisfactorily for different experiments even on varying the initial concentration in the ratio 1:10. There is, then, every justification for utilizing these curves for an interpretation based on thermodynamical considerations.

There is a slight difference between the two amines with respect to the third method. In the tetramethyl compound the overlapping of the first and second steps of oxidation is somewhat greater than in the dimethyl compound. This is recognizable by the relatively earlier beginning of the drifting part of the curve. This disadvantage is, however, compensated by the fact that the potentials of the tetramethyl compound, before the drifting part of the curve begins, are even more stable than for the dimethyl compound. The tetramethyl compound, during the first, not drifting, part of the curve, can be titrated with the same leisure as any good reversible system; furthermore, even when the drift begins, this drift is so slow (within some tenths of a millivolt per minute) that the uncertainty of the potential value may lie only within one millivolt. Here the drift does not cause so much a time distortion of the curve, but

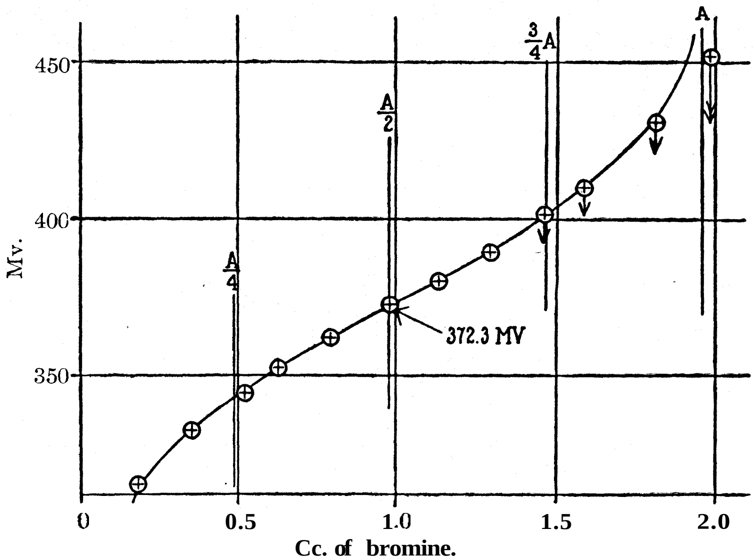

Fig. 3.—1.0 × 10^{-5} mole of tetramethyl-*p*-phenylenediamine hydrochloride dissolved in 15 cc. of acetate buffer and titrated with bromine. Designations as in Fig. 1. The short arrows signify a drift of the potential of about 0.1 millivolt per minute; the long arrow, a drift of several millivolts per minute. Potentials without arrow are perfectly stable.

rather shows the beginning of an overlapping and marks that part of the curve beyond which the potentials can no longer strictly obey the simple formula calculated for *a* one-step oxidation without overlapping.

These E_0 values must be considered as being strictly indicative of a free energy level of the system, and from the shape of the curve it can be decided with safety which one of the two reactions

$$\text{1 mole reduced form} \rightleftharpoons \text{1 mole oxidized form} + \epsilon \qquad (1)$$

(Wurster's red as semiquinone)

$$\text{2 moles reduced form} \rightleftharpoons \text{1 mole oxidized form} + \epsilon \qquad (2)$$

(Wurster's red as meriquinone)

(ϵ is one electron) takes place. The first of these two possibilities, then, is found to be the correct one.

Two titration experiments are shown for dimethyl-*p*-phenylenediamine graphically in Figs. 1 and 2. The initial concentrations differ in these two cases in the ratio 1:5, the greater one being 0.01 molar. Two experiments are shown for tetramethylphenylenediamine, one as a graph (Fig. 3) and another in the form of Table I. The initial concentrations in these two experiments differ in the ratio 1:7.5, the greater one being 0.003 molar.

TABLE I

1.3×10^{-6} MOLES OF *TETRAMETHYLPHENYLENEDIAMINE* HYDROCHLORIDE DISSOLVED IN 15 CC. OF ACETATE BUFFER, PH 4.62, AND TITRATED WITH BROMINE

E calculated according to the formula $E = 0.1303 + 0.0601 \log \frac{X}{1.660 - X}$ volts

X (cc. of Br solution)	Percentage of oxidation, the whole first step of oxidation taken as 100%	Drift of the potential in millivolts per minute (approximately)	E in volts referred to the normal hydrogen electrode Observed	Calcd.
0.280	16.9	0	+0.0882	+0.0887
.465	28.0	0	.1048	.1057
.620	37.3	0	.1160	.1168
.805	48.5	0	.1285	.1287
.990	59.6	0	.1401	.1405
1.154	69.5	0	.1517	.1518
1.320	79.4	0.1	.170	.1658
1.610	98.0	5.0	.201	.1961

Summary

It is shown by mathematical analysis of the potential curve obtained by oxidative titration with bromine that Wurster's red and Wurster's blue are not molecular compounds of one molecule of a quinoid type with another molecule of a hydroquinoid type, but true semiquinones, *i. e.*, radical-like compounds intermediary between quinone and hydroquinone and of the same molecular size as each of these two. Such a compound must possess an odd number of electrons. One may express the situation

by saying that the two nitrogen atoms of the dye are linked by a chemical bond which consists of a single electron instead of a pair.

NEW YORK, N. Y.

[COMMUNICATION NO. 64, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

THE REACTION BETWEEN OXYGEN AND ACETYLENE IN THE PRESENCE OF NITROGEN OXIDES

BY SAMUEL LENHER

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Comparatively little work has been done on the catalyzed oxidation of the simple hydrocarbons. Study of the slow combustion of acetylene[1] led to isolation of the intermediate compounds, glyoxal, formaldehyde, and formic acid, and indicated the probable steps in the reaction. As the influence of a homogeneous catalyst is to lower the temperature at which measurable reaction begins, and thus to increase the stability of the partially oxidized products, study of the effect of gas catalysts in oxidations promised to give further information on the course of reaction.

The present investigation was a study of the effect of nitric acid vapor and its decomposition products on the slow thermal oxidation of acetylene. The oxides of nitrogen have been used repeatedly in the partial oxidation of the hydrocarbons.[2] It was assumed in these papers and patents that the action of the nitrogen oxides was catalytic, that is, that the nitrogen oxides were not destroyed in the reaction. This assumption was not directly tested, although Frolich, Harrington and Waitt[2f] stated that in the oxidation of methane with nitrogen peroxide and oxygen the loss of nitrogen peroxide by complete decomposition to elementary nitrogen was of the order of 1% per pass, and Bibb and Lucas[2g] indicated in an experiment that nitric acid was consumed in the oxidation of methane. It appears now from a recent paper by Smith and Milner[3] that in the partial oxidation of methane in the presence of nitrogen oxides the nitrogen oxides are consumed in the reaction and that their action cannot be considered catalytic. The writer has found in an investigation of the oxidation of ethylene, which will be communicated shortly, that nitrogen oxides react chemically with ethylene at the temperature of the slow oxidation reaction and that their action is not one of catalysis.

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[1] (a) Kistiakowsky and Lenher, THIS JOURNAL, 52, 3785 (1930); (b) Spence and Kistiakowsky, *ibid.*, 52, 4837 (1930).

[2] (a) Bailey, U. S. Patent 1,319,748 (1919); (b) Bibb, U. S. Patent 1,392,886 (1921), reissue 15,789 (1924); *(c)* Chemische Fabriken Worms **A.** G., British Patent 156,252 (1921); (d) Atack, British Patent 182,843 (1921); (e) Layng and Soukup, *Ind. Eng. Chem.*, 20, 1052 (1928); (f) Frolich, Harrington and Waitt, THIS JOURNAL, 50, 3216 (1928); (g) Bibb and Lucas, *Ind. Eng. Chem.*, *21*, 633 (1929); (h) Bibb, Canadian Patent 302,672 (1930).

[3] Smith and Milner, *Ind. Eng. Chem.*, 23, 357 (1931).

The catalytic action of nitrogen oxides in gaseous oxidations must be that of an active oxygen carrier which is alternately reduced in the reaction and oxidized by oxygen, or which can initiate long reaction chains from one primary reaction.

Experimental Results

The oxidation of acetylene in the presence of nitrogen oxides was studied by the flow method at atmospheric pressure. Oxygen and acetylene at a regulated rate of flow were mixed in a capillary at the entrance of the reaction vessel. Oxygen from a commercial cylinder was used without further purification. Acetylene (Prest-O-Lite) was passed through two spiral wash-bottles containing water to remove acetone and was dried with calcium chloride. Nitric acid vapor was introduced into the gas mixture by passing the oxygen through a wash-bottle containing 100 cc. of 90% nitric acid containing only 0.046% nitrogen peroxide. The concentration of nitric acid in the gas was controlled by the vapor pressure of the acid.[4] The temperature of the acid was kept constant to ±2° with a water-bath. The cylindrical Pyrex reaction vessel, 20 mm. in diameter, was heated in an electric tube furnace. Reaction temperatures were read by means of a chromel–alumel thermocouple in a thin-walled glass tube in the center of the vessel.

The reacted gases passed through a U-tube cooled in solid carbon dioxide–methanol mixture, and a spiral wash-bottle containing a standardized barium hydroxide solution to absorb carbon dioxide, and were collected in a water gasometer. The gas was analyzed as described by Kistiakowsky and Lenher (Ref. 1a, p. 3786). The organic products condensed in the cooled U-tube were practically negligible as determined by oxidation with standard potassium dichromate in strong sulfuric acid and back-titration with sodium thiosulfate. The U-tube contained appreciable amounts of nitric acid and nitrogen oxides, and in many experiments drops of inky blue nitrogen trioxide (N_2O_3) were seen. The organic acid content could not be determined because of the nitric acid. Quantitative analysis of the aldehyde content was not possible because of the very small amounts of both glyoxal and formaldehyde. Accordingly, after several tests showed that less than 3% of the acetylene went to formic acid and formaldehyde, the contents of the U-tube were omitted from further quantitative analysis. A solid deposit was formed in the exit tube of the reaction vessel at the end of the furnace. The amount of this deposit was determined by weighing. This deposit showed the general physical properties of trimeric glyoxal.[5] Monomeric glyoxal was prepared from a sample of one gram of

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[4] Taylor, Ind. Eng. *Chem.*, **17**, 633 **(1925).**

[5] Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, 1918, 4th ed., Vol. I, p. 759.

the deposit by heating it with phosphorus pentoxide[6] in a small distilling flask with a condenser cooled to −78°. On warming the flask the green vapor of glyoxal which condensed in the receiver to fine yellow needles was noted.

A weighed sample of the solid glyoxal product from several experiments was dissolved in 20 cc. of warm water. Thirty cc. of 50% acetic acid solution of *p*-nitrophenylhydrazine was added and thesolution was allowed to stand for thirty-six hours. The precipitate of the nitrophenylhydrazones was filtered on a small Biichner funnel, washed with warm 10% sodium carbonate solution and water, dried in powder form and weighed. The weighed precipitate was then extracted for two hours at room temperature with dry chloroform to dissolve the *p*-nitrophenylhydrazone of formaldehyde, and was then filtered, dried and .weighed. The weight of phenylhydrazones in one experiment was 0.6533 g. before treatment with chloroform and 0.6319 g. after extraction, which showed that the precipitate was 96.7% the di-*p*-nitrophenylhydrazone of glyoxal, whose melting point was 302°. The precipitate gave the characteristic Bamberger test of a blue coloration with alcoholic potassium hydroxide. The weights of glyoxal given in Table I are the actual weights of the solid deposit from the reaction on the assumption that the deposit was trimeric glyoxal.

A gas mixture containing equal volumes of acetylene and oxygen was used. The rate of flow of each gas was 0.05 cc. per sec., corresponding to an average time of contact of 180 seconds for the 30-cc. vessel at an average

TABLE I

REACTION OF OXYGEN AND ACETYLENE IN THE PRESENCE OF NITRIC ACID VAPOR

Average time of contact, 180 seconds

		Reaction products			
Temp., °C.	HNO_3 in mixture, %	CO_2, cc.	CO, cc.	Hz, cc.	Solid deposit (glyoxal), g.
		180 cc. of 1 acetylene:1 oxygen mixture used			
210	1.7	0.3	5.2	0.0	0.0132
230	1.7	1.1	4.2	.2	.0130
230	1.7	1.3	1.2	.2	.0134
230	1.7	0.6	2.4	.4	.0113
240	1.7	1.2	3.5	.5	.0131
240	2.3	1.8	2.6	.0	.0183
210	4.1	3.4	18.1	.8	.0362
210	4.1	3.6	16.4	1.0	.0301
230	4.1	6.0	19.8	1.4	.0295
230	4.1	6.2	20.1	0.8	.0418
		180 cc. of 1 acetylene:1 air mixture used			
210	4 1	2.7	4.9	3.4	0.0194
210	4 1	1 6	...	0 8	.0231
230	4 1	4 0	6 5	1.7	.0253

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[6] Harries and Temme, Ber., 40, 165 (1907).

temperature of 230°. One hundred and eighty cc. of acetylene–oxygen mixture was used. The nitric acid wash-bottle in the oxygen line was kept at 0° until the furnace was at the desired temperature and the gas flow was adjusted; then the acid was warmed to the temperature of the experiment. From Table I it is seen that the main products of the reaction are glyoxal and carbon monoxide with smaller amounts of carbon dioxide, hydrogen and water.

These experiments show that the principal reaction product is glyoxal, for the glyoxal recovered corresponds to 50–60% of the acetylene oxidized.

Experiments with a different time of contact and with different gas mixtures are given in Table II.

TABLE II

EFFECT OF TIME OF CONTACT AND GAS COMPOSITION ON REACTION OF ACETYLENE WITH OXYGEN IN THE PRESENCE OF NITRIC ACID VAPOR

180 *cc.* of **gas** mixture used

Temp., °C	HNO_3 in mixture, %	Time of contact, seconds	Composition of gas, %		Reaction products			
			C_2H_2	O_2	CO, cc.	CO_2, cc	H_1, cc.	Solid deposit (glyoxal), g
210	4.1	180	50	50	16.4	3 6	1.0	0.0301
210	4.1	90	20	40	4 0	...	0.4	.0201
210	4.1	90	13.5	43	1.9	...	.6	.0229
210	4 1	45	50	50	...	...	...	.0268
230	4 1	45	50	50	...	Explosion		

The rate of reaction in the presence of nitrogen oxides appears to depend on the concentrations of acetylene, oxygen and nitrogen oxides, as shown by the experiments with air and with different amounts of nitrogen oxides in Table I and with low acetylene concentrations and the same concentration of nitrogen oxides in Table II. The rate is not dependent on the square of the acetylene concentration, as in the uncatalyzed reaction,'" and the reaction is not retarded by an excess of oxygen or air.

In the above experiments with 4% of nitric acid in the gas mixture, reaction was observed below 170° by the formation of the solid deposit of glyoxal and the formation of carbon dioxide. Experiments carried out above 250° using over 2% of nitric acid vapor in the gases resulted in explosions. The sensitivity of gas containing nitric acid vapor varied with the time of contact; for example, numerous runs were made at 230° with times of contact from 90 to 180 seconds, but increasing the flow to give a time of contact of about forty-five seconds brought about explosions which shattered the reaction vessel. Dixon[7] observed that a lower ignition temperature was obtained when a gas mixture was passed rapidly into a hot tube than when the tube was gradually heated while the gas mixture was passing through it. It may be that the phenomenon noted here is caused by a lowering of the ignition temperature as observed by Dixon.

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[7] Dixon, *Rec. trav. chim.*, 44, 305 (1925).

A number of experiments were carried out to see if nitrogen peroxide in small amounts lowered the explosion temperature of acetylene-oxygen mixtures as it did the explosion temperatures of hydrogen–oxygen mixtures[8] and of carbon monoxide–oxygen mixtures.[9] A 1 acetylene–1 oxygen mixture was used containing from 0.010 to 0.45% of nitrogen peroxide. Only the slow thermal reaction was observed in the range 260–315°. As a 1 acetylene–1 oxygen mixture exploded frequently at 325° and always at 340°, it was concluded that small amounts of nitrogen oxides (below 0.5%) did not lower the explosion temperature or the temperature range of the slow oxidation reaction.

Examination of the solid reaction product and the contents of the cooled trap by the sodium fusion test gave no evidence that the nitrogen oxides had entered into chemical combination, forming organic nitrogen compounds.

The reaction of nitric oxide and acetylene was studied under the conditions of the oxidation experiments in the absence of other nitrogen oxides and oxygen. Nitric oxide, which was stored over water, was passed through the system before the run to sweep out traces of nitrogen peroxide and oxygen. The reaction was tested using a mixture of 1 nitric oxide–1 acetylene with a time of contact of thirty seconds at 260°. No reaction was observed between nitric oxide and acetylene under these conditions; the gases leaving the reaction vessel were colorless, which showed the absence of nitrogen peroxide, there was no formation of carbon oxides, and the washings from the trap cooled to $-78°$ gave no evidence of the presence of organic oxidation products. As nitric oxide does not react with acetylene under the conditions of the reaction between acetylene and oxygen in the presence of nitric acid vapor (and its decomposition products), it was concluded that the nitrogen oxides are not reduced by acetylene beyond nitric oxide in the catalyzed oxidation.

Discussion

The presence of nitrogen oxides in concentrations greater than 0.5% by volume causes a marked lowering of the temperature of the slow thermal reaction between acetylene and oxygen; this lowering is as much as 80° for concentrations of 4% nitrogen oxides. As the rate of reaction is not greatly influenced by a change in the concentration of acetylene or oxygen, and as the rate of oxidation increases with increasing concentration of nitrogen oxides up to 4%, it appears that the rate-determining process is a reaction with a nitrogen oxide. At the temperature of these experiments, nitric acid vapor in the presence of oxygen is partially dissociated into water and nitrogen peroxide. The initial process is probably a reaction of

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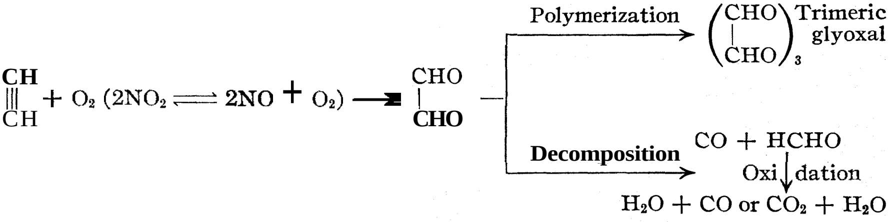
[8] Gibson and Hinshelwood, *Trans. Faraday Soc.*, 24, 559 (1928).

[9] Sagulin and Semenoff, *Chem. Reviews*, 6, 350 (1929).

nitrogen peroxide with acetylene. Acetylene is oxidized with the formation of nitric oxide. This nitric oxide is oxidized by oxygen to nitrogen peroxide. Thus the action of the nitrogen peroxide is one of true catalysis, involving alternate reduction with acetylene to nitric oxide and oxidation of the nitric oxide with oxygen to nitrogen peroxide.

The predominance of glyoxal as a reaction product indicates that its formation is a principal primary reaction. In fact, the yields of glyoxal of 50% or more of the acetylene oxidized suggest that it is the primary product. The occurrence of large amounts of carbon monoxide and of only traces of formic acid, formaldehyde and hydrogen points to the thermal decomposition of glyoxal to carbon monoxide and formaldehyde, $OHC—CHO \longrightarrow CO + HCHO$, as the main source of the carbon monoxide. The formaldehyde may be either oxidized to formic acid, which decomposes to water and carbon monoxide, $HCOOH \longrightarrow H_2O + CO$, or may be oxidized directly to water and carbon monoxide by nitrogen peroxide, $HCHO + NO_2 \longrightarrow CO + H_2O + NO$, in a reaction similar to the primary reaction of nitrogen peroxide with acetylene. The hydrogen and carbon dioxide may come from the decomposition of formic acid, $HCOOH \longrightarrow H_2 + CO_2$. The course of the reaction as shown by these experiments may be given by the scheme



Summary

The reaction between acetylene and oxygen in the presence of nitrogen oxides proceeds between 170 and 250° as a homogeneous reaction catalyzed by nitrogen peroxide. The main product is trimeric glyoxal; the other products are formaldehyde, formic acid, carbon oxides, hydrogen and water.

WILMINGTON, DELAWARE

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

THE SYNTHESIS OF AMMONIA IN THE LOW VOLTAGE ARC

BY A. KEITH BREWER AND R. R. MILLER

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A detailed study of the synthesis of ammonia in the glow discharge[1,2] has shown that the rate of formation is proportional to the current passing through the discharge, and is independent of the pressure between wide limits. The maximum rate of reaction was obtained for a $2H_2$–N_2 mixture.

From these considerations an electrochemical equivalence law was proposed for the glow discharge which is comparable to Faraday's laws for electrolytes. This law is expressed as $dP/dt = \propto \mathbf{I}$, where P is the equivalent ammonia pressure, I the current and $\propto$ a constant. This law has more recently been shown to have a universal application to the glow discharge.

The technique employed was such that a fair estimation of relative reactivities of atoms, excited molecules and positive ions could be made. The results showed that no reactivity could be assigned to active states other than positive nitrogen ions under the conditions of these experiments.

The present research was undertaken to test the following points: (1) Can the electrochemical equivalence law be applied to the low voltage type of arc? (2) Can any significance be given to the fact that a maximum rate was obtained for a $2H_2$–N_2 mixture? (3) What is the relative reactivity of the 16.8 volt nitrogen ion as compared to the 24.5 volt ion? (4) Can the presence of various active states other than N_2^+ ions be detected under conditions where the voltage of the exciting electron can be controlled?

The activation of nitrogen and hydrogen by controlled electron impacts has been studied by several investigators. Kunsrnan[3] obtained no reactivity for electron speeds under 17 volts. Storch and Olsen[4] report synthesis to start at about 15 volts. Their voltage–rate curves showed a sudden break near 23 volts and breaks for every four volts' increase thereafter. Caress and Rideal[5] detected a synthesis beginning at 13 volts with breaks at 17, 23, 30 and 34 volts. From this they assigned the reactive states to be H', N_2^+ and Nf, successively, the breaks at 30 and 34 volts being due to combinations of the lower voltages. Recently

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[1] Brewer and Westhaver, J. Phys. Chem., 33, 883 (1929).

[2] Brewer and Westhaver, *ibid.*, 34, 153 (1030).

[3] C. H. Kunsman, *Phys. Rev.*, 31, 301 (1925).

[4] Storch and Olsen, THIS JOURNAL, 45, 1605 (1923).

[5] Caress and Rideal, *Proc. Roy. Soc.* (London), 115, 684 (1927).

Brett[6] has obtained voltage rate curves which he interprets as indicating breaks at 17, 18.5, 20.5, 24.5 and 27 volts, that correspond to the production of N_2^+, $H + H^+$, $N_2^{+\prime}$, $N + N^+$ and $N' + N^+$, respectively. He observed reactivity in the absence of an applied field. From these observations he assumes the mechanism of synthesis to be the interaction of atomic hydrogen with one or the other of the active states cited.

Apparatus and Method of Procedure

The tube and electrical hook-up used are illustrated in Fig. 1. The capacity of the tube was 300 cc, while that of the McLeod gage and leads was 175 cc. Both two- and three-electrode tubes were tried. The presence of a grid may be a help in the case of simple electron excitation; however, it only introduced complications in the presence of an arc. The results presented in this paper were taken with the two-electrode arc.

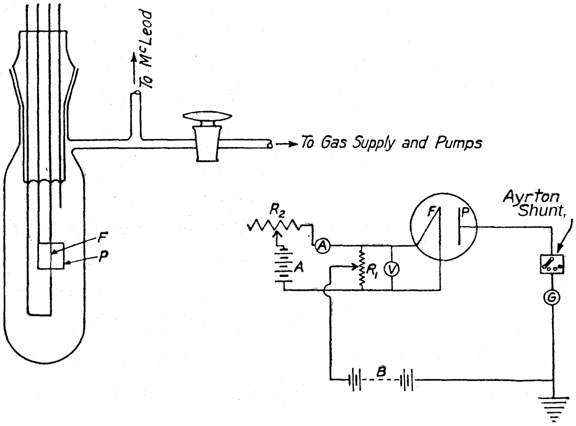

Fig. 1.—Tube with electrical connections.

Several types of filaments were tried, including tungsten, thoriated tungsten and barium and strontium coated platinum. The latter type obtained from the Bell Telephone Laboratories proved the most satisfactory. Most of the filaments were from 1 to 2 cm. in length, although longer filaments were used on occasions. The drop of potential along the filament was usually less than 0.5 volt. All filaments were thoroughly reduced in hydrogen before the experiments were started. The life of a filament was often as long as seventy-five runs with an average length of forty minutes each.

The $3H_2$–N_2 mixture was purified by passing over heated copper and glowing tungsten and through liquid air. Helium was purified by charcoal at liquid air temperature. Spectroscopically pure neon was used directly. The argon was purified by standing in contact with heated calcium for hours.

The method of procedure was essentially the same as that described for the glow discharge. The system was filled to the desired pressure with the gas mixture to be studied. The tube was then immersed in liquid air and an arc was struck between F and **P.** The pressure was thereafter read at regular intervals, usually five minutes; the decrease in pressure with respect to time was taken as the rate of ammonia synthesis. During each run both the current and liquid air level were maintained constant.

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[6] Brett, *Proc. Roy. Soc.* (London). 129, 319 (1930).

Results

The Effect of Pressure.—The influence of pressure on the rate of synthesis for a $3H_2$–N_2 mixture is illustrated by line 1 of Fig. 2. The line is identical to similar time–pressure curves obtained in the glow discharge in that the rate is independent of the pressure over a wide range. The rapid dropping of the rate to zero at some minimum pressure characteristic of the discharge tube is common also to both types of arcs. It will be noted that the rate remains constant to 0.04 mm. pressure while no synthesis could ever be detected under 0.02 mm. with a plate diameter of 1 cm. or less.

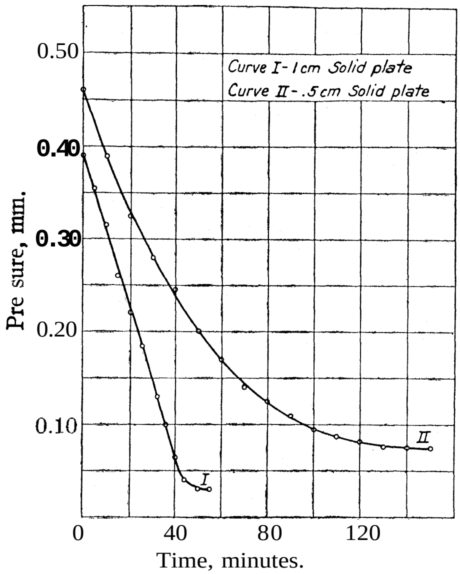

Fig. 2.

The Effect of Current.—The relationship between current and rate is illustrated in Fig. **3.** The low voltage arc is again similar to the glow discharge in that the rate of synthesis is proportional to the current flowing through the arc. The electrochemical equivalence law, $dP/dt = \propto I$, has, therefore, a general applicability to both types of discharges.

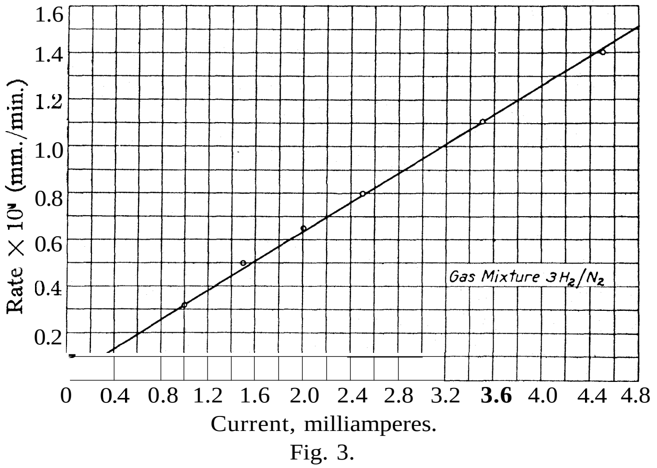

Fig. 3.

The Effect of Voltage.—The effect of varying the applied voltage between the filament and plate on the rate of clean-up is shown in Fig. 4.

The voltages given are not corrected for contact p. d. A direct measurement of the contact p. d. by voltage just necessary to stop electron emission showed the filament to be between 1.5 and 2.0 volts electronegative to the plate depending upon the conditions of the experiment. To obtain the correct voltages, therefore, the values given should be shifted about 1.5 volts to the right or raised by this amount.

These results were obtained with a filament which had been thoroughly reduced and on which over twenty runs had been made before any of the points given were taken. The general contour of curves obtained with new filaments is similar to that illustrated except that the total emissivity changes from time-to-time, tending to give breaks in the curve which in reality are due entirely to variations in the emissivity of the filament. These changes in emissivity are absent in a well worked-in filament.

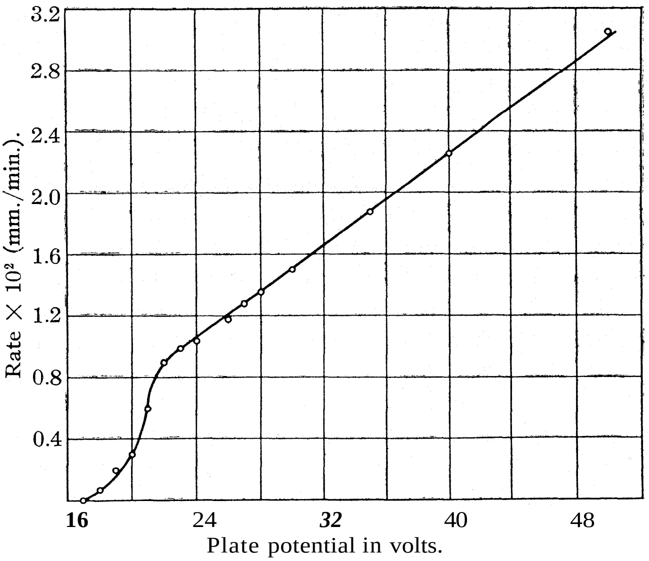

Fig. 4.

It will be seen from the curve that the reactivity at 17 volts is very small, no synthesis being detected at appreciably lower voltages. The rate increases rapidly with potentials between 17 and 23 volts, but thereafter the rate of change is linear over the range investigated.

In some instances a clean-up was detected under 17 volts, but the product frozen out on the walls invariably showed the vapor pressure of water. The clean-up could always be traced to an improperly reduced filament or to oxygen in the $3H_2$–N_2 mixture.

The Effect of the Filament.—The reactivity of a given filament appears to be affected both by its age and its length. Filaments 1 cm. in length gave a faster rate than did those 2 cm. in length, while 8-cm. filaments were even slower. The length of the region over which the arc played was not materially changed by lengthening the filament. It seems possible that the slower rates observed with the longer filaments are due to decomposition of the positive ion clusters on the heated filament. The enhanced rates obtained with old filaments are probably due to the changes in the potential gradient around the filament since it becomes smooth and thin with use; all visible oxide drops off after about fifteen runs and the base metal appears thin and bright.

The Effect of the Plate.—Various types and dimensions of plates were tried. Curve I of Fig. 2 was taken with a solid cylindrical nickel plate 1 cm. in length and 1 cm. in diameter, while curve II was taken with a similar plate except the diameter was 0.5 cm. Tests with several diameters showed that at high pressures the rate was approximately the same irrespective of the diameter. At low pressures, however, the rate decreased with the diameter, while the minimum pressure to which the synthesis could be carried was raised.

An increase in the length of the plate beyond the length of the filament had no appreciable effect on the rate, *i. e.*, Curve I of Fig. 2 would be the same whether the plate was 1 or 2 cm. in length. An increase in length of both the filament and plate apparently decreased the rate, for the reasons stated under the effect of the filament.

Both solid, screen and spiral wire plates were tried. The results were the same at the higher pressures irrespective of the type of plate. At the lower pressures, however, the rate was much more constant for the open plate, *i.* e., an open spiral plate of the dimensions used for Curve II of Fig. 2 gave a line quite similar to curve I. At the high pressures the arc for the spiral wire plates was entirely between the plate and the filament, while at the lower pressure it spread for an appreciable distance through and beyond the plate.

The Ratio of Hydrogen to Nitrogen.—The effect of varying the gas mixture on the rate of synthesis is illustrated in Fig. 5. These results were taken with comparatively new filaments to which the coating still adhered. For this reason the rates are somewhat lower than those given for the old filament in Fig. 4.

It will be seen that the maximum rate occurs in **a** mixture containing 83% nitrogen and 17% hydrogen for both the 19 and 30 volt arcs. In the case of the glow discharge the maximum rate was obtained with a mixture containing 33% nitrogen. The two arcs are similar, in that the rate in both cases is speeded up by excess nitrogen, although the acceleration is much more pronounced in the case of the low voltage arc.

Effect of Inert Gases.—The results obtained when helium, neon and argon are added to a $3H_2–N_2$ mixture are illustrated in Fig. 6. The rates in each case were measured at 0.3 mm. pressure, hence this point is taken as 100% added gas.

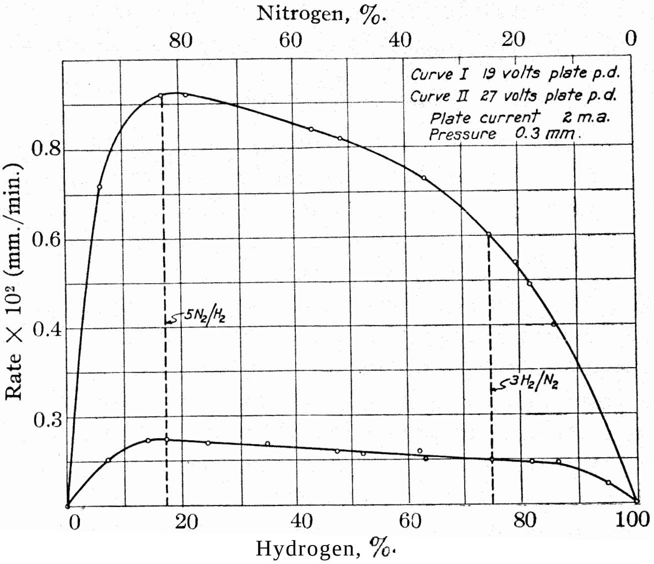

Fig. 5.

The helium and neon results could be duplicated without trouble, while argon, on the other hand, had a peculiar effect on the filament. After a run had been made with argon present, the rate for a pure $3H_2$–N_2 mixture

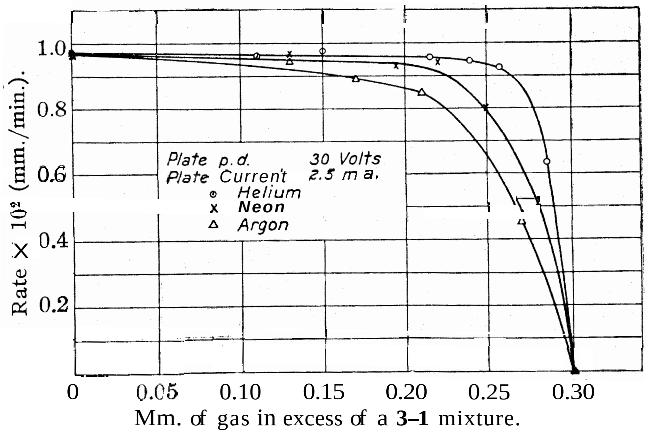

Fig. 6.

might be as much as twice that usually obtained; it returned to normal in the course of two or three runs in the absence of argon. For this reason the argon curve probably does not represent constant arc conditions.

The curve for helium is very similar to that obtained in the glow discharge, in that it shows no appreciable effect on the rate until the amount present is more than 80%. Argon in the glow discharge, however, slowed down the rate of reaction almost in proportion to the amount present.

Discussion of Results

The results just given are strikingly similar in nature to those presented previously for the glow discharge, in that the rate of synthesis (1) is proportional to the current flowing through the discharge, (2) is independent of the gas pressure over a wide range; and **(3)** is accelerated by excess nitrogen and retarded by excess hydrogen.

The similarities just mentioned necessitate the assignment of the same reaction mechanism to the two types of arcs. The fact that the electrochemical equivalence law ($dP/dt = \propto I$) holds for the low voltage arc is definite proof that the reaction is initiated by ions formed in the discharge, since the rate of production of atoms and excited molecules is neither proportional to the current nor independent of the pressure.[7]

Recent experiments in the glow discharge[8] have furnished direct proof that the oxidations of hydrogen, methane and carbon monoxide take place around positive ions formed in the discharge. Since the present reaction is similar in every respect, the mechanisms of reaction are evidently identical.

A comparison of line 1, Fig. 2, with similar lines for the glow discharge[2] shows that the synthesis may be carried to a much lower pressure in the low voltage arc, *i. e.*, 0.02 mm. for the arc as contrasted with 0.1 for the glow. This difference results from the fact that the life of an N_2^+ ion is much longer in the low voltage arc due to the absence of high fields driving ions to the electrodes and to the walls. The N_2^+ ion, therefore, is capable of making many more collisions with hydrogen molecules at a given pressure before becoming neutralized.

The acceleration in the rate of synthesis by the addition of excess nitrogen to the combining mixture, as shown in Fig. 5, is even more pronounced in the low voltage arc than in the glow discharge. This is again evidence in favor of the contention that the reaction is initiated primarily by N_2^+ ions and that H_2^+ ions are comparatively inert. The reason for the more pronounced effect of excess nitrogen in the present case lies in the fact, just pointed out, that the longer life of the N_2^+ ion enables the necessary collisions with hydrogen molecules to be made even when the partial pressure is very low.

The relationship between voltage and rate, as shown in Fig. 4, is a still

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[7] Lowe, *Trans. Roy. Soc. Canada,* 20, 271 (1926); *Hughes* and *Skellett, Phys. Rev.,* 30, 11 (1927); *Crew* and *Hulbert, ibid.,* 29, 843 (1927); 30, 124 (1927).

[8] *Brewer* and Kueck, *J. Phys. Chem.,* 35, *1281* (1931); 35, 1294 (1931).

further proof that the reaction is initiated by N_2^+ ions, since no reactivity was detected under the ionization potential of nitrogen.

The present voltage–rate curves are in agreement with the results obtained by Kunsman[3] for electron bombardment in that no reactivity was detected under the ionization potential of nitrogen. Wansbrough-Jones[9] also obtained very similar results for the oxidation of nitrogen in the low voltage arc. The interpretation given his results is in complete agreement with that presented for the synthesis of nitrogen dioxide in the glow discharge.[10]

The results reported by Brett, however, are materially different from those presented in Fig. 4, not only in the presence of breaks but also in that he observed a clean-up even at zero voltage. The technique used in the two cases was not the same, which may account for the discrepancies. Brett made runs of but four minutes' duration; we were never able to obtain a temperature equilibrium under five minutes. His observed clean-up under 17 volts may have been due to temperature changes, or to an improperly reduced filament, or to oxygen in the $3H_2$–N_2 mixture. In regard to the breaks observed by Brett we have found that a given filament which has not had long use will be subject to changes even greater than those given. Further, no mention is made of the correction for contact potential, which is between −1.5 and −2.0 volts under the conditions of his experiments. Brett assumed breaks at 24.5 volts although his .curves show near breaks only at 23.5 and 26.5 volts. The break at 23.5 volts is doubtless the one due to the second ionization potential of nitrogen; the other breaks, therefore, must be shifted by a similar amount. In this event the assigning of active states to the possible breaks and the attributing of chemical reactivity to these states is highly speculative.

Calculation **of** M/N Ratio,--The computation of the number of ions formed per electron of current involves uncertainties as to the percentage of the current carried by positive ions, as to the number of positive ions formed per electron, and as to the distribution of ions between the nitrogen and hydrogen. Neglecting the positive ion current, which probably does not introduce an error of more than a factor of two, the total number of positive ions formed per electron of current can be estimated from the data of Langmuir and Jones.[11] The distribution of ions between the two gases can be calculated from the probability of ionization per collision as given by Compton and Van Voorhis[12] and the collision frequency as given by Hughes and Klein.[13]

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[9] Wansbrough-Jones, *Proc. Roy. Soc.* (London), 127, 511 (1930).

[10] Westhaver and Brewer, *J. Phys. Chem.*, 34,554 (1930).

[11] Langmuir and Jones, Phys. *Rev.*, 31,357 (1925).

[12] Compton and Van Voorhis, *ibid.*, 27, 724 (1926).

[13] Hughes and Klein, *ibid.*, 23,450 (1924).

The collision frequencies in nitrogen and hydrogen are of the ratio of 1.92 to 1.00; in a $3H_2$–N_2 mixture, therefore, an electron will make 1.56 collisions in hydrogen for every collision in nitrogen. A total of 1.5 ions for a 100 volt electron in a $3H_2$–N_2 mixture was taken as a standard from which the total number and distribution of ions was calculated from the probabilities of ionization for the various accelerating voltages. The results as computed from Fig. 4 are tabulated in Table I. $M/\text{min.}$ represents molecules per minute, M/e, molecules per electron, N_2^+/e, positive nitrogen ion per electron, and M/N_2^+ molecules of ammonia per nitrogen ion.

TABLE I

COMPUTED RESULTS

Volts	$M/\text{min.}$[a]	M/e	N_2^+/e	M/N_2^+
18	0.1366	0.0145	0.01127	1.288
20	0.5766	.0612	.0487	1.256
22	1.730	.1835	.0816	2.25
30	2.885	.306	.1945	1.57
40	4.350	.462	.345	1.34
50	5.770	.613	.487	1.258

[a] $\times 10^{-17}$.

It will be seen from the table that the M/N ratio rises rapidly to a maximum near the second ionization potential of nitrogen and thereafter decreases slowly with increasing voltage. Below 20 volts the ratio is practically constant.

The increase in rate between 18 and 20 volts is evidently due to an increase in production of N_2^+ ions. The decrease in the M/N_2^+ ratio above the second ionization potential of nitrogen is interesting in that it shows the effect of dissociation of N_2^+ ions on the rate of synthesis. A 24.5 volt N_2^+ ion while showing only a very slight dissociation on the primary impact dissociates into $N + N^+$ upon collision with neutral molecules. Since the N^+ ion is capable of forming but one ammonia molecule while an N_2^+ ion can form two, the decrease in rate is to be expected. This is further evidence for the relative inactivity of neutral atoms.

The value $M/N_2^+ = 2.25$ at 22 volts is evidently high since it is difficult to see how the ratio could exceed two on the basis of any mechanism that can be postulated. The error may be a general one arising from the manner of calculating N, or it may result from an added source of N_2^+ ions found above 18 volts, for instance, the ionization of nitrogen by collision of neutral molecules with the 18.2 volt hydrogen ion.

The Mechanism of Reaction.—The data presented in this paper, as well as correlative data obtained with the glow discharge, show clearly that the reaction mechanism may be divided into two parts: I, the formation of a positive nitrogen ion, and II, the interaction of the ion with neutral hydrogen molecules to form ammonia.

The evidence is definite regarding part I. It indicates that the reactivities of N_2^+ and N^+ are very great as compared to any other possible active state that might be present.

The process by which the ammonia molecule is built up around the positive ion is only indirectly indicated by the data in hand.

The results, on the whole, are entirely in line with the demands of a cluster mechanism, wherein hydrogen molecules are attached to the nitrogen ion. There is no indication of any intermediate compound formation. It seems probable from the *M/N* ratios obtained, that two molecules of ammonia are formed in the cluster about an N_2^+ ion, and one molecule about the N^+ ion cluster. This may be expressed by the equation for the N_2^+ ion

$$N_2^+ + 3H_2 = (N_2H_6)^+ \quad (1)$$

$$(NH)^+ + e = 2NH_3 \text{ (wall or gas phase)} \quad (2)$$

for the N^+ ion

$$N^+ + 2H_2 = (NH_4)^+ \quad (1)$$

$$(NH_4)^+ + e = NH_3 + H \quad (2)$$

It cannot be said that the above mechanism is the only one by which ammonia is formed in the arc. The results show definitely, however, that in the arc where atoms, excited molecules, metastables, and ions of both reactants are present, the reactivity around the nitrogen ions is so rapid that any possible reactivity of the other active states appears negligible in comparison. It is a matter of conjecture whether a mechanism of this type can be carried over to other conditions, such as the interaction of nitrogen and hydrogen on an iron catalyst. However, the possibility exists that the same work may be done by the surface forces in catalysis as is done by the electron in the arc.

The writers are indebted to Dr. C. H. Kunsman for the constructive interest he has taken in this research.

Summary

1. The synthesis of ammonia in the low voltage arc is shown to obey the electrochemical equivalence law, $dP/dt = \propto \mathbf{I}$, derived for the glow discharge, *i. e.*, the rate of ammonia formation is independent of the pressure between wide limits, and is proportional to the current flowing through the arc.

2. Synthesis does not take place for arc voltages under the ionization potential of nitrogen. Between 17 and 23 volts the rate increases rapidly with the voltage, while above 23 volts the increase is nearly linear.

3. A maximum rate of synthesis occurs in a mixture containing **83%** nitrogen. The addition of hydrogen to a $3H_2$–N_2 mixture decreases the rate almost in proportion to the amount of hydrogen added.

4. The effect of various inert gases is discussed.

5. The results are interpreted as indicating that the reaction takes place around N_2^+ and N^+ ions. H_2^+ ions, neutral atoms, and excited molecules are relatively inactive.

6. **A** method of calculating the rate of ion formation, as well as the distribution of ions between the nitrogen and hydrogen, is presented.

7. A ratio of $M/N_2^+ \sim 2$ is obtained below 23 volts (24.5 volts when corrected for contact p. d.). A ratio for $M/N^+ \sim 1$ seems the most probable for the monatomic ion.

8. It is suggested that the reaction goes to completion in a cluster of hydrogen molecules around the nitrogen ions.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 264]

VAPOR PRESSURES AND LATENT HEATS FOR THE SYSTEM: $BaCl_2 \cdot 8NH_3$–$BaCl_2$–NH_3

BY LOUIS J. GILLESPIE AND ELI LURIE

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Introduction

In the experimental study of the thermodynamic properties of ammonia in gaseous solutions of ammonia and nitrogen[1] the substances $BaCl_2 \cdot 8NH_3$ and $BaCl_2$ were chosen as the materials to be used to avoid the necessity of a semipermeable membrane, because the high ammonia content of the octammine, the high decomposition pressures at temperatures below 50°, as well as the formation by barium chloride of only one ammine, are very desirable properties from an experimental standpoint.

Hüttig and Martin[2] had studied the 0° isotherm of barium chloride and ammonia, and had shown that barium chloride forms only one ammine, the octammine. They also determined the decomposition pressures of the octammine in the temperature range between 0 and —15.5°.

The large deviations of ammonia from the ideal gas law make the equilibrium an interesting one to study, and we have determined the pressures of ammonia in equilibrium with barium chloride and its octammine from 0 to 50°. One of us has recently discussed equations for representing, as a function of the temperature, the decomposition pressure of solid compounds capable of evolving a gas that deviates from the ideal gas law;[3] we have applied to our data the new equations for the pressures and the latent heats.

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[1] Lurie and Gillespie, THIS JOURNAL, 49, 1146 (1927).

[2] Hüttig and Martin *Z. anorg. Chem.*, **125**, 269 (1922).

[3] **Gillespie,** ***Proc. Am. Amd. Arts Sci*****,** ***66 (No.***3), 153 (1930).

Preparation of Materials.—Liquid ammonia was treated with metallic sodium in a steel vessel. After it had been standing for several months, during which time gas was occasionally drawn off, ammonia was withdrawn and was fractionally distilled three times. After each distillation the ammonia was frozen by means of liquid air and any permanent gas removed by evacuation with a mercury diffusion pump backed with an oil pump. The middle fraction from the distillation was stored in a steel bomb as liquid ammonia.

"C. P." barium chloride was recrystallized from distilled water three times and dried at 110°.

Experimental Procedure and Measurements.—For the determination of the decomposition pressures above three atmospheres an all-steel apparatus was used. About one gram of dry barium chloride was placed in the steel reaction bomb and the entire system was evacuated. The reaction bomb was then connected through the proper steel stopcocks with a liquid ammonia reservoir and the ammine was prepared by causing ammonia to distil over into the reaction bomb. Before measuring the pressure, some ammonia gas was removed from the reaction bomb--enough to insure the presence of barium chloride as one of the phases. The pressures were measured by a piston gage and the temperatures by a platinum resistance thermometer.

The measurements at the lower temperatures and pressures were made using an all-glass apparatus and a mercury manometer. A thermostat of rather large dimensions was necessary in order to keep the temperature constant day and night.

In all cases the temperatures were constant to 0.02°.

The data were taken in three groups, the octammine being prepared separately (though from the same stock of barium chloride) in the three reaction vessels used at 0°, from 7.48 to 19.92°, and from 38.28 to 49.95'. The decomposition pressures are given in Table I in atmospheres, together with those (listed as "calcd. A") calculated by means of the simple equation

$$\text{Log}\, p = -1998.04/T + 7.13333 \qquad (1)$$

where p is the pressure in atmospheres, T is the absolute temperature (t + 273.13), and the logarithm is to the base ten. The percentage deviation is the observed minus calculated, divided by the observed, and multiplied by 100. The average percentage deviation without respect to sign is 0.21%.

In Table II are the decomposition pressures in millimeters of mercury obtained by Hiittig and Martin compared with the results from the same equation. Although the agreement at 0° is good, the divergence at lower temperatures is large, though irregular.

The Smoothing of the Pressures and the Calculation of the Heats.—As is well known, the linear relation between log @ and $1/T$ shown in equation (1) can be justified theoretically if we assume that the gas is an ideal gas, that the change of heat capacity attending the reaction is zero, and that the volume of the solids can be neglected. Gibbs[4] and others have given an equation for the case that the gas is ideal, and the change of heat capacity is not zero (though constant), and the volume of the solids is not zero (though constant). This equation is

$$\log p = A - B \log T - C/T \qquad (2)$$

In the present case the gas is ammonia, which deviates greatly from the ideal gas law, and the pressure rises above eight atmospheres. In such a case the deviation from the ideal gas law should probably be taken into account in the smoothing of the pressures, and is certainly important in the calculation of the heat absorbed in the decomposition of the ammine.

When the ideal gas law is used to calculate the molal volume of ammonia at the temperature and the corresponding vapor pressure of the ammine system, the errors are about 0.9, 2.7 and 7.6% at 0, 25 and 50°, respectively. In the calculation of the latent heat from the Clapeyron equation the error introduced by the use of the ideal gas law for computing the change of volume will be nearly as large. In the use of an equation which assumes the ideal gas law for smoothing the pressures and thus obtaining dp/dT there will be an error, which may be significant even when the linear equation (1) happens to appear satisfactory for the calculation of the pressures.[5]

These considerations apply with more force to the present data than to probably any previous data. Higher decomposition pressures have previously been measured, but not for a gas deviating so greatly from the ideal gas law as ammonia.

As a result of these considerations one of us has recently given general thermodynamic equations for the vapor pressures and latent heats as functions of the temperature, as well as special equations for the case of solids which can evolve a gas.[3] The approximate equations are

$$\log p = \log p_0 - \frac{M(C_p - \bar{c})}{R}\left[\frac{1}{M}\log\frac{T_0}{T} + 1 - \frac{T_0}{T}\right] + \frac{M\lambda_0}{R}\left[\frac{1}{T_0} - \frac{1}{T}\right] + M\left[\frac{\bar{v} - B_0}{RT} + \frac{A_0}{R^2T^2} + \frac{c}{RT^4}\right](p - p_0) \qquad (3)$$

$$\lambda = T\lambda_0/T_0 + \frac{T}{M}(C_p - \bar{c})\log\frac{T}{T_0} - \frac{RT}{M}\log\frac{p}{p_0} - Q\left[\frac{A_0}{RT} + \frac{3c}{T^3}\right](p - p_0) \qquad (4)$$

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[4] Gibbs, "Scientific Papers I Thermodynamics," Longmans, Green and Co., New York, 1906 and 1928, footnote beginning on page 152.

[5] This statement would not be true, were we dealing with data of infinite precision. But when the precision of the data is limited and can only be judged by their consistency we can find more than one function, which will represent the body of data with practically the same average precision, though they will not represent any given datum with the same precision and the derivatives of the functions will in general differ at any given point. In such a practical case, we need what help can be obtained from rational equations.

In these equations T_0 is an arbitrary standard temperature, in the present case 0°C., p_0 is the corresponding vapor pressure (obtained from a preliminary smoothing of the data in any convenient manner), and λ_0 is the latent heat at the same temperature and pressure. M is the modulus of logarithms, common logarithms being denoted by log. The constants A_0, B_0 and c are the constants of principal importance in the Beattie–Bridgeman equation of state[6] and have for ammonia the values 2.3930, 0.03415 and 476.87×10^4, respectively, the units being liters per mole, atmospheres and degrees centigrade absolute ($T = t + 273.13$).[7] Q is the conversion factor: 24.2122 cal_{15}/liter-atm.[8] T, p and λ are the variable temperature, vapor pressure, and corresponding value of the latent heat, respectively. C_p is the molal heat capacity of the gas and $\bar{c}$ is the partial molal heat capacity of ammonia in the solids (equal to one-eighth of the excess of the molal heat capacity of the octammine over that of the barium chloride),[3] both at the constant pressure p_0. $\bar{v}$ is the partial volume of ammonia in the solids (equal to one-eighth of the excess of the molal volume of the octammine over that of the barium chloride). When equation (3) is applied to data in the manner previously discussed, λ_0 and $C_p - \bar{c}$ will be found in liter-atmospheres, and may be converted into calories by multiplication by Q. In the use of equation (4) it will be convenient to take the heats and heat capacities in calories, and for R the value 1.9869 cal_{15}, except when R occurs in the denominator of a fraction containing a constant of the equation of state, when it should be taken as 0.08206.[9]

Equations (3) and (4) are based on the following assumptions: (1) the equation of state used for the gas is the Beattie–Bridgeman equation in the volume form;[10] (2) the difference of heat capacities $C_p - \bar{c}$ is constant at the pressure p_0; **(3)** the partial molal volume of ammonia in the solids $\bar{v}$ is constant; and (4) terms involving squares and cubes of the pressures p and p_0, arising from the equation of state but not appearing in equations **(3)** and (4), are negligible. Such terms were found to affect the pressure by not more than 0.03% in any instance and to have a negligible effect on the latent heats.

Equation (3) looks more complicated than equation (2), but the difference is largely due to the fact that equation (2) is not in a form suitable for the graphic treatment of data when the coefficient B is unknown.

Equation **(3)** was applied to our data. The quantity $\bar{v}$ was known as

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[6] Beattie and Bridgeman, Proc. *Am. Acad.* ***Arts*** *Sci.*, 63, 229 (1928); THIS JOURNAL, ***50*, 3133 (1928).**

[7] Beattie and Lawrence, THIS JOURNAL, 52, 6 (1930); Beattie and Bridgeman, *Z.* ***Physik,*** **62,** 95 (1930).

[8] "International Critical Tables," 1926, Vol. **I,** p 24.

[9] This exception was unfortunately not mentioned in the previous discussion, page 163 of reference 3.

[10] Bcattie, ***Proc. Nat. Acad. Sci.*, 16,** 14 **(1930).**

21.53 cc./mole at 25°.[11] The quantities λ_0 and $C_p - \bar{c}$ were treated as adjustable constants and were determined by drawing a straight line as explained in reference **3.** The value found for $C_p - \bar{c}$ is –7.050 cal., which corresponds to a value of $\bar{c}$ of about 16 calories per mole of ammonia in the solids. This appears to be a reasonable value, judging by the value $\bar{c} = 11$ calories per mole found for the system $AlCl_3 + AlCl_3{\cdot}6NH_3$, the only value obtainable from data for ammines reported in "International Critical Tables."[12] The value for λ_0 is 9074.0 cal_{15} per mole of ammonia, which may be compared with 9141, the value according to the simple equation (1).

The pressures thus calculated are entered as "calcd. (B)" in Table I. The average percentage deviation is 0.15. This may not seem to be a great improvement over equation (1), but the deviation for every point is less by equation **(3)** than by equation (1), provided that we do not count three cases in which equation (1) is closer by a negligible amount, 0.03% or less. **A** deviation plot shows that equation (1) fails to represent the slope at the higher temperatures, whereas equation **(3)** gives much improvement. Hence the latent heats calculated from equation (3) (by means of equation (4) should be much better than those calculable from equation (1), even if in the latter case an exact value of the volume change is computed for use in the Clapeyron equation.

As regards the data obtained by Hüttig **and** Martin for lower tempera-

TABLE I

OBSERVED DECOMPOSITION PRESSURES IN ATMOSPHERES AND THOSE CALCULATED (A) BY EQUATION 1 AND THOSE CALCULATED (B) BY EQUATION 3. THE PERCENTAGE DEVIATION = 100 (OBS.—CALCD.)/OBS.

t	Obs.	Calcd. (A)	% Dev.	Calcd. (B)	% Dev
0	0.6576	0.6576	0.00	0.6576	0.00
7.48	1.031	1.030	.00	1.031	.00
9.28	1.148	1.144	.35	1.144	.35
11.95	1.337	1.332	.37	1.333	.30
14.95	1.574	1.576	–.13	1.576	–.13
19.92	2.063	2.066	–.15	2.066	–.15
38.28	5.195	5.215	–.38	5.205	–.19
40.40	5.747	5.762	–.26	5.753	–.10
42.10	6.209	6.237	–.45	6.228	–.31
44.00	6.797	6.807	–.15	6.800	–.04
46.00	7.471	7.455	.21	7.453	.24
46.52	7.637	7.632	.07	7.630	.09
46.78	7.726	7.721	.06	7.722	.05
48.07	8.200	8.181	.23	8.187	.16
49.95	8.916	8.891	.28	8.905	.12

The average percentage deviations are (A) 0.21, and (B) 0.15.

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[11] Gillespie and Gerry (unpublished).

[12] "International Critical Tables," 1929, Vol. V, p. 95.

tures, reference to Table II shows that equations (1) and (3) are in practical agreement at these temperatures. The distribution of the percentage deviations is such as to suggest that the fault lies in the experimental values. At lower temperatures it appears more difficult to obtain equilibrium. This interpretation is suggested also by the deviation plots of our own data.

TABLE II

OBSERVED DECOMPOSITION PRESSURES IN MILLIMETERS OF MERCURY AT LOWER TEMPERATURES (HÜTTIG AND MARTIN) AND THOSE CALCULATED (A) BY EQUATION 1, AND THOSE CALCULATED (B) BY EQUATION 3. EQUATIONS 1 AND 3 GIVE 499.8 MM. AT 0°

t	Obs.	Calcd. (A)	% Dev.	Calcd. (B)	% Dev.
0	500	500	0	500	0
–10.8	287	250	13	249	13
–15.0	193	188	3	187	3
–15.5	189	181	4	180	5

In Table III are given values of the decomposition pressures and the latent heats for every ten degrees from 0 to 50° centigrade, as well as for 25°, as calculated from equations (3) and (4). The calculations of the heats were checked by the method already outlined.[3]

TABLE III

DECOMPOSITION PRESSURES IN ATMOSPHERES AND LATENT HEATS IN 15° CALORIES, CALCULATED FROM THE DATA BY MEANS OR EQUATIONS 3 AND 4

t..............	0	10	20	25	30	40	50
Pressure........	0.658	1.193	2.074	2.696	3.476	5.646	8 925
Heat............	9074	8990	8901	8853	8804	8696	8575

Summary

The decomposition pressures of the system $BaCl_2{\cdot}8NH_3$–$BaCl_2$–NH_3, were measured from 0 to 50° with an average precision of about 0.2%. The results were interpreted by means of a vapor pressure equation previously derived,[3] which can be regarded as the equation $\log p = A - B \log T - C/T$ with added terms for the deviation of ammonia gas from the ideal gas law.

Interpolated values for the pressure and calculated values of the corresponding latent heat of decomposition are given in Table III.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE COBB MEMORIAL LABORATORY. UNIVERSITY OF VIRGINIA, No. 77]

THE KINETICS OF GAS REACTIONS AT CONSTANT PRESSURE

BY ARTHUR F. BENTON

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The classical equations of reaction kinetics, relating the velocity of reaction to the concentrations of the reacting substances, were originally developed to describe the behavior of reactions occurring in liquid systems. In such systems the volume remains approximately constant. In the hands of van't Hoff, Bodenstein and others, the same equations were found to be applicable to gaseous reactions occurring at constant volume. In this period the kinetics of gas reactions were almost invariably studied by the so-called "static" method, in which the volume is maintained constant, and the progress of reaction is followed by noting the change in pressure.

In recent years there has been an increasing tendency to employ the flow method, which consists in streaming the gases through the reaction space, and determining the extent of reaction by analysis of the exit gases. This method differs essentially from the static method in that the reaction takes place at constant pressure. Nevertheless, it has been a common practice to apply to results obtained by this method the kinetic equations which hold for reactions at constant volume.

It is the object of the present paper to point out that kinetic equations for reactions at constant volume are not necessarily applicable to reactions at constant pressure, and to indicate how the latter are to be correctly treated.

Homogeneous, Unimolecular Gas Reactions.—Reactions of the first order are defined in two different ways, either (1) as those in which a constant fraction of the material reacts in unit time, or (2) as those in which the rate of change of concentration is proportional to the concentration of reacting substance. Accordingly, if n_A, n_B denote the number of moles of substances A and B, respectively, present in volume V, and c_A, c_B their respective concentrations, the rate of the reaction, $A \longrightarrow \nu B$, could be expressed in either of the following ways

$$-\frac{dn_A}{dt} = k_1 n_A \qquad (1)$$

$$-\frac{dc_A}{dt} = k_2 c_A = k_2 n_A/V \qquad (2)$$

If the reaction is carried out at constant volume, $dc_A(=d(n_A/V)) = (1/V)dn_A$, and the two expressions are equivalent. For reactions conducted at constant pressure, however, the volume does not remain constant (except in the special case where $\nu = 1$). Under this condition, therefore, Equations 1 and 2 are not equivalent. The difference between them can best be seen in their integrated forms

$$k_1t = \ln n'_A/n_A \qquad (1a)$$

$$k_2t = \ln c'_A/c_A = \ln \frac{n'_A}{n_A}\cdot\frac{V}{V'} \qquad (2a)$$

where the primes represent the conditions at zero time. If the gas consists of pure A at the start, V/V' varies from unity at $t = 0$, to ν at $t = \infty$. From this it can readily be shown that $k_2 = \nu k_1$ at $t = 0$, while at $t = \infty$, $k_2 = k_1$. Hence if either k_1 or k_2 is actually constant, the other will vary by a factor of ν during the course of the reaction.

While it is clear that these equations can not both be correct, they have been employed indiscriminately in the literature. Thus, for example, of three recent papers by different authors dealing with the homogeneous, unimolecular decomposition of hydrocarbons at constant pressure, one employs rate constants calculated by means of Equation 1 and two by means of Equation 2.

The generally accepted theory of homogeneous, unimolecular reactions leaves no doubt that Equation 1 rather than Equation 2 is the correct form. Of the total number of molecules of reactant, n_A, a given fraction are in the necessary activated state, and of this fraction a further fraction suffers reaction in unit time independent of the concentration.[1]

Homogeneous, Unimolecular Reactions in Flow Systems.—There are two methods by which reactions may be carried out at constant pressure, (1) the "flow" method, and (2) a method involving a closed system of variable volume. Equation 1a, obtained by direct integration of Equation 1, is obviously in suitable form for application to Method 2. On the other hand, its utility in the flow method is limited by the fact that the "time of contact" is not a directly measurable quantity. If the rate of flow of the entering gases is maintained constant, the time of contact t depends on the extent to which the volume changes during the progress of the reaction.

Let the volume of the reaction space be V_b, and let V' represent the volume of gas, at the temperature and pressure of the reaction space, entering per unit time. If there were no change in volume due to the reaction, the time of contact would be simply V_b/V'. However, in the reaction $A \longrightarrow \nu B$, the volume changes from $V' = (RT/P)n'_A$ to $V = (RT/P)(n_A + n_B) = (RT/P)(\nu n'_A - [\nu - 1]n_A) = V'(\nu - [\nu - 1]n_A/n'_A)$, where n'_A is the number of moles of A entering the reaction space per second, and n_A is the number passing any given point per second. If, under these conditions, we treat V_b as a variable, we may write

$$\frac{dV_b}{dt} = V = V'(\nu - [\nu - 1]n_A/n'_A)$$

Substitution of dt from this equation in Equation 1 gives

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[1] Equation 1 probably applies strictly only to an ideal gas. In real gases it would seem that the fraction of the molecules in an activated state cannot be independent of the concentration, and it is further possible that the fraction of the activated molecules which decompose in unit time may also depend to some extent on concentration.

$$-V'\left(\nu - [\nu - 1]\frac{n_A}{n'_A}\right)\mathrm{d}n_A = k_1 n_A \mathrm{d}V_b$$

On integration,

$$k_1 V_b/V' = \nu \ln \frac{n'_A}{n_A} - (\nu - 1)\left(1 - \frac{n_A}{n'_A}\right)$$

where V_b is the volume of the whole reaction space, out of which n_A moles of *A* issues per second. If F represents the fraction of A which reacts, then

$$k_1 V_b/V' = \nu \ln \frac{1}{1 - F} - (\nu - 1)F \qquad (3)$$

In treating reactions in flow systems it has been the common practice hitherto to calculate the time of contact as the ratio of the volume of the reaction space to the average of the entering and exit rates of flow.[2] While this procedure gives a fair approximation when the fractional conversion is not too great, the simplicity and exactness of Equation 3 would seem to make approximations needless.

First Order, Catalyzed Reactions.—When we turn to first order gas reactions which are catalyzed by a solid surface, we find that when the volume varies neither Equation 1 nor Equation *2* is correct. This fact will be apparent from the following derivation.

We may assume that the reaction is of the first order either because (1) the velocity is determined by the rate of collision of (activated) molecules of reactant with the surface, or because (2) a small portion of the surface is occupied by adsorbed molecules, a given fraction of which are transformed in unit time. In Case (1) the rate of reaction, that is, the number of moles of reactant disappearing in unit time, is a given fraction of the number colliding with the surface, and this in turn is equal to $(v/4)Sc_A$, where S is the surface area, v is the average velocity of the molecules, and c_A is their concentration. Thus, at a given temperature

$$-\frac{\mathrm{d}n_A}{\mathrm{d}t} = k_3 \cdot \frac{v}{4} Sc_A = kSn_A/V \qquad (4)$$

It may be noted that this equation is dimensionally correct, since k_3 is dimensionless and both sides reduce to number per unit time.

In Case (2) the rate is proportional to the amount of gas adsorbed, and the latter is also determined by S and the concentration in the gas phase. Thus for small adsorption the result is the same as for Case (1). The principle is, of course, the same whether the adsorption is small or large, but in the latter event the order of reaction will differ from the first, and we should have to write

$$-\frac{\mathrm{d}n_A}{\mathrm{d}t} = k'S\frac{c_A}{1 + ac_A}$$

where a is the constant of the Langmuir adsorption equation.

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[2] Pease [THIS JOURNAL, 51, 3470 (1929)] has, however, already elaborated the proper treatment of time of contact, and has applied it to the bimolecular polymerization of acetylene.

To integrate Equation 4 it is necessary to express V as a function of n_A. Let us assume that the reaction is $A \longrightarrow \nu B$, and that the gas entering the reaction space per second occupies the volume V', and is composed of n'_A moles of A and no B. Then, as before, $V = V'(\nu - [\nu - 1]n_A/n'_A)$ and $dt = (I/V)dV_b$, where V_b now represents the free space in the reaction tube not occupied by the catalyst. With these values of dt and V substituted in Equation 4, integration gives

$$\frac{kSV_b}{V'^2} = \nu^2 \ln \frac{n'_A}{n_A} - 2\nu(\nu - 1)\left(1 - \frac{n_A}{n'_A}\right) + \frac{(\nu - 1)^2}{2}\left(1 - \frac{n^2_A}{n'^2_A}\right)$$

Because of the somewhat complex nature of this exact expression, it is often preferable in practice to substitute an approximate equation previously suggested,[3] which may be written in the form

$$-\frac{\Delta n_A}{\Delta t} = kS\bar{c}_A$$

where $\bar{c}_A$ is the average concentration of A in the entering and exit gases, and At is V_b divided by the average rate of flow. This equation necessarily fails at high percentage conversions, but ordinarily involves only a negligible error for conversions up to at least 50%.

Bimolecular Reactions.—The treatment of homogeneous, bimolecular gas reactions at constant pressure is complicated to some extent because of the fact that the rate of collision in a gas whose volume is changing does not appear to have been studied, The correct form of velocity equation may readily be obtained, however, by considering a homogeneous, reversible reaction which is unimolecular in one direction and bimolecular in the other. Thus, in the reaction $A \rightleftarrows 2B$, the rate to the right is

$$-\frac{dn_A}{dt} = k_1 n_A$$

If we assume that the rate to the left is given by the expression

$$\frac{dn_A}{dt} = k_2 V c^2_B \qquad (5)$$

then, at equilibrium where the two rates are equal

$$k_1 n_A = k_2 V c^2_B, \text{ or } c^2_B/c_A = k_1/k_2 = K$$

where K is the equilibrium constant. Since, as may readily be shown, the usual ways of writing the bimolecular velocity equation do not give this necessary result, it may be assumed that Equation 5 is correct.

In the case of a catalyzed, bimolecular reaction, it may be shown by reasoning exactly analogous to that used in the corresponding unimolecular case that Equation 5 has the proper form. The equation can readily be applied by expressing n_A, V and dt in terms of n_B, V_b and the initial conditions, followed by integration. In practice, however, if the percentage conversion is not too great, it will usually be sufficient to employ the approximation

[3] Benton, *Ind. Eng. Chem.*, **19,494 (1927).**

$$\frac{\Delta n_A}{\Delta t} = k_2 \overline{V} \bar{c}_B^2$$

where $\overline{V}$ and $\bar{c}_B$ are the average volume and the average concentration of B, based on the entering and exit gases.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. V. THE POLYMETHYLENE BROMIDES

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These measurements upon compounds containing two dipoles separated by a carbon chain of varying length were undertaken with the object of studying the effect of the carbon chain upon the positions of the dipoles relative to one another and thus of extending our knowledge of the shape and behavior of the chain. The bromide doublets were used as being simple dipoles obtainable in compounds with chains of different length. Subsequent measurements have been made upon the diethyl esters of dicarboxylic acids[1] and upon the glycols,[2] in both of which classes of compounds the dipoles are more complex.

Apparatus

The dielectric constants of the solutions of the substances under investigation have been measured with a capacity bridge, part of which was presented by the Bell Telephone Laboratories. This part consisted of two fixed resistance arms with small adjustable resistances and capacities for balancing small inequalities and shielded in-put and out-put transformers, the whole mounted in a case with the parts carefully shielded. The other two arms of the bridge consisted of two condensers with series resistances as used previously in this Laboratory.3 The source of current was a Western Electric Company variable oscillator, which was operated at a frequency of 50,000 cycles in these measurements. The balance of the bridge was obtained by passing the current through a six-tube amplifier with a detector and a multimeter, adjustable to read microamperes, as null instrument. The condenser in which the liquid was measured consisted of concentric gold-plated cylinders fitting closely into a small glass vessel similar to that used in earlier measurements.[4] The densities of the liquids were determined with a pycnometer of the type previously employed[5] and

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[1] Smyth and Walls, THIS JOURNAL, 53,527 (1931).

[2] Smyth and Walls, *ibid.*, 53,2115 (1931).

[3] Smyth, Morgan and Boyce, *ibid.*, 50, 1536 (1928).

[4] Smyth and Stoops, *ibid.*, 51, 3312 (1929).

[5] Smyth and Morgan, *ibid.*, 50, 1547 (1928).

the temperatures were controlled with a special form of thermostat also used before.[5] The solutions of ethylene bromide were measured at a wave length of 600 meters with a slightly more accurate bridge, which has been previously described,[6] and the measurements on decamethylene bromide were checked at 1000 meters on a heterodyne beat apparatus also previously described.[1,2]

Preparation of Materials

Heptane and benzene were purified as in earlier work.[7]

Ethylene Bromide.—Ethylene bromide from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, sodium carbonate solution and water, and, after drying with calcium chloride, was fractionally distilled. The middle fraction, boiling at 131.0° (756 mm.), was used; n_D^{20} 1 53801; d_4^{20} 2.1760.

Trimethylene Bromide.—Trimethylene bromide from the Eastman Kodak Company was washed with sodium carbonate solution and water and, after drying with calcium chloride, was fractionally distilled under reduced pressure. The middle fraction, boiling constantly at 80.5° (50 mm.), was used; n_D^{20} 1.52319; d_4^{20} 1.9790.

Pentamethylene Bromide.—Pentamethylene bromide was loaned by Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company; b. p. 122–125° (36 mm.); n_D^{20} 1.5126.

Decamethylene Bromide.—Decamethylene bromide, loaned by Dr. Carothers. was distilled under reduced pressure (b. p. 172–174° (12 mm.)) and recrystallized.

Experimental Results

The dielectric constants, ϵ, and the densities, d, are given in Table I together with the polarizations, P_2, of the bromides calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_1} + P_1$$

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 dielectric constants were actually measured at intervals of about 10° and the densities at intervals of about 20°, with the exception of the measurements upon the benzene solutions of ethylene bromide which were made at the stated temperatures. Although the data were graphically interpolated to obtain values at definite 10° intervals, the results are shown, for the most part, at 20° intervals only, in order to save space. The values for the pure solvents, which have been repeatedly determined, are omitted also for the same reason.

The values of P_2 have been plotted against those of c_2 and extrapolated to $c_2 = 0$ to obtain the values of P given in Table II as P_∞. The values of P_∞ when plotted against $1/T$ should give a straight line, 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 $b = 4\pi N\mu^2/9k$, N

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[6] Smyth and Dornte, THIS JOURNAL, 52,3546 (1930).

[7] Smyth and Rogers, *ibid.*, 52, 2227 (1930).

being the Avogadro constant, 6.061×10^{23}, μ, the electric moment, and k, the molecular gas constant, 1.372×10^{-16}. As the temperature range possible in these measurements is not as wide as might be wished for the accurate establishment of the $P_\infty - 1/T$ curves and as b is not constant for some of these substances, P_A is neglected and a set equal to MR_D. b is then obtained approximately as $(P_\infty - MR_D)T$ and the moment is calculated from the relation $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$. At the bottom of the set of data for each substance in Table II, the very approximate values of P_A and of the moments obtained from the $P_\infty - 1/T$ curves are given in parentheses. The measurements of the decamethylene bromide solutions made with a heterodyne beat apparatus at 1000 meters wave length as a check gave values of the moment of 2.73×10^{-18} at 25° and 2.72×10^{-18} at 50° in excellent agreement with those in Table II.

TABLE I

INTERPOLATED VALUES OR DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATION OF POLAR COMPONENTS

	Heptane–Ethylene Bromide			Benzene–Ethylene Bromide		
Mole fr. of $C_2H_4Br_2$ = t, °C.	0.0303	0.0650	0.0913	0.0258	0.0487	0.0490
−40	2.030	2.053				
−30	2.018	2.044	2.066			
−10	1.996	2.023	2.047			
10	1.969	1.996	2.024	2.378	2.428	2.428
30	1.940	1.967	1.997	2.337	2.387	2.393
50	1.906	1.935	1.965	2.290	2.336	2.333
70	1.870	1.901	1.930	2.243	2.286	2.285
90	1.832	1.866	1.892			
				d		
−40	0.7628	0.7962				
−30	.7545	.7874	0.8122			
−10	.7370	.7697	.7944			
10	.7197	.7515	.7761	0.9212	0.9496	0.9503
30	.7019	.7330	.7570	.8991	.9270	.9278
50	.6839	.7145	.7380	.8761	.9044	.9052
70	.6648	.6954	.7073	.8545	.8815	.8822
90	.6445	.6749				
				P_2		
−40	40.5	36.1				
−30	42.3	40.8				
−10	47.2	43.4	43.6			
10	47.8	44.3	45.4	67.7	62.5	62.2
30	50.1	45.7	47.3	68.9	64.1	67.3
50	47.4	45.6	47.5	66.6	62.4	61.3
70	43.3	44.6	47.2	65.8	60.9	60.2
90	37.2	43.1	46.5			

TABLE I (*Continued*)

Heptane–Trimethylene Bromide

Mole fr. of $C_3H_6Br_2$ = t, °C.	0.0325	0.0340	0.0353	0 0363	0.0413	0.0507	0.1471
				ϵ			
–30	2.146	2.148	2.156	2 159	2.180	2.231	2.694
–10	2.109	2.112	2 120	2.122	2.141	2.184	2.603
10	2.071	2.075	2.081	2 084	2.102	2.141	2.518
30	2.033	2.035	2.041	2.045	2.062	2.097	2.437
50	1.994	1 997	1.999	2.006	2.020	2.053	2.360
70	1.955	1.957	1.957	1.965	1.979	2.011	2.285
				d			
–30	0.7561	0.7575	0 7580	0.7604	0.7646	0.7742	0.8806
–10	.7391	,7403	.7410	.7428	.7474	.7564	.8514
10	.7216	.7231	.7241	.7252	.7300	.7385	.8320
30	.7040	.7056	.7067	.7074	.7122	.7288	.8129
50	.6863	.6875	.6887	.6896	.6943	.7026	.7927
70	.6678	.6692	.6692	.6719	.6756	.6839	.7726
				P_2			
–30	133.9	131.6	134.1	131.0	130.5	133.6	120.4
–10	130.4	129.3	131.8	128.9	127.5	128.7	119.3
10	126.8	126.2	127.2	126.1	124.6	125.5	114.9
30	123.8	120.7	122.7	123.2	1218	121.7	110.5
50	117.9	117.0	115.6	118.4	116.0	116.9	106.4
70	111.9	109.0	109.0	110.6	110.8	112.7	101.6

Heptane–Pentamethylene Bromide

Mole fr. of $C_5H_{10}Br_2$ = t, °C.	0.0311	0.0361	0 0492	0.0665
		ϵ		
–40	2.193	2.222	2.294	2.392
–30	2.173	2.203	2 271	2.366
–10	2.135	2.164	2.225	2.314
10	2.097	2.124	2.179	2.261
30	2.058	2.081	2.132	2.208
50	2.018	2.038	2.085	2.154
70	1.974	1.995	2.036	2.097
		d		
–40	0.7642	0.7694	0.7826	0.7996
–30	.7557	.7610	.7741	.7910
–10	.7386	.7436	.7565	.7738
10	.7214	.7264	.7391	.7556
30	.7042	.7091	.7216	.7376
50	.6864	.6912	.7041	.7194
70	.6680	.6730	.6864	.7007
		P_2		
–40	171.5	170.4	166.3	164.2
–30	169.3	169 5	164.5	162.6
–10	166.0	166.9	160.6	158.3
10	161.9	163.4	156.1	154.2
30	158.6	158.0	151.2	150.0
50	152.1	151.9	144.7	144.0
70	144.6	144.2	135.9	136.2

TABLE I (Concluded)

Ileptane–Decamethylene Bromide

Mole fr. of $C_{10}H_{20}Br_2$ = t, °C.	0.0329	0.0355	0.0435	0.0475	0.0574	0.0675
				ϵ		
0	2.164	2.182	2.227	2.251	2.315	2.370
20	2.126	2.139	2.180	2.207	2.264	2.315
40	2.083	2.095	2.134	2.160	2.213	2.258
60	2.039	2.050	2.087	2.113	2.161	2.201
80	1.994	2.003	2.041	2.063	2.106	2.143
				d		
0	0.7342	0.7380	0.7449	0.7488	0.7597	0.7690
20	.7171	.7200	.7279	.7317	.7424	.7515
40	.6996	.7021	.7103	.7141	.7245	.7335
60	.6820	.6843	.6924	.6961	.7065	.7155
80	.6637	.6665	.6744	.6781	.6884	.6977
				P_2		
0	216.9	215.3	212.9	211.8	211.8	207.3
20	213.8	212.1	207.5	209.1	207.4	203.4
40	208.3	206.4	202.1	204.2	202.1	198.0
60	199.3	197.3	194.9	198.4	195.8	191.0
80	192.2	189.2	189.2	191.3	189.0	184.1

TABLE II

VALUES OF P_∞ $(P, - MR,)$ T, AND THE MOMENT

	$C_2H_4Br_2(MR_D = 27.0)$ (in C_7H_{16})			(in C_6H_6)			$C_3H_6Br_2(MR_D = 31.O)$		
T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$P,$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$P,$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
243	43	3890	0.79				140.2	26540	2.07
263	48	5520	0.94				130.2	27670	2.11
283	48	5940	0.98	74.0	13300	1.46	132.0	28580	2.15
303	49	6660	1.04	74.3	14330	1.52	128.7	29600	2.18
323	48	6780	1.05	72.0	14550	1.52	122.8	29650	2.19
343	47	6860	1.05	70.7	14990	1.55	(115.8)	(29090)	(2.17)
				($P_A = 17.5$; $\mu = 1.12 \times 10^{-18}$)			($P_A = 45$; $\mu = 1.56 \times 10^{-18}$)		

	$C_5H_{10}Br_2(MR_D = 40.6)$			$C_{10}H_{20}Br_2(MR_D = 64.6)$		
T, °A.	$P,$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
233	178.8	32200	2.28			
253	174.4	33850	2.34			
273	169.8	35270	2.39	229	44880	2.69
293	156.6	36620	2.43	221	45830	2.73
313	161.6	37870	2.47	214.5	46920	2.75
333	155.0	38100	2.48	206.0	47090	2.76
353				197.0	46740	2.75
	($P_A = 60$; $\mu = 1.60 \times 10^{-18}$)			($P_A = 37$; $\mu = 2.40 \times 10^{-18}$)		

Discussion of Results

The values of P_2 for ethylene bromide in dilute solution in heptane increase with rising temperature, pass through a maximum at about 30°, and then decrease, although, according to the Debye equation, P_2 should be a linear function of $1/T$. Obviously, it is useless to attempt to determine b as the slope of the $P_\infty - 1/T$ curve since b is not a constant. When the moment is calculated as $\mu = 0.0127 \times 10^{-18}\sqrt{(P_\infty - MR_{\text{D}})T}$, it is found to increase with rise of temperature. The measurements of ethylene bromide in benzene solution give much higher values of the polarization, a difference analogous to that found by Meyer in the case of ethylene chloride.[8] The polarizations in benzene solution also show a maximum at 30°, but, as the only values below this temperature were determined not far above the freezing point, where the tendency toward association is greater, great significance cannot be attached to this. The temperature range is here too short for an accurate determination of the moment from temperature variation, but the 30, 50 and 70° values lie on an approximately straight line, which gives $\mu = 1.12 \times 10^{-18}$ and $P_{\text{A}} = 17.5$. It is more satisfactory to use the refraction to obtain the values of the moment given in Table II, where the temperature variation of μ from 30 to 70° is negligible.

The polarizations of the higher bromides in dilute solution do not increase with rising temperature even at the lowest temperatures investigated, but the values of b obtained on the slope of the $P_\infty - 1/T$ lines give surprisingly large values of P_{A} and, consequently, low values of the moment. When the molar refraction is used in the calculation of the moment, the values obtained for trimethylene bromide show a small increase with rising temperature at the low temperatures. Pentamethylene bromide shows a more appreciable increase with temperature and decamethylene bromide a negligible increase. An increase in the moment with rising temperature, while tending to cause a departure from linearity in the $P_\infty - 1/T$ curve, would at the same time reduce the slope of the curve and hence reduce the value of b and increase P_{A}, which, as it is obtained by a long extrapolation, is very dependent upon the slope of the curve. The value of P_{A} for pentamethylene bromide which shows the most marked temperature variation of the moment, is the highest of the three, while that for decamethylene bromide, which shows negligible temperature variation of the moment, is much the lowest. Actually, one would expect the large molecule of decamethylene bromide to have the largest value of P_{A}. It appears probable,[9] therefore, that these apparent values of P_{A} are much too high, although the value for decamethylene bromide is less than double those found for some of the alkyl halides.[10] Considerable doubt must, however, exist as to whether these latter values are not too high.[9] Morgan and Lowry[11] obtained a value of 21.4 for the P_{A} of methyl bromide from the

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[8] Meyer, *Z. physik. Chem.*, [B] **8**, 27 (1930).

[9] Cf. Smyth, THIS JOURNAL, 51, 2051 (1929).

[10] Smyth and Rogers, *ibid.*, 52, 2227 (1930).

[11] Morgan and Lowry, *J. Phys. Chem.*, 34, 2385 (1930).

temperature variation in solution and a value of 2.8 from the polarization of solid methyl bromide. The reason for this discrepancy is not apparent. In view, however, of the uncertainty which exists in regard to the P_A values for these bromides, it seems best to use the values of the moments calculated from $(P_\infty - MR_D)$. They are presumably a little high because of the neglect of P_A, but, for the most part, this cannot materially alter the conclusions to be drawn from them.

In order to interpret the results, it is necessary to know the moment of the dipole at each end of the carbon chain. The moment of methyl bromide reported by Morgan and Lowry[11] is 1.45×10^{-18}, but, in obtaining this value, they used the curve which gave the high value, 21.4, for P_A. As P_A has been neglected in the values of the moments which we are to interpret, it is best to use for our purposes the value of the moment obtained from a calculation in which the almost negligible value of P_A, 2.8, found from the solid, is used. The result of this calculation is 1.7×10^{-18}. Eucken and Meyer[12] have used a value of 1.5×10^{-18} for the moment of the C–Br bond obtained as the moment of bromobenzene and a value of 0.4×10^{-18} for that of the C–H bond calculated from that of toluene. The assumptions underlying the assignment of the values to these bonds are exceedingly doubtful in character, although the empirical method used by Eucken and Meyer is often effective in calculating moments. As the use of these bond moments gives the decidedly high value 1.9×10^{-18} for methyl bromide, it is best to adopt tentatively the value 1.7×10^{-18} as the moment of the dipole at each end of the carbon chain.

Williams[13] has treated the molecule XCH_2CH_2X as containing two dipoles, each of moment m, with their axes in the lines joining the carbon nuclei to the X groups, these lines making an angle with the extension of the line joining the carbon nuclei. The mean effective moment of the molecule is then calculated as $\mu = 1.41\ m \sin \theta$. The values which Williams observed for molecules of this type were all much lower than the calculated, a fact which he attributed to repulsion between the X groups and consequent decrease in θ. Meyer[8] has considered the mutual potential energies of the doublets and obtained a much more complicated expression, which, when the mutual potential energies are small in comparison with the energy of rotation of the dipoles around the C–C line, may be simplified to the equation given by Williams. When the distance between the doublets is small, the mutual potential energy is large, and it is only at very high temperatures, not practically obtainable, that the energy of rotation around the C–C line is sufficient to make the doublets independent of one another. As the mutual potential energy is a minimum when the doublets oppose one another, it is evident that the moment of the

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[12] Eucken and Meyer, *Physik. Z.*, 30, 397 (1929).

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

molecule as a whole will increase as rising temperature gives a rotational energy which tends to overcome this effect of the mutual potential energy.

Meyer has found that the polarization of ethylene chloride in solution in hexane shows a variation with temperature in conformity with the requirements of his equation, deviating from the linearity required by the simple Debye equation. So many approximations and assumptions are necessary in a treatment of this sort that even an exact quantitative agreement between a single set of observed and calculated values is not necessarily convincing, but Meyer has experimentally demonstrated the success of his equation in predicting an increase in the moment of ethylene chloride with rising temperature. The results of the present work show a similar increase in the moment of ethylene bromide with rising temperature.

It is interesting to calculate the moment for the limiting case in which the rotational energy is large in comparison to the mutual potential energy of the doublets, or, expressed in another way, in which all positions in the rotation about the C–C bond are equally probable. Assuming the usual tetrahedral carbon valence angles and taking the moment of each dipole as $m = 1.7 \times 10^{-18}$, we may apply the simple equation of Williams to this limiting case: $\mu = 1.41 \times 1.7 \times 10^{-18} \sin 70° = 2.25 \times 10^{-18}$. The large difference between this value and those observed for ethylene bromide shows how far the actual conditions are from those assumed in the derivation of the equation. The reduction of the moment of each dipole by the inductive effect of the other has been neglected in this calculation. The moment of ethyl bromide has been found to be 1.86×10^{-18}.[5] The rounding off of this figure to 1.9×10^{-18} makes it comparable with the values of the moments in the calculation of which P_A has been neglected. The difference of 0.2×10^{-18} between this value and the moment of methyl bromide may be attributed mainly to the moment induced in the second carbon in the former.[10] This suggests that in ethylene bromide each dipole tends to induce a moment in the second carbon from it opposite to that induced by the other dipole. It would seem reasonable, therefore, to subtract a moment of at least 0.2×10^{-18} from the value 1.7×10^{-18} used for m in the calculation. If m is taken as 1.5×10^{-18}, the result obtained for μ is 2.0×10^{-18}, still much higher than the observed values, which should approach this value with rising temperature.

The temperature variation of the moment of ethylene bromide in benzene solution is small and uncertain and the moment is higher than that found in heptane solution. Meyer observed a similar difference in the case of ethylene chloride, finding a larger moment without temperature variation in the benzene solutions. The reason for this discrepancy probably lies in the effect of the benzene upon the forces between the dipoles in the molecule for results, as yet not published in detail,[14] confirm the tem-

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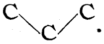
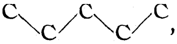
[14] Smyth and Dornte, THIS JOURNAL, 53, 2005 (1931).

perature variation of the moment in the cases of ethylene chloride and ethylene chlorobromide, in at least qualitative conformity with the prediction of Meyer's equation.

In trimethylene bromide, the 110° valence angle of the central carbon should bend the chain thus, . This should tend to reduce the opposition between the dipoles at the ends of the chain and so increase the resultant moment. If we take 1.52 Å. as the internuclear separation of the carbons and 1.85 Å. as the separation of the carbon and the bromine nuclei,[15] we may calculate the distance which would separate the two bromine nuclei if they were able to lie on the inside of the angle of the carbon chain in the plane of the three carbon atoms, the 110° valence angles being maintained throughout. The result of this calculation, 1.53 Å., is considerably smaller than the atomic diameter of bromine, 2.18 Å., calculated from x-ray data,[16] which shows that this particular arrangement of the atoms in the molecule is impossible without great distortion of the valence angles. A similar calculation for ethylene bromide gives 2.79 Å. for the separation of the bromine nuclei when they lie on the same side of the molecule in the plane of the carbon atoms. Evidently there is reason to expect a moment for trimethylene bromide larger than that of ethylene bromide and showing some increase as the increasing energy of rotation about the C–C bonds accompanying rising temperature tends to overcome the effects of the mutual potential energy of the dipoles and the repulsion between the bromine atoms.

If the carbon chain in pentamethylene bromide were the zigzag structure, , with the carbons all in the same plane, its moment should differ from that of trimethylene bromide only as the result of an increase of 2.5 Å. in the separation of the two dipoles. This obviously should increase the moment and decrease its variation with temperature. Actually, there is no reason why there should not be turning about the other C–C bonds and it is easy to picture this turning as sometimes giving rise to a ring structure in which the dipoles overlap and oppose one another. This is somewhat analogous to the ring structure suggested to account for the lowering of the moment and its increase with rising temperature in the case of diethyl succinate.[1] The existence of a portion of the molecules in this ring structure, which would diminish with rising temperature, would account for the fact that the increase of moment on going from trimethylene to pentamethylene bromide is not greater and that the increase of moment with rising temperature is not inconsiderable. However, this must be regarded as a very tentative and speculative explanation rather than as definite evidence of ring formation. There is uncertainty in the experi-

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[15] Pauling, *Z. Krist.*, **67**, 377 (1928).

[16] Huggins, *Phys. Rev.*, 28, 1086 (1926).

mental accuracy of the temperature variation of the moments of trimethylene and pentamethylene bromide. In the latter it may be merely that the mutual potential energy of the dipoles renders less probable those positions in which the chains are bent by turning around the C–C bonds so as to bring the two dipoles near together on the same side of the molecule and give increased moment. Increasing rotational energy with rising temperature would then overcome the effect of the mutual potential energy of the dipoles and increase the moment.

Probably in pentamethylene bromide and, certainly, in decamethylene bromide, it is justifiable to assign to the dipole at each end of the chain the moment of ethyl bromide, 1.9×10^{-18}, which has been found indistinguishable from that of heptyl bromide in value. If the carbon chain is rod-like with the 110° valence angles maintained, we can apply the simple equation used to calculate the limiting value of the moment of ethyl bromide, that is, $\mu = 1.41 \times 1.9 \times 10^{-18} \sin 70° = 2.5 \times 10^{-18}$. In decamethylene bromide, the dipoles are so far apart that we should expect no lowering of the resultant moment because of their mutual potential energy and, therefore, no temperature variation of the moment because of this effect. The difference between the observed and the calculated values of the moments is no greater than the possible absolute error in the observed value and the absence of appreciable variation of the values with temperature accords with the theoretical prediction. As any considerable permanent bending of the chain would cause a moment larger than that calculated and, probably, varying with temperature, which should affect the bending, it may be concluded that the long carbon chain in the liquid does not differ much from the rod-like shape commonly assigned to it. Another conclusion to be drawn is that the chain does not bend appreciably in the electric field used in measuring the dielectric constant, for such bending would increase the effect of the dipoles and give an apparent increase in the value of the electric moment observed.

In conclusion the writers wish to express their gratitude to the Bell Telephone Laboratories for a portion of the apparatus used in these measurements and to Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company for the loan of the pentamethylene and decamethylene bromide.

Summary

The dielectric constants and densities of heptane solutions of dibromides with two, three, five and ten carbon atoms between the bromines have been measured over a range of temperature and the results have been used to calculate the electric moments of the molecules.

The moment of ethylene bromide is found to increase with rising temperature in accordance witht heoretical predictions. The moments of methyl

and ethyl bromide are used to calculate the moments which might be expected in the molecules. The observed values are lowered by proximity of the two bromide dipoles, which also gives rise to the temperature variation of the moment. In decamethylene bromide the two dipoles are so far apart that the observed and calculated moments agree satisfactorily and the moment shows no variation with temperature.

Rotation around the C–C bonds probably causes some bending of the carbon chain, but there is no evidence of pronounced bending of the supposedly rod-like structures of the long chains, even in the external electric fields used in the measurement of the dielectric constants.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH]

THE GLASS ELECTRODE. THE STUDY OF VARIOUS CHARACTERISTICS

BY H. KAHLER AND FLOYD DEEDS

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Introduction

The theory of the glass cell which so far is the most widely accepted is that of Haber.[1] He derived several expressions for the potential difference across a glass membrane when the two surfaces are in contact with solutions whose hydrogen-ion concentrations (activities) are 1a and Ib. All of these expressions may be summarized into the equation E = RT log $(1a/1b) - F(G)$, where by $F(G)$ is meant a function of the glass, when immersed in different solutions.

The difference between the equations of Haber as well as between different hypotheses which have since been stated, arises from differences assumed for $F(G)$. When $F(G)$ is a small constant the glass is said to be "good," since it then has the theoretical slope for the calibration curve and also a small zero correction. Haber made the hypothesis that the glass is hydrated at its surfaces, this hydrated layer having the product $[H^+][OH^-]$ constant. In his paper, under certain conditions, $F(G) =$ RT log (IIa/IIb), where II*a* and II*b* are the hydrogen-ion concentrations (activities) in the two hydrated layers. $F(G)$ then is small only when II*a* is nearly equal to II*b*, which occurs when the hydrated layer is uninfluenced by the successive solutions coming in contact with the glass, or $[H^+]$ and $[OH-]$ are constant. Hughes[2] pointed out that this constancy could be attributed to the sodium silicate buffer system in the hydrated layer at the phase boundary. It is also evident that any increase in the buffer capacity of the hydrated layer improves the electrode performance.

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[1] Haber and Klemensiewicz, *Z. physik. Chem.*, 67, 385 (1909).

[2] Hughes, *J. Chem. Soc.*, 491 (1928).

Horovitz and collaborators[3] showed that certain glasses exhibited metal electrode functions for ions other than H^+ and OH^- when the glasses contained the metal whose ion was being measured in solution.

It has been observed by nearly every worker that thin glass electrodes give better results than thick glasses, though no one has shown any good reason for this. MacInnes[4] has gone so far as to use glasses only 1 micron thick, the membranes exhibiting interference colors. It is obvious from a practical standpoint that thick glasses having great mechanical strength would possess advantages in most applications.

We discuss thickness, resistance, zero correction, deviation and temperature coefficient, following the experimental technique generally employed by others as described in the literature. Following this, we show how some of these results may be greatly modified by using the methods outlined in this paper.

Chemical Composition of Glass.—On the basis of the work of Hughes and of MacInnes and Dole, the glasses we selected were those whose composition approached Corning Glass 015. Four such glasses are shown in Table I. The first glass to be used is unknown in origin and it has been designated "A." A second glass designated as 015 (Al) was obtained from the Corning Glass Company, and its designation is given the suffix Al because analysis showed the presence of aluminum. A third batch of glass called 015 is a sample of Corning soda lime glass and differs from 015 (Al) in that it yields electrodes having a calibration curve very close to the theoretical. Glass "M" is a sample prepared by Dr. G. W. Morey of the Geophysical Laboratory from c. p. ingredients.

TABLE I

RESULTS OF EXPERIMENTS

Designation	SiO_2, %	CaO, %	Na_2O, %	$(Al, Fe)_2O_3$, %	Al_2O_3, %	Other constituents, %	Analyst
"M"	72	6	22				G. W. Morey
015	72	6	22				Corning Glass Works
015(Al)	69.8	6.1	21.6	2.2		PbO 0.3	W. Taylor
"A"	70	4.5	22.7		0.3	Fe_2O_3 0.3 Mn_2O_3 0.2 MgO 1.7	E. Wherry

Resistance and Thickness Measurements.—Glass bulbs whose thickness was 10 microns and over were measured by Dr. W. R. Earle with a microscope having a vertical adjustment calibrated in microns.[5] In measuring the thickness of the glass its thickness was determined at four different places. When the glass was not sufficiently uniform, the

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[3] Horovitz, Z. *Physik*, 15, 369 (1923).

[4] MacInnes and Dole, THIS JOURNAL, 52, 29 (1930).

[5] Gage, "The Microscope," 1925; Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley and Sons, Inc., New York, 1930, Vol. I, p. 407.

sum of the reciprocal thicknesses was made $1/T = 1/t_1 + 1/t_2 + 1/t_3 + 1/t_4$ in order to compare with the resistance of several parallel resistances $1/R = 1/r_1 + 1/r_2 + 1/r_3 + 1/r_4$. On measuring the area of the bulb and its total resistance the specific resistance ρ could be obtained. The total resistance R was measured by an electrometer–capacity method as follows (Fig. 1).

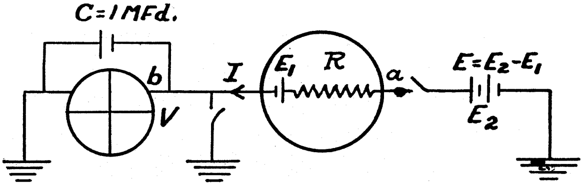

Fig. 1.—Resistance measurement: V, voltage of electrometer; E_1, potential difference across glass cell for zero current; E_2, voltage applied by potentiometer; E, excess potentiometer voltage for zero current; I, current; R, glass cell resistance.

The cell being first balanced by the null method, at a given time let the earth connection of b be broken and the excess potential R from the potentiometer applied so that the electrometer charges up at a certain time rate. This rate is observed and the resistance computed according to the equation

$$R = -\frac{t}{2.3C \log (E - V)/E}$$

R is the resistance, t is seconds where C is the capacity of the shunt condenser; E is the applied voltage, V is the electrometer voltage. This method has the great advantage that low applied voltages may be used and small currents flow, thus causing a minimum polarization.

As a result of such experiments the glass 015 Al gave a specific resistance of $2.0 \times 10^{+10}$ ohms/cm. cube, while glass "A" gave a specific resistance of $6.5 + 10^{+10}$ ohms/cm. cube. We estimate from the data of MacInnes and Dole for glass 015 that they would get about 1.2×10^{10}. For 015 we find $\rho = 3.6 \times 10^{10}$ at 22.3°. Horovitz obtained for various German glasses 10^{+7} to 10^{+10} for the specific resistance, the former of which seems remarkably low.

In some cases the glass electrode was provided with a guard ring and connected as in the well-known method. A check on the work is the graphs obtained for different cells of the same glass. These show that the resistance is proportional to the thickness of the glass. In passing it may be remarked that the guard ring is necessary for a short shanked glass electrode or a damp glass surface but for a well dried glass insulating surface in a fairly dry atmosphere and a length of shank of 10 cm. there is little need of the guard ring except in measurements of high precision or when the cell membrane has a very high resistance.

It can readily be seen that the leakage is related to the ratio of the surface resistance to the resistance of the glass membrane for electrolytic currents. If the latter be taken at 10^8 ohms, then the shank should be long enough so that the former would have a resistance of 10^{11} ohms with a humidity of 60%. The measurements were made at a measured humidity of 55%, the room being provided with an air dryer.

Resistance and Temperature.—The variation of resistance over the temperature range from 5 to 55° was ascertained. At 55° the resistance is only a fraction of the value obtained at 5°. Thus a cell which at 5° showed a resistance of over 1200 megohms at 55" had a resistance of only 12 megohms.

Potential Measurements.—In measuring potential differences across the glass membrane, the solution on each side of the membrane is electrically connected to a saturated calomel half cell by means of an agar–potassium chloride bridge. In the ensuing experiments a potentiometer and Compton type electrometer were used interchangeably with vacuum tube voltmeters. Three vacuum tube amplifiers were used. The first is of the previously described[6] type, using a 201-A tube critically balanced in the first stage for a minimum grid current, followed by a two-stage resistance coupled amplifier with a microammeter in the output of the last stage. The second amplifier was used with the FP-54 General Electric tube in the first stage followed by 222 and 212 tubes in successive stages. A third amplifier used the German Osram double grid (E series) tube with the control grid inserted in the tube through an amber plug, followed by 222 and 212 tubes.

In an electrometer–potentiometer system of small electrostatic capacity and small leakage the sensitivity of the system is independent of resistance in the circuit so long as a sufficient current flows to charge up the quadrant, since in the final steady state the current approaches zero. However, when leaks occur on the electrometer side of the potentiometer, the sensitivity of the equipment drops. The chief effect of increase in resistance is to increase the time necessary to get the final steady reading.

Similar considerations with regard to the glass cell, keeping the Haber theory in mind, might indicate that the resistance or thickness of the cell as such could play no part other than the time factor in the potential measured since, at the time of the final reading, there is no current flowing except that due to unavoidable insulation leakage.

However, experiments now to be described, as well as those previously reported in the literature, show that this is not the case, *viz.,* resistance (thickness) appears to affect the performance of the glass cell indirectly, at least under some conditions.

In measuring the hydrogen-ion activities of solutions, one of the first

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[6] Kahler, DeEds, Rosenthal and Voegtlin, Am. *J. Phys.,* **91,** *225* (1930).

steps is to measure the potential when the same solution is on both sides of the glass. This gives the zero correction, also called the strain value by some writers, and the asymmetry value by other writers. By changing the solution simultaneously on both sides, a relation between the observed potential and the *P*H value of the solutions was obtained. This curve is shown in Fig. 2. This particular graph illustrates the manner in which a very poor cell may show a large change in zero correction with *P*H. The interpretation of this is that the slopes of the calibration curves on the two sides differ since the difference in slopes $S_2 - S_1 = Z_2 - Z_1$ the difference of zero corrections at two *P*H levels.

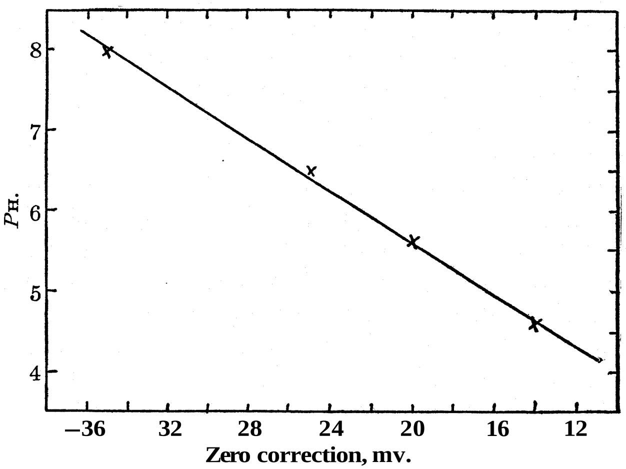

Fig. 2.—Glass "A," thick bulb.

Relation between Resistance (Thickness) and Zero Correction.—By taking a large number of cells of the Haber bulb type of the same kind of glass but differing in thickness and total resistance, it was shown that usually the higher resistant (thicker) cells have the larger zero corrections when using a liquid of *P*H 4 on each side if the outside surface is only immersed to the top of the bulb.

Deviation and Resistance (Thickness).—By keeping the fluid on the inside of the glass cell constant and varying the *P*H of the solution on the outside, a calibration curve for the cell outer surface may be obtained. It is found that as the resistance of the glass cell increases for the same glass composition, the curve for the glass cell markedly deviates from the theoretical relationship. In order to have a definite criterion for this effect, we take as a convenient measure of the deviation from the theoretical the difference between the hydrogen electrode and glass electrode reading for unit *P*H change: $E_H - E_G = \Delta(\text{H.G.})$. A perfect electrode has a difference of 0. MacInnes and Dole,[4] using thin membranes, were able to get a difference of zero over a range *P*H 1 to 9.8. At PH values for which the glass is attacked all glasses deviate markedly from the theoretical, as has been shown by many workers including Horovitz, Hughes, MacInnes and Dole.

The relation between Δ(H.G.) and thickness for different glasses on their outer surfaces is shown in Fig. 3. As can be seen, the "A" glass containing no aluminum is quite similar to 015(Al).

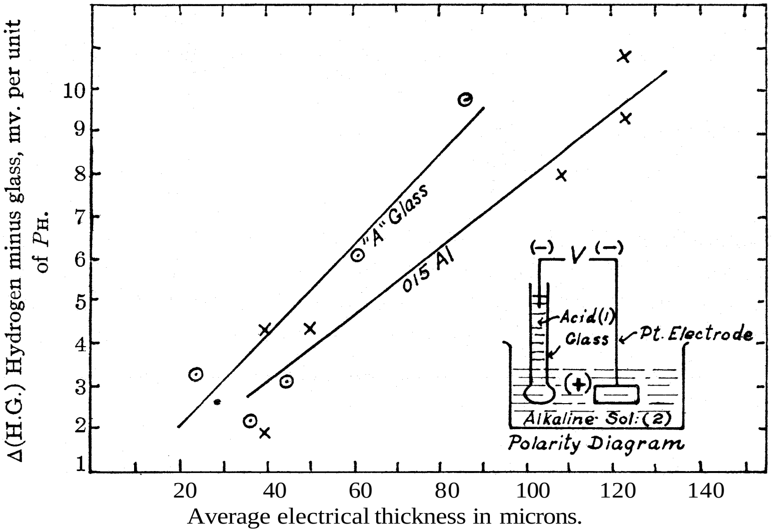

Fig. 3.—Polarity: when inside solution in glass cell is acid with respect to the outside—inside is negative. (Both calomel half cells are omitted in the diagram.)

For reasons to be pointed out later, it should be here stated that these measurements were all made when the outer glass surface was immersed only about 1 cm. below the surface of the solution.

Effect of Hydrofluoric Acid Treatment.—If the surfaces of the glass bulbs are etched with hydrofluoric acid, the thickness may be reduced at will. Experiments were performed with the idea of testing whether the zero correction and deviation from the theoretical would follow the thickness (resistance) deviation curves. The results for several glass cells are shown in Table II.

At this point it is well to make clear that all the above-mentioned experiments were made with a large area of wetted glass on one side of the membrane and a small area on the other side. The shank and bulb were of the same glass and the statement refers to the total combined areas. It seems likely that most of the work reported in the literature was done under somewhat comparable conditions.

TABLE II

HYDROFLUORIC ACID TREATMENT

Electrode	Thickness, microns	PH 4 zero correction	Δ(H.G.)	Time in hydrofluoric acid, minutes
"A" 21	233	0.078	0.028	0
	146	.011	.011	15
	116	.009	.008	12
"A" 38	121	.031	.015	0
	83	.009	.006	4
	70	.009	.003	15
015A1 12	225	.063	.052	0
	220	.020	.026	5
	110	−.003	.003	28
"A" 34	71	.047	?	0
	68	.011	?	3
	67	.011	.001	3

Temperature.—Literature describing the use of the glass electrode for the measurement of H^+ has contained little discussion of the influence of temperature changes upon the observed potential. In making these measurements both the electrometer and a vacuum tube voltmeter were used. Curves showing the relationship between zero correction and temperature are shown in Fig. 4, these measurements being made with the electrometer. In Fig. 4, 08 is a thin electrode; N2 and N6 are thicker electrodes. Additional measurements on a good electrode in a buffer

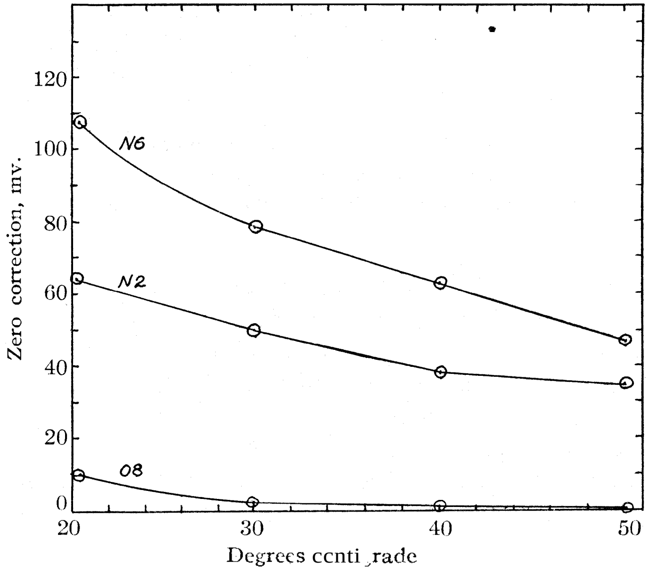

Fig. 4.

system at three different temperatures showed that as the temperature was elevated the slope of the calibration deviated a little more from the theoretical.

Effects of Surfaces upon Potential Measurements.—Experiments were performed to see if a given glass electrode gave the same calibration curve on the two sides of the bulb when the outside immersed surface was only a fraction of the inside wetted area. Although a difference in calibration on the two sides, without exception, was found on twenty electrodes, to conserve space we give the data on only a single electrode in the form of a matrix (Table III).

TABLE III

THICK ELECTRODE C 60. VOLTS MEASURED ON VACUUM TUBE VOLTMETER

Reading in volts

P_H outside	3.97 P_H Inside	748	Inside diff.
3.97	0.1842	-0.020	0.2042
748	.300	.096	.2040
Outside diff.	.1158	.1160	Theor. diff. = 0.2046 volt

This evidence shows clearly that an electrode may have different calibration curves on the two sides. A large number of experiments testing the importance of such factors as method of blowing the bulb, hydrostatic pressure at time of measurement and surface curvature gave negative results.

The important factor in determining the electrode characteristic was finally found to be the detailed conditions connected with the geometry of the wetted surfaces. Before discussing these details, however, it is first necessary to determine whether these phenomena are connected with states of non-equilibrium or equilibrium.

Time Required to Reach Equilibrium.—Most electrodes giving a poor performance show time lag in reaching a steady value. To study this, fourteen similar tube type electrodes were made, by sealing one end of 30-cm. lengths of 7-mm. diameter tubing of 1 mm. wall, and tested in buffer solutions. It was found that under similar experimental conditions all behaved alike. In going from one buffer to another, on the side of small immersion, the initial value was poor, improving on standing for the first and subsequent days (Table IV). This leaves little doubt that the de-

TABLE IV

TUBE TYPE ELECTRODE. P_H 3.97 INSIDE. INSIDE LENGTH WETTED 21 CM.; OUTSIDE LENGTH IMMERSED 4 CM. (VOLTS MEASURED ON ELECTROMETER)

Time of immersion before reading	P_H outside 3.97 volts	8.24	Outside A	Theor.
Immediately	0.909	0.800	0.109	
24 hours	.980	.760	.220	0.252

viation effects are transient phenomena, disappearing when the system ultimately reaches equilibrium.

Potential Dependence on the Geometry of the Two Wetted Surfaces.—It was first established that in the tube type of electrode the larger surface gives the theoretical slope or something near thereto, and the smaller surface gives a calibration considerably under the theoretical. This effect is roughly proportional to the thickness. In the case where a glass tube electrode is partially immersed in a fluid so that the height is the same on both sides, the electrode also gives a good value (Table V).

TABLE V

EXPERIMENTAL DATA

Height inside, cm	Height outside, cm.	A outside	Theoretical
5.5	5.5	246.5[a]	246.3
8.75	5.5	201	
8.75	8.75	245.9[a]	
19.00	8.75	240.7	
19.00	5.50	217.8	
19.00	19.00	246.5[a]	
30.00	4.50	191.5; 152.9; 176.5[b]	

[a] Close agreement with theoretical value when levels are equal. [b] Erratic value when levels are markedly different.

The most careful checks were made to test the influence of instrument leakage and it was definitely settled that the relations mentioned in the preceding paragraph were a function of the glass electrode itself and could not result from any deficiency of the measuring equipment.

The electrical capacity of the electrode was also eliminated as a factor in the deviations of the measurement from the theoretical value.

Next, tubes were made with equal areas on the two sides of the glass wall but in such a relationship to each other that no immersed surfaces would be directly opposite each other. Changing the solution inside gives the correct slope but changing the solution outside has practically no influence on the potential measured. Now an inspection of Figs. 5 and 6 showed that the current which flows through such an electrode must pass up a film on the surface of the glass, since the resistance through the glass would be several times the actually. measured value. This indicates the existence of an aqueous conducting film on the glass above the solution line which we simply call the deviation film, since we attribute most of the deviations to it.

Between this film and the glass there must be a phase boundary potential and between the film and main body of the solution a small diffusion potential. The deviation film through the process of diffusion gradually takes a PH value depending in part at least on the PH of the solution.

The measured potential difference is therefore the result of the parallel electromotive forces existing at the phase boundaries between the solution and glass and between the deviation film and glass, to the latter of which is added a small diffusion potential. In the simplest case of two parallel e. m. f.s, the measured potential, neglecting the diffusion potential, is $(Er + eR)/(R + r)$, where E, e and R, r are the potential differences and resistances in the two regions, respectively. Thus the higher the relative resistance of the submerged part of the electrode, the greater is the effect of the deviation film above the solution surface and hence the greater the deviation. This explains the resistance effects experimentally given in preceding paragraphs. A thick glass may therefore be used providing a large immersed area is used to lower the resistance.

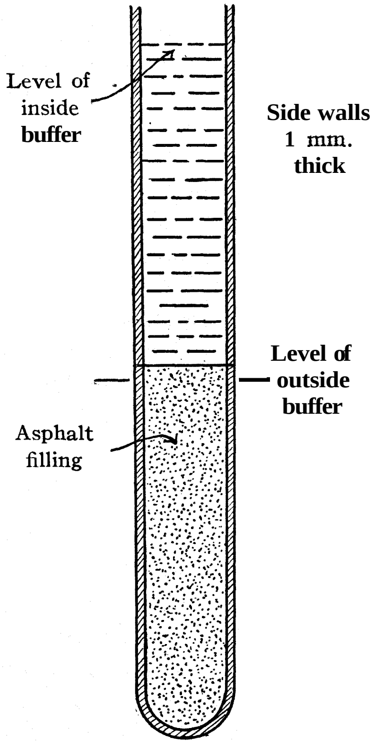

Fig. 5.

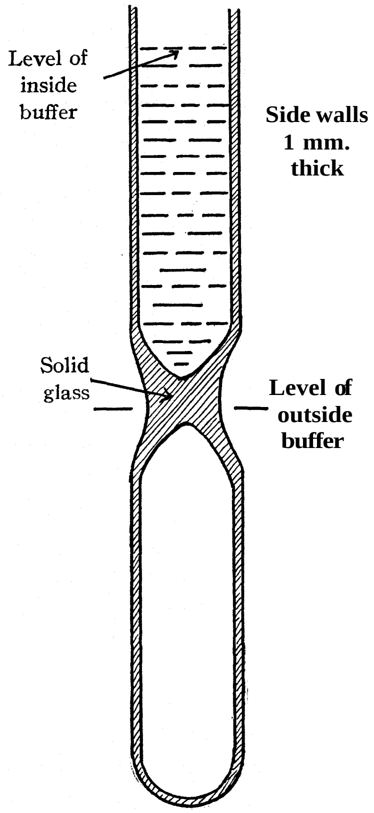

Fig. 6.

Two further tests of the deviation film hypothesis were (1) a tube which had stood in a solution for a week with a fixed level on the outside was found to give the theoretical difference for the solutions measured. The solution on the outside had been P_H 8.24. The tube was held horizontally and painted above the immersion line with a hydrochloric acid solution, care being taken to keep well above the line of top immersion. The tube was now wiped off with a towel and put back in the original position. The e. m. f. was now too low by 70 mv., showing the importance of the film above the liquid line. The value slowly recovered in the course of a day.

(2) If the deviations ordinarily found are to be attributed to films above the line, then by painting on a dry tube a layer of insulating paint, asphalt or paraffin, and just immersing to the edge of the coat, it should be possible to eliminate the spurious effects. A tube was so painted and it then gave the theoretical slope with only one-sixth the outside area immersed. This was verified in perhaps thirty cases.

Glass Cells with Solid Poorly Conducting Coats.—A few tests on the response of poorly conducting coats to change in *PH* of the solution were made. The coating should have two properties. (1) By simply adding resistance to the region covered it would give protection as pointed out in the preceding paragraphs. (2) If the coating itself does not respond to *PH* changes, it should give protection irrespective of resistance. In order to study the response of the coats to *PH* the entire bulb of a Haber–Klemensiewicz type electrode was coated with the material in question. Thin films of paraffin about 5μ thick, collodion, flexible collodion, oleic acid and stearic acid were put on the outer wall of the glass bulb as in Fig. 7. Shellac, DeKhotinsky cement and asphalt were also tried.

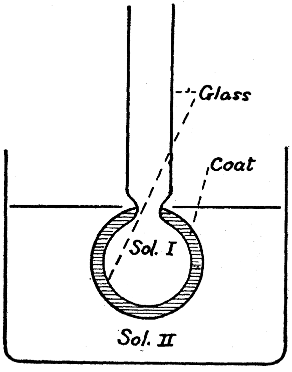

Fig. 7.

It was found that varying the *PH* of solution I in contact with the bare glass gave the usual calibration curve for a good electrode. The bulbs used in these tests were of large area and were quite thin (20μ). The resistance of the combination was usually measured. It was found that changing the PH of solution II in contact with these coatings had little effect on the potential of the chain, but changing the salt concentration in solution II had a marked influence on the readings. Table VI shows some typical experiments. The case of electrode **A-81** shows that readings can be duplicated from day to day.

An inspection of the table shows that for the coatings mentioned change of *PH* of the solution in contact with the coated side of the glass has little effect on the potentials measured. It is reasonable therefore to use such coatings in an attempt to cut out the change in potentials occurring above the level of immersion of the glass.

Practically we find that most paints are worthless after a few hours of immersion due to the fact that water penetrates between the paint and the soft alkaline glass.

TABLE VI

ELECTRODE NO. A-81. PARAFFIN COAT. RES. = 150 MGS.

Date	PH inside	PH outside	Volts measured	Diff.	Theor.	Temp.. °C.
4– 8–30	3.97	7.94	0.364			
4–10–30	3.97	10.3	.365	0.230	0.230	19
	7.94	10.3	.135			
4–12–30	3.97	7.94	.361			
4–14–30	3.97	3.97	.363			
	3.97	7.94	.363	.233	.233	23
	7.94	7.94	.130			
	7.94	7.94 + NaCl	.069			
Electrode No. A-83. Collodion Coat						
	4	7.94	0.155			
	4	4	.156			
Electrode No. A-31. Stearic Acid Coat						
	3.97	3.97	0.200			
	3.97	7.94	.200			
Electrode No. A-32. Stearic Acid Coat						
	3.97	7.94	0.200			
	3.97	7.94 + NaCl	.150			
			.120	5 minutes later		
	3.97	7.94	.200	In 20 minutes		
Electrode C-20 + Paraffin Wax Coating						
	3.97	7.94	0.406	0.046		
	3.97	7.94 + NaCl	.360			
	3.97	7.94	.401			
Electrode N-17. Collodion Coating						
	3.97	7.96	0.334	0.058		
	3.97	7.96 + NaCl	.276			

Electrode A-61. Parafiin Coating

Mg. added KCl	M. v.
	0.165
100	.170
100	.164
100	.159
100	.155

Influence of Ions Other than Hydrogen and Hydroxyl.—There are statements in the literature to the effect that at least certain glasses, when made into thin membranes, are capable of measuring potential changes due to alterations in the concentration of ions other than hydrogen and hydroxyl. Horovitz and Schiller, in their widely known papers, showed for the special glasses they examined that sodium, potassium, silver and zinc electrode functions were exhibited. This is a matter of considerable significance, and we have, therefore, studied this phenomenon especially with reference to the sodium electrode function of the glasses in our possession.

For the purpose of studying the sodium electrode function, Horovitz in one case used a sodium acetate buffer. To this buffer varying amounts of sodium chloride were added. It was observed by him that the potential changes, indicated by the glass electrode, upon the addition of successive amounts of sodium chloride, could be accounted for by assuming that the glass membrane had a sodium electrode function.

In our work we found large sodium electrode effects, if we assumed that the PH of the buffer remained constant. On the basis of a consideration of ionic activities, such an assumption was not justified, and we therefore modified the experimental procedure as follows. A 50-cc. bottle was provided with a rubber stopper having holes to permit insertion of a hydrogen electrode, a glass electrode, an agar–potassium chloride bridge, an inlet for purified hydrogen gas and an escape for the gas. This arrangement made it possible to measure the potential of either the hydrogen electrode or the glass electrode in conjunction with a saturated calomel half-cell. Using this technique, the potentials were obtained on 25 cc. of a buffer solution, after all traces of oxygen had been eliminated as

TABLE VII

EXPERIMENTAL DATA

Solution used	NaCl added, %	ΔEh^a	ΔEg^a	PH[b]	$\Delta Eg - \Delta Eh$
M/20 acid potassium phthalate	5	0.0355	0.036	3.97	+0.0005
Phosphate buffer[c]	5	.0335	.0305	7.48	− .0030
Phosphate buffer	5	.0320	.0335	8.24	+ .0015
Phosphate buffer[d]	5	.0545	.0570	10.77	+ .0025
Phosphate buffer	5	.0545	.0565	10.77	+ .0025
Phosphate buffer	5	.0545	.0590	11.19	+ .0045
Phosphate buffer	10	.0790	.0785	11.19	− .0005
Phosphate buffer	5	.0525	.0555	11.4	+ .0030
Phosphate buffer	10	.0735	.0765	11.4	+ .0030
Phosphate buffer	10	.0470	.064	11.94	+ .0170
Glycine buffer	5	.0220	.0370	11.97	+ .0150
Glycine buffer	10	.0375	.0630	11.97	+ .0255
Glycine buffer	1	.0055	.0180	12.26	+ .0125
Glycine buffer	5	.0205	.0460	12.26	+ .0255
Glycine buffer	1	.0045	.0190	12.55	+ .0145

[a] ΔEh and ΔEg are the changes in potential of the hydrogen and glass electrodes, respectively, due to the addition of the salt. [b] The PH column refers to the values before addition of the salt. [c] Buffer system composed of varying ratios of monosodium phosphate and disodium phosphate. [d] Buffer system composed of varying ratios of disodium phosphate and trisodium phosphate. These mixtures and the glycine series yield buffer mixtures having buffer capacities characteristic for each series; hence the difference in magnitude of salt effect noted on the hydrogen electrode.

judged by the constancy of the hydrogen electrode reading. A weighed amount of sodium chloride was then introduced and the potentials again observed. The data of a series of such experiments covering a PH range from 3.97 to 12.55 are given in Table VII.

Similar effects were obtained when electrodes were constructed so that equal areas were used on both wetted sides.

It is seen that the change in voltage at the glass electrode unaccounted for by the change in hydrogen-ion activity is definite but very small in the lower PH range. Only in alkaline solutions does the glass 015 show a significant sodium electrode function and even then it is far below the hypothetical magnitude. Similar experiments showed an even smaller effect produced by potassium.

The fact, here brought out, that the sodium effect becomes important only when the glass buffer properties begin to break down favors the idea that the salt is simply interfering with the hydrogen-ion measuring system.

Referring back to the introductory paragraph, it now appears that so far as Haber's theory is concerned, in the equation $E = RT \log (Ia/Ib) - F(G)$, $F(G)$ is probably the term involved in the deviation of the electrode calibration at extreme PH values, while the deviations at intermediate PH levels are due to the deviation film and have no special relation to the Haber hypothesis.

Conclusions and Summary

1. The specific resistances of several glasses were determined as well as decrease of resistance with rise of temperature.

2. It was shown that without waiting for the system to come to complete equilibrium, glasses give deviations from the theoretical calibration curve (volts against PH) which are roughly proportional to the thickness on the side of smaller fluid immersion. On the larger side the calibration is close to the theoretical.

3. This effect was shown to be caused by the formation of a hygroscopic deviation film on the glass surface above the water lie. It is suggested that the potential measured is the value of the spurious film potential and the true value of the immersed glass connected in parallel.

4. By changing the character of the film above the line, the values given by the electrode could be changed.

5. By suppressing the film through coats of dielectric paints, the deleterious effect could be practically eliminated as long as no water penetrated under the coating.

6. Potentials were measured through various thin semi-conducting coatings on glass bulbs. The potential on the coated side of the glass shows only a slight dependence on the PH of the solution and large salt effects. The opposite side of the glass wall, however, shows its usual calibration.

7. The change in salt effects for a PH range from 3.97 to 12.55 was determined. Specific salt effects over the secondary hydrogen ion change only become important in the extreme range of PH values.

WASHINGTON, D. C.

NOTES

The Atomic Weight of Chlorine. The Solubility of Silver Chloride.—I am grateful to Messrs. Scott and Johnson[1] for calling my attention to an erroneous statement in the paper by Hönigschmid and Chan[2] on the atomic weight of chlorine.

Our reason for deciding that it was unnecessary to apply a correction for the silver chloride removed in making the nephelometric tests, when the precipitate was subsequently to be weighed, was that we had assumed its solubility under the conditions of the analysis at 0° to be 0.05 mg. per liter. At that time we had not determined this value ourselves but, through an error in reading, had taken from the paper by Richards and Willard[3] this value instead of the true one, 0.5 mg. per liter. After reading the communication of Scott and Johnson, we determined this solubility in analyses both of sodium and potassium chlorides at the equivalence point, after the usual shaking and cooling in ice for several days. Portions of the perfectly clear solution were pipetted into nephelometer tubes and, after addition of silver and chloride ion, respectively, showed the same opalescence as a standard containing 0.53 mg. of silver chloride per liter, thus completely confirming the work of Richards and Willard. When an excess of 0.3 mg. of silver was added, the solubility was 0.42 mg. or only 80% as much. This common ion effect makes the correction uncertain.

The nature of the precipitate obtained by us was probably different from that obtained by Scott and Johnson, and this doubtless accounts for the lower solubility found by us. In making the correction we prefer to use our own value because we consider it more applicable.

A calculation of the correction to be applied was easily made by referring to the laboratory notebook which contained all the data. Usually only two or three tests were necessary, because the proper amount of silver was carefully weighed to within 0.1 or 0.2 mg. It was assumed that 100 cc. of the solution contained 0.05 mg. of silver chloride, as already determined, because although it may have been less in the first test, when an excess of one ion was present, this value is certainly a maximum. Each nephelometer tube contained 22 cc. The corrections are shown in Table I.

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[1] Scott and Johnson, THIS JOURNAL, 52, 3586 (1930).

[2] Honigschmid and Chan, *Z. anorg. allgem. Chem.*, *163*, 315 *(1927)*.

[3] Richards and Willard, THIS JOURNAL, 32, 4 (1910).

TABLE I

CORRECTION VALUES

No.	No. of neph. tests	Vol. of soln. removed, cc.	AgCl in soln., mg.	Corr. wt. AgCl in vac., g.
1	2	88	0.044	11.54010
2	2	88	.044	9.11889
4	3	132	.066	9.94704
5	4	176	.088	13.58106
6	4	176	.088	11.96637
7	3	132	.066	8.94863
8	3	132	.066	12.30290
9	3	132	.066	8.80133

In Table II are shown the corrected gravimetric values for the atomic weight of chlorine, together with the weights of silver plus chlorine taken and found.

TABLE II

THE ATOMIC WEIGHT OF CHLORINE

No.	Wt. of Cl in vac., g.	Wt. Ag in vac., g.	Wt. AgCl in vac., g.	Diff., mg.	Cl:AgCl	At. wt., Cl
1	2.85458	9.68543	11.54010	−0.09	0.2473618	35.4558
2	2.25569	6.86312	9.11889	− .08	.2473645	35.4563
4	2.46049	7.48635	9.94704	− .20	.2473590	35.4553
5	3.35955	10.22139	13.58106	− .12	.2473702	35.4574
6	2.96007	9.00620	11.96637	− .10	.2473657	35.4565
7	2.21357	6.73502	8.94863	− .04	.2473641	35.4562
8	3.04333	9.25949	12.30290	− .08	.2473669	35.4568
9	2.17711	6.62409	8.80133	− .13	.2473615	35.4558
	21.32439	64.88109	86.20632	− .84	.2473646	35.4563

The average value for the atomic weight of chlorine is 35.4563, and that obtained nephelometrically is 35.4567. The average deviation between the weight of silver chloride found and calculated is 0.10 mg. and the total for eight gravimetric determinations is 0.84 mg.

Because silver chloride retains traces of other salts, it is probable that the weight obtained in the gravimetric process tends to be too great and that an exact agreement between the gravimetric and volumetric methods, if it occurs, is due to a chance compensation of errors in both directions.

In most of our atomic weight determinations the error due to uncertainty in the amount of silver chloride removed for nephelometric tests is, as shown above, very small, because the solution is almost always so near the equivalence point that very few tests are necessary.

CONTRIBUTION FROM THE
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Note on the Third Law Calculation of the Entropy and Free Energy of Ammonia.—A calculation of the molecular entropy and free energy of formation of ammonia has been made by means of the third law of thermodynamics using the low temperature heat capacity data of this compound. The calculated molecular entropy and free energy of formation are, respectively, 46.7 entropy units, and —4150 calories at 298.1°K.

There has been considerable uncertainty regarding the proper value of the entropy of hydrogen to be used in thermodynamic calculations in combination with other molecular entropies obtained by means of the third law. For this purpose, Giauque[1] has recommended a value derived from the absolute entropy of ordinary hydrogen obtained from spectral data, modified by the principle of nuclear spin cancellation.[2] This value has been found satisfactory for systems of monatomic and diatomic substances, but has not been conclusively tested for larger molecules. Since the thermal data and equilibrium in the ammonia synthesis, $^1/_2N_2(g) + 1^1/_2H_2(g) = NH_3(g)$, are known with a high order of precision,[3] and since there are now sufficient measurements upon ammonia at low temperatures to permit a calculation of the molecular entropy, this substance serves as a test of the applicability of the third law, and more particularly of Giauque's value for the entropy of hydrogen.

The low temperature heat capacity measurements used in the present calculation are those of Clusius, Hiller and Vaughen,[4] also Eucken and Karwat.[5] Heats of vaporization and fusion were taken from the work of Eucken and Donath.[6] Extrapolation to 0°K. was carried out by the Debye function with $\Theta = 215$. For the heat capacity of the gas, the values of Osborne[7] and associates were used. The molecular entropy thus obtained is 46.7 entropy units at 298.1°K.

Assuming Giauque's value of 31.23 for the entropy of hydrogen, and 45.6 for that of nitrogen,[8] the entropy change accompanying the formation of ammonia is —22.9 E. U. The heat of formation, $\Delta H_{298.1}$, which is equal to —10,985 calories, is obtained from Lewis and Randall's equation[3]

$$AH = -9500 - 4.96T - 0.000575T^2 + 0.0000017T^3$$

The free energy of the ammonia synthesis can be derived from the above results by means of the second law, and is found to be: $\Delta F^{\circ}_{298.1} = -4150$,

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[1] Giauque, This journal, 52, 4816 (1930).

[2] Gibson and Heitler, Z. Physik, 49, 465 (1928).

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co.. Inc., New York, 1923, pp. 556-557.

[4] Clusius, Hiller and Vaughen, Z. physik. Chem., 8B, 427 (1930).

[5] Eucken and Karwat, ibid., 112, 467 (1924).

[6] Eucken and Donath, ibid., 124, 181 (1926).

[7] Osborne, Stimson, Sligh and Cragoe, Bur. Standards Sci. Paper No. 501, Washington, D. C., 1925.

[8] Lewis and Randall, Ref. 3, p. 464.

which may be compared with the experimental ΔF°_{298} = —3910 given by Lewis and Randall.[8] If the previously accepted value[8] of 29.6 for the entropy of hydrogen be used instead of that later recommended by Giauque,[1] $\Delta F^\circ_{298.1} = -4900$ is obtained. It is obvious that Giauque's value gives the better agreement with experiment.

Villars[10] has calculated the molecular entropy of ammonia from spectroscopic data. His figure, 44.0 E. U., is not given on the same basis as the above value. When Villars' result is made comparable with the entropy of hydrogen used here (31.23), his value becomes 46.5, in close agreement with the 46.7 given above.

CONTRIBUTION FROM THE
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The Analysis of Chlorine Monoxide–Chlorine Mixtures.—Chlorine monoxide may be determined by absorption in potassium iodide solution and titration of the iodine liberated.

$$Cl_2O + H_2O + 4I^- \longrightarrow 2OH^- + 2Cl^- + 4I$$

It is necessary to acidify the solution before titrating with thiosulfate.[1]

$$Cl_2O + 4I^- + 2H^+ \longrightarrow 4I + 2Cl^- + H_2O$$

The liberation of OH− provides a further means for the determination of chlorine monoxide and indicates a method for the analysis of chlorine monoxide-chlorine mixtures.

$$Cl_2 + 2I^- \longrightarrow 2I + 2Cl^-$$

Excess of standard sulfuric acid is added and after titration of the total iodine with thiosulfate the excess acid is found by back titration with standard alkali. Bowen[2] used methyl orange as indicator. while Hinshelwood[3] used $N/10$ baryta and phenolphthalein. If x cc. of thiosulfate is used and then y cc. of sulfuric acid is required to neutralize the OH−; Cl_2O a y and Cl_2 a $x - 2y$. Acid, base and thiosulfate must all be of the same normality or correcting factors are necessary.

The analysis can be simplified by an adaptation of the method used by Bodenstein[4] for the analysis of chlorine-ozone mixtures.

As before, the gases are absorbed in potassium iodide solution and excess standard $N/10$ sulfuric acid added and the total iodine found.

[9] Giauque and Wiebe, THIS JOURNAL, 50, 121 (1928).

[10] Villars, *ibid.*, 53, 2006 (1931).

[1] Kistiakowsky, Z. *physik. Chem.*, 116, 371 (1925).

[2] Bowen, J. *Chem. Soc.*, 123, 1203 (1923).

[3] Hinshelwood, *Proc. Roy. Soc.* (London), A131, 177 (1931).

[4] Bodenstein, Schumacher and Padelt, Z. *physik. Chem.*, 5B, 209 (1929).

The excess sulfuric acid is estimated by addition of a slight excess of $N/10$ potassium iodate solution and titration of the iodine liberated.

$$IO_3^- + 51- + 6H^+ \longrightarrow 61 + 3H_2O$$

The acid may be standardized by addition of potassium iodide and a slight excess of $N/10$ potassium iodate solution, the results agreeing very well with those by other methods.

The agreement between this method and that used by Hinshelwood[3] may be seen by comparing the amounts of standard $N/10$ sulfuric acid used to neutralize the $OH-$ liberated by the chlorine monoxide contained in 5 cc. of a solution of chlorine monoxide-chlorine in carbon tetrachloride.

	Solution A	Solution B	Solution C
H_2SO_4 estimated by KIO_3 method, cc......	7.40	5.67	7.88
H_2SO_4 estimated by baryta method, cc......	7.42	5.74	7.89

Doing duplicate experiments showed an agreement to about one-half of one per cent. but the method could be brought up to the usual accuracy of iodine titrations using calibrated apparatus and greater care than in these preliminary experiments. The concentrations of chlorine monoxide and chlorine were between 0.05 and 0.30 g. moles per liter in these experiments.

This method would appear to have the advantage of speed, simplicity and a convenient end-point. Since the acid can be standardized in terms of the thiosulfate, only the latter need be determined absolutely and, furthermore, the ratio of chlorine to chlorine monoxide can be found without a knowledge of the actual normality of the thiosulfate.

The method could also be used for the analysis of chlorine dioxide–chlorine mixtures, the excess acid being determined as above by addition of potassium iodate solution.

$$ClO_2 + 51- + 4H^+ \longrightarrow Cl^- + 51 + 2H_2O$$

Bowen[2] analyzed chlorine dioxide–chlorine mixtures by absorption in potassium iodate solution, followed by thiosulfate titration in acid and in neutral solution according to Bray's[5] method.

$$ClO_2 + 51 + 4H^+ \longrightarrow Cl^- + H_2O + 51$$
$$3ClO_2 + 5I^- \longrightarrow 2IO_3^- + 3Cl^- + 31$$

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[5] **Bray,** *Z. physik. Chem.*, 54,731 (1906).

The Ultraviolet Light Absorption of Ethyl Alcohol Purified by Different Methods.—According to Bielecki and Henri[1] the first ultraviolet absorption band of pure ethyl alcohol begins at about λ2500 Å., and extends, with increasing strength, down at least to 2100 Å. On the other hand, many of the impurities ordinarily found in ethyl alcohol (*e. g.*, aldehydes, resins, etc.), shows trong absorption bands at longer wave lengths. It follows that measurements of the absorption coefficients of ethyl alcohol in the threshold region, λ2500–3000 Å., should provide a very delicate method for the detection of impurities of this type.

We have observed a considerable variation in the absorption spectra in the threshold region of samples of ethyl alcohol purified by different methods, and believe that absorption measurements can be used to determine to some extent the efficiency of different methods of purification.

In Table I, and on Fig. 1, are compared the absorption coefficients of samples of ethyl alcohol which have been subjected to the following treatments. All distillations were made through a fractionating column, only the center portion of the distillate being collected in each case.

A. Stock 95% ethyl alcohol, without purification.

B. Alcohol "A" was dried over calcium oxide, then 1 g. of iodine added per liter of alcohol. The solution was allowed to stand for several days and then distilled. To this was added 1 g. per liter of pure powdered zinc, the mixture being refluxed for several hours and again distilled.[2]

C. To alcohol "A" was added, per liter, 25 cc. of 12 N sulfuric acid. The mixture was refluxed for several hours and distilled.

D The product from "C" was treated with 20 g. of potassium hydroxide and 10 g. of silver nitrate per liter, the mixture being refluxed and distilled.

E. Alcohol "D" was allowed to stand for one week over specially prepared pure calcium oxide, then distilled slowly on a water-bath.

F. Treatment same as in "E" except that the solid matter (calcium oxide and hydroxide) was filtered off before distillation.

G. Same as "E" except that the whole process, from first addition of calcium oxide, was carried out in an atmosphere of pure nitrogen.

H. Alcohol "D" was allowed to stand for one week over active aluminum amalgam, filtered and distilled.

The absorption measurements show clearly that the treatment of stock alcohol with dilute sulfuric acid, followed by distillation, produces a tremendous improvement in purity (curve C). Another marked improvement is produced by the treatment with alkaline silver oxide (curve D). This is no doubt due principally to the removal of aldehydes.

If the next step be distillation in air from calcium oxide, after standing, in the usual manner, a very pronounced increase in absorption is observed (curve E), indicating the formation of some absorbing impurity. Upon filtering off the calcium oxide before distillation, a less marked

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[1] Bielecki and Henri, *Ber.*, 45,2819 (1912); *Compt. rend.*, 155,456 (1912).

[2] Castille and Henri, *Bull. soc. chim. biol.*, 6,299 (1924).

TABLE I

ABSORPTION COEFFICIENTS

$\kappa \times 10^3$

A	A Stock 95%	B I_2 + Zn method	C H_2SO_4 + H20 distillation	D "C" + Ag_2O	E "D" + CaO distillation	F "D" + CaO filtered	G "D" + CaO in N_2	H "D" + Al amal.	I Henri values
3710	2.8		...		..				
3500	8.2		...		..				
3320	13.0		1.1		2.9				
3160	18.1		1.9		3.1				
3020	25.1		2.9	...	9.7		..		
2890	34.8	0.5	3.1	0.02	10.2	...	0.15	..	
2780	50.4	2.0	5.1	.4	13.7	1.7	.43	0.30	
2675	77.5	3.8	5.5	.5	15.1	3.1	.65	.45	..
2585	..	6.0	6.7	.9	17.6	4.5	1.2	.58	4.0
2500		8.8	9.6	2.0	20.3	6.4	2.2	1.33	6.2
2430		12.4	14.5	3.3	24.8	9.7	3.5	2.85	10.0

increase in absorption is obtained (curve F), and upon keeping the alcohol in an atmosphere of nitrogen during the entire treatment and distillation, no change in absorption is observed (curve G).

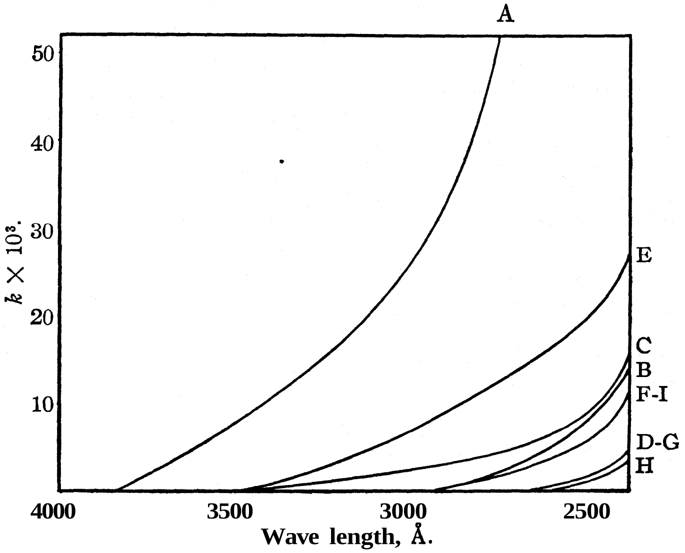

Fig. 1.—Absorption coefficients for various alcohol samples.

This suggests that the alcohol is oxidized by calcium oxide in the presence of air, the reaction proceeding very slowly at room temperature, and much more rapidly during distillation. The oxidation does not occur in the absence of oxygen, and hence the drying of ethyl alcohol over calcium oxide should be carried out in nitrogen.

Drying over aluminum amalgam gives the lowest absorbing, and hence the purest alcohol of any of the methods used here. It should be pointed out, however, that non-absorbing impurities, such as water, are not detected by absorption measurements. The electrical conductivity may be used to detect the presence of small amounts of water, and a comparison of the conductivities of the different samples indicated that aluminum amalgam is fully as efficient a drying agent as calcium oxide. Metallic calcium, used as a drying agent, failed to give any better results than calcium oxide, either for light absorption or conductivity.

The iodine–zinc method of purification (curve B) does not give quite as good results as the other methods.

It is of interest that the absorption measurements of Bielecki and Henri (column I) which are the lowest hitherto reported, agree almost exactly with our alcohol F, while our samples D, G and H show a lower absorption in this threshold region.

In short wave lengths, however, where alcohol itself absorbs strongly, one would expect the difference between the various samples to be slight.

Summarizing, light absorption measurements indicate that the standard practice of drying ethyl alcohol over calcium oxide should be carried out in an oxygen-free atmosphere. The highest degree of purity, as measured by the absorption spectrum, is obtained by the use of aluminum amalgam for drying.

CONTRIBUTION FROM THE
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[CONTRIBUTION FROM THE PURE OIL COMPANY]

SOME FACTORS AFFECTING THE CATALYTIC ACTIVITY OF COBALT OLEATE IN THE AUTOXIDATION OF PENTENE-2[1]

BY JULIUS HYMAN AND C. R. WAGNER

RECEIVED DECEMBER 12, 1930 PUBLISHED AUGUST 5, 1931

(A) Introduction

In a paper published some months ago,[2] the authors noted the catalytic activity of certain substances on the autoxidation of cracked gasolines. It was ascertained at that time that hydrogen chloride, for example, was a strong autoxidizing catalyst, whereas acetic acid was almost without effect. These reactions, as well as numerous other indications, prompted the authors[2,3] to propose a new theory of autoxidation based on the acidic

[1] Presented before the Petroleum Division of the American Chemical Society at Cincinnati, Ohio, September 9–13, 1930.

[2] Wagner and Hyman, 10th Annual Meeting, A. P. I. Report, 3rd section, pages 118–123.

[3] Hyman and Wagner, J. *Inst. Pet. Tech.*, 15, 645 (1929).

character of the autoxidation catalysts, as well as on the possibility of oxonium compound formation in the cases where peracids were felt to act as catalysts.

Among the compounds showing a decided catalytic activity was reported a mixture of cobalt and nickel acetate crystals, despite their apparent insolubility in gasoline. In work reported in a recent paper,[4] the authors have made use of this fact, using cobalt oleate as a catalyst in the autoxidation of the pentenes. Cobalt oleate (provided it is not removed too completely from its original solvent) is readily soluble in hydrocarbons.

Since the time that certain compounds were discovered to have a positive catalytic effect on the formation of pseudo-gum in cracked gasoline, the authors have felt that "promoted" autoxidation (*i.e.*, autoxidation which has been promoted by a foreign substance purposely added) could be brought under the same viewpoint as the "unpromoted" autoxidation. It is believed that the material to be presented in this paper tends to justify such an opinion.

The cobalt soaps have for years been used as "driers" in paints and varnishes and, according to various authorities,[5] are the most active of all the soaps in this respect. Kissling[6] recognized the action of the drying of an oil film to be in part, at least, an oxidation, and Fahrion[7] was quick to apply Engler and Weissberg's extension of the original Engler-Bach theory of autoxidation[8] to this problem. According to Fahrion's interpretation, the metals may act as carriers of atmospheric oxygen, transferring this oxygen either between two "acceptors"—olefin bonds of a drying oil—or else allowing half the oxygen to combine with water to form hydrogen peroxide. The manner in which such transfer was to take place was left moot, although Fahrion believed that the metal-oxygen combination was in the form of a metallic peroxide or hydro-peroxide. The theory, regarding the action of driers, which appears to have gained the most popularity is that of Ingle.[9]

Ingle's theory is an alteration and extension of Fahrion's theory, the most striking point of which is the postulation that only those metals act as siccatives (in the form of their soaps) which possess multiple valence states, and only then when the salts corresponding to the lower valence state are more stable than those corresponding to the higher state. In

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[4] Hyman and Wagner, THIS JOURNAL, 52, 4345 (1930).

[5] Fokin, *Seif.-Ztg.*, 34, 821 (1907); Eibner and Pallauf, *Chem. Umschau*, 32, 97 (1925); Mackey and Ingle, *J. Soc. Chem. Ind.*, 36, 317 (1917).

[6] Kissling, *Z. angew. Chem.*, 4, 395 (1891).

[7] Fahrion, *Chem.-Ztg.*, 1196 (1904).

[8] Engler and Weissberg, "Kritische Studien ueber die Vorgaenge der Autoxydation," Braunschweig, 1904.

[9] (a) Mackey and Ingle, *J. Soc. Chem. Ind.*, 35, 454 (1916); (b) 36, 317 (1917); (c) Ingle, *ibid.*, p. 319.

order to distinguish between the drying activities of the various metals possessing multiple valence states, Ingle further postulated that the more valence states a metal could assume, the more active it would be as a drier.[10]

That Ingle's scheme cannot express the action of driers completely is obvious, as its author admitted.[9b] For example, cobalt, having but two valence states is more active (in its soaps) as a drier, than is vanadium, with at least four. Furthermore, soaps of aluminum, calcium, sodium and silver act as driers to some extent, despite the fact that these metals possess but one valence state. The authors believe, with Ingle,[9] that their use of metal catalysts with unsaturated hydrocarbons parallels to quite an extent the use of such catalysts with the vegetable oils. In fact, metal catalysis in atmospheric oxidation does not seem to be limited to these fields at all, but appears to play a very important role in other branches of chemistry as well, as for example, in physiological chemistry.[11]

As a matter of fact, in the petroleum industry, metal catalysis in autoxidation is undoubtedly present. As a very minor but immediate example, the use of a copper dish for gum determination leads to inordinately high gum values, which can be accounted for only by assuming a catalytic activity of the copper, *i. e.*, the copper compounds formed by interaction of the acids present in the oxidized gasoline with the copper dish.

(B) Preliminary Preparations

It is now common knowledge that aldehydes such as benzaldehyde and acetaldehyde, when exposed to sunlight in the presence of oxygen, are converted partially at least into peroxides. In the absence of light a somewhat similar but much slower reaction takes place.

If, however, acetaldehyde is dissolved in alcohol to which a crystal of cobalt acetate and a few drops of acetic acid have previously been added, and if such a solution is permitted to stand under oxygen in the dark, the peroxide formation is even more rapid than in sunlight. During the reaction, the light pink solution is changed to olive-green. This reaction suggests that one of the reasons for the autoxidation of acid-free aldehydes in the dark may lie in the presence of traces of metallic salts as impurities.

It was decided to prepare a sample of cobalt oleate, free from solvent. This was tried both by methods of fusion and precipitation. The former method, however, never made a product free from fatty acid, and therefore the latter method was used throughout the work. The general method of preparation was, first, to make the potassium soap by allowing U. S. P. oleic acid, diluted with alcohol, to react with a 10% excess of potassium hydroxide dissolved in a large portion of distilled water. To this solution,

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[10] Fokin[5] also assumed this latter generalization.

[11] O. Warburg, *Ber.*, *58*, 1001 (1925).

after being filtered, was added either a slight excess or a slight insufficiency of C. P. $Co(C_2H_3O_2)_2\cdot 4H_2O$, also previously dissolved in considerable distilled water, and filtered. The precipitate of the cobalt soap formed immediately upon mixing. It was taken up in as little ether as possible, centrifuged, the ether extract filtered, and alcohol added until an ether–soap layer formed. A cobalt oleate solution, such as the layer just mentioned represents, is a deep purple, very heavy solution which hardens immediately on contact with air. The hardening is not due to oxidation, apparently, but rather to evaporation of the ether. If the ether–soap solution is evaporated in *vacuo*[12] a solid substance is formed, which, however, is not the pure soap but a combination of soap, alcohol and ether. If this material is heated on the water-bath in vacuum until the odor of alcohol is gone, a purple colored rubbery substance is formed which appears to be the cobalt oleate itself. The fact that it shows a cobalt content of 10.2–10.3% (the cobalt soap being ignited to the oxide, which is then reduced to metallic cobalt by hydrogen, and weighed as such), whereas theoretically cobalt oleate should contain but 9.48% of the metal, indicates that the U. S. P. oleic acid contains acids of molecular weights lower than that of pure oleic acid.[13] However, for the purposes of this work, it was necessary only to avoid the presence of free fatty acid, and therefore no attempt was made to purify the oleic acid further.

For the preparation of the cobalt oleate used in the main experiments, it was found advantageous to use chloroform instead of ether as a solvent, chiefly because of the very low solubility of water in the former. It was also found unnecessary to wash the chloroform extract with alcohol; thus, the chloroform solution was evaporated *in vacuo* in a water-bath heated to 60°, and the danger of decomposing the soap, consequently, considerably reduced. Such soap also shows a cobalt content of 10.2–10.3%. In the work herein reported the cobalt oleate was never freed from the original chloroform solvent but, rather, more chloroform was added to the solution.

(C) Experimental

If cobalt oleate catalyzes the autoxidation of the olefin bond, it should be an autocatalyst of itself, that is, it should hasten its own oxidation. Indeed, the induction period in this particular autoxidation should disappear entirely, for it is impossible to imagine a negative catalyst present in so large an amount as to prevent completely, even for a very short while,

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[12] A simple and satisfactory arrangement for vacuum evaporation consists of a heavy-walled lipless Pyrex dye beaker, a funnel whose rim fits the inner part of the rim of the beaker, and a ring of thin sheet rubber, used as a gasket. The suction pump hose is connected to the stem of the funnel. Care must be taken to prevent excessive foaming of the soap solution.

[13] Of course, there is always the possibility of the formation of a mixed soap, namely, cobalt aceto-oleate, in fairly constant proportions.

the autoxidation of so fairly pure a soap solution as the cobalt oleate solution prepared by us. Cobalt oleate, however, is not oxidized immediately, if exposed to oxygen in the dark. In fact, the oxidation does not become noticeable until a lapse of twelve to fifteen hours. The oxidation of cobalt compounds in organic media is readily visible by the color change. The original purple color changes first to brown, and then rapidly to an olive green. The experiment previously alluded to was carried out by allowing several drops of a chloroform solution of cobalt oleate to drop onto a piece of quantitative filter paper. The chloroform was evaporated by blowing with compressed oxygen, and the paper then placed in a four-ounce oil bottle, which was filled with oxygen and kept in the dark. The results obtained indicate quite clearly that some compound other than cobalt oleate is the real catalyst in the reaction. This compound seems to form slowly in the soap, induced perhaps through traces of impurities; for once oxidation has begun, it appears to proceed very rapidly. It usually appears to begin at the fringes of the spot of cobalt oleate. A drop of distilled water in the bottle seems to delay oxidation slightly; a trace of acetic acid appears to hasten the oxidation considerably; on the other hand, a drop of aqueous ammonia retards the oxidation for several days. The authors believe these exploratory experiments to be of considerable importance, for while the present-day tendency might be to interpret these results solely in the light of surface activity and hydrogen-ion concentration, the authors feel that a simpler and more fundamental viewpoint lies in assuming, on the one hand, the interaction of fatty acid and the cobalt oleate, at least minutely, to produce a complex acid possessing catalytic powers, while the ammonia, on the other hand, would tend to bind these acids, or even form amine-cobalt complexes so as to prevent the formation of complex acids.[14] The experiments previously spoken of were continued by determining the rate of autoxidation of pentene-2 in the presence of cobalt oleate alone, as well as in the presence of stearic acid and triethylamine. Pentene-2 was prepared from *sec.*-amyl alcohol and sulfuric acid.[15] It is the simplest of the amylenes to prepare with a fair degree of purity and has been shown by the authors[4] to be oxidized by molecular oxygen with comparative ease. The manner of carrying out the experiments and the mode of titration used was the same as that used by the authors in the paper just referred to.

The results in Table I substantiate the results obtained by noting the action of acetic acid and ammonia on drops of cobalt oleate solution taken up by filter paper (see page 3022). A very interesting point to note in Table I, however, is the initial "induction period," during which time oxida-

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[14] Mackey and Ingle[5] suggested that partial valences of the soap ions might play a part in the catalytic action of metal driers.

[15] Norris and Joubert, THIS JOURNAL, 49, 873 (1927).

TABLE I

RESULTS OF EXPERIMENTS

	Material	Cc. of 0.01 *N* $Na_2S_2O_3$ used after 4 hrs.	21 hrs.	45 hrs.	69 hrs.	117 hrs.	165 hrs.
1	Pentene-2, blank	0.00	0.00	..	..	0.00	0.00
2	No. 1 + 2 drops 14.4% soln. of $Co(oleate)_2$ in $CHCl_3$	.00	0.00	..	0.00	3.60	8.90
3	No. 2 + 2 drops 10% soln. of stearic acid in pentene-2	.00	1.30	3.20	5.40	..	..
4	No. 2 + 2 drops 10% soln. of $N(C_2H_5)_3$ in pentene-2	.00	0.00	..	..	0.00	0.00

tion does not appear to take place (see the first column of Table I). If the idea of complex acid formation is adhered to, it is at once apparent that the tremendous catalyzing influence of cobalt soaps cannot depend on the action of a complex cobaltous acid in such quantities as might be found by simply mixing a cobaltous soap with a fatty acid. The remaining possibility is the activating influence of a complex cobaltic acid.

The fact that normal cobaltic salts are quite unstable excepting in strongly acid solution makes the preparation of cobaltic soaps by precipitation a rather difficult task. Fusion methods were felt by the authors to be unsatisfactory for this work, because of the possibility of formation of decomposition products which might mask the character of the results. It was therefore decided to oxidize a chloroform solution of cobaltous oleate, in the presence of oleic acid, using hydrogen peroxide of 10% strength as the oxidizing agent. The calculated amount of oleic acid was used, and 50% more hydrogen peroxide than the theoretical equation would require. The resulting product, which is of an olive-green color, was washed repeatedly with water, to remove the excess hydrogen peroxide, then heated for a half hour on the water-bath, any excess oleic acid removed by repeated extraction with ethyl alcohol, and the remaining ethyl alcohol and chloroform evaporated in *vacuo* as previously described. A cobalt determination gave the very surprising result of 13.4% cobalt in the new product, whereas the cobaltous material showed only 10.3% cobalt. The cobaltic material made without the addition of the oleic acid showed a similar analysis.

The most plausible explanation for the above-mentioned analysis lies in the assumption that the cobaltic compound formed from the oxidation of cobaltous oleate immediately splits off oleic acid, a certain amount of which is removed by alcohol extraction. A simple analogous experiment may be conducted as follows.

Dissolve a few crystals of cobalt acetate in a little 95% alcohol. Add a few drops of 10% hydrogen peroxide. The purple solution becomes olive-green so rapidly that the intermediate brown state is scarcely perceptible. If a little of this clear solution is poured on a piece of fine filter paper, the color distributes itself evenly over the entire blot. As the alcohol evaporates, the odor of acetic acid may be noticed. After standing overnight, the solution will have turned brown, and if a few drops are poured onto a piece of filter paper, the brown color will not spread with the liquid. This indicates that the (apparently) basic cobaltic acetate has hydrolyzed completely to form colloidal cobaltic hydroxide. It is logical to assume that a similar series of changes takes place with the oxidized cobaltous oleate. The complete hydrolysis, however, seems to take place very slowly, if at all. If a piece of cobalt oleate is exposed to the air for several days, the surface becomes sticky. If the surface is washed with alcohol, and the alcohol evaporated, a pale yellow film, evidently of oleic acid, remains behind.

In this way, then, the oxidation of a cobalt soap may produce its own fatty acid. Numerous series of tests similar to that recorded in Table I have been made, using a chloroform solution of the green cobalt*ic* oleate compound as a catalyst. A representative run appears in Table II. Because of the fact that only those values at the beginning of the runs are of immediate interest, only these have been noted. As the runs continued, the values for the various titrations merge into one another.

TABLE II

DATA OF A REPRESENTATIVE RUN

		Cc. of 0.01 N Na_2SO_3 used after		
	Material	**4 hrs.**	**28 hrs.**	**78 hrs.**
1	Pentene-2, blank	0.00	0.00	0.00
2	No. 1 + 2 drops 8.2% soln. of Co^{+++} compound in $CHCl_3$ + 4 drops pure $CHCl_3$	0.80[a]	5.20	10.00
3	No. 1 + 2 drops Co^{+++} soln. + 4 drops 10% stearic acid soln. in $CHCl_3$	0.90	5.55	11.95
4	No. 1 + 2 drops Co^{+++} soln. + 4 drops normal soln. NH_3 in $CHCl_3$	0.00[b]	0.00	7.10

[a] No. 2, titrated at the beginning of the test, showed practically no iodine liberation.

[b] Two drops of N ammonia solution added to sample after portion for first titration had been removed, to allow for ammonia lost by evaporation. No ammonia added thereafter for the remainder of the run. The amount of ammonia used at the beginning in series No. 4 was approximately double that needed to form a compound $(Co(NH_3)_6)X_3$.

The results of the experiments recorded in Table II attract attention in more than one respect. The most striking feature is the lack of an induction period in series 2 and 3.

Again, the influence of acidic and basic substances is apparent, quite in accordance with the authors' viewpoint. The fact that the plain cobaltic solution shows a high initial catalytic influence the authors would ascribe to the formation of a fairly stable complex cobaltic acid during the preparatory oxidation. The powerful inhibiting effect of ammonia leads the authors to the conclusion that so long as a strong free base is present, cobaltic soaps will not function as catalysts. As a concluding remark relevant to these experiments, therefore, it appears probable that when a cobalt soap acts as a catalyst, the oxidized soap is the active principle; furthermore, the most apparent explanation for the nature of this active principle is to assume the formation of a complex cobaltic acid.

(D) Theory

Provided one may then assume the active principle of a cobalt soap to be a complex cobaltic acid, and provided, furthermore, that one may generalize the case of cobalt soaps to driers in general, a logical picture of "promoted autoxidation" may be gained, somewhat as follows.

If the metals, present in their soaps, have several valence states, and if the metals were present originally in their lowest valence states, then the peroxides formed by autoxidation may raise the metals to higher valences. For example, Co^{++} will be raised to Co^{+++}, Mn^{++} will be raised to Mn^{++++} or higher and Pb^{++} will be raised to Pb^{++++}, which will be the normal valence states for these metals so long as any peroxides are present. If, therefore, complex acids are to be formed, the nuclear atoms will be Co^{+++}, Mn^{++++} and Pb^{++++}. Now, although Mn^{++++} and Pb^{++++} have not received much investigation regarding their complex-forming tendency, Co^{+++} is known as the ion possessing the greatest tendency in this respect. Cr^{+++}, which also possesses a high complex-forming tendency, is oxidized by peroxides to a higher valence state. Pt^{++++}, another complex-forming ion, acts as a rather good drier in the form of its soaps.

In 1899, Abegg and Bodländer[16] made the important observation that, in general, metallic cations form complexes more readily, the weaker their electro-affinities. This is equivalent in the case at hand to saying that the greater the oxidation potential exerted when a metallic ion existing in the presence of peroxides is reduced to its next lower valence state, the greater will be the tendency of that ion to form complexes. The very incomplete data on this subject[17] indicate clearly that the active siccative ions possess high potentials, the cobaltic ion heading the list. Thus, a bridge may be formed between the tendency toward complex formation and the drying powers of metallic soaps. It can hardly be doubted, however, that the stabilities of the individual acids (formed under the conditions of the autoxidation) play an important role in determining the activity of the soap in question.

As to the acidity of such complex acids, they all[18] belong to the class known as true acids, that is, compounds showing acidic tendencies even in so-called non-ionizing media, as distinct from the pseudo-acids,[19] to which category the plain fatty acids belong.

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[16] Abegg and Bodlander, *Z. anorg. allgem. Chem.*. 20, 471 (1899).

[17] See "International Critical Tables," 1st ed., Vol. VI, pp. 332–333.

[18] Hantzsch, *Z. Elekfrochem.*, 29, 231 (1923).

[19] Ref. 18, p. 227.

Conductivity experiments made some time ago in their laboratory by the authors has shown that vapor-phase gasoline which had undergone oxidation possessed to a very appreciable degree the ability to conduct the electric current. Hence, it is apparent that ions actually are present in such *a* medium. This information has been of value to the authors in explaining the results of their investigation on the autoxidation of the amylenes,[4] assuming that the atmospheric oxidation of amylenes also produces ions, or maintains ionization.

(E) Summary

1. Cobalt soaps of oleic acid have been prepared, and their catalytic effects studied.
2. It has been shown that the cobaltic soap is responsible for the great catalytic activity of cobalt soaps in promoting autoxidation.
3. It has further been shown that bases exert a negative whereas fatty acids exert a positive catalytic effect on autoxidation in the presence of a cobalt soap.
4. The activity of cobalt soaps has been explained on the assumption of the formation of a complex cobaltic acid.

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SALTS OF THE AMMONO-ENOLIC MODIFICATION OF QUINALDINE[1]

BY F. W. BERGSTROM

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Introduction

Since the group —CH=N— is related to ammonia as —CH=O is related to water,[2] it follows that the heterocyclic nitrogen compounds, pyridine, quinoline, isoquinoline and quinoxaline are aldehyde-acetals of an ammonia system. The aldehydic properties of pyridine, quinoline and isoquinoline are not marked, because of the stability of the six-membered ring they contain. Nevertheless, Mr. McAllister and the author have shown that all three of these compounds react with the Grignard reagent in ether at 150°.[3] Ziegler and his co-workers have quite recently

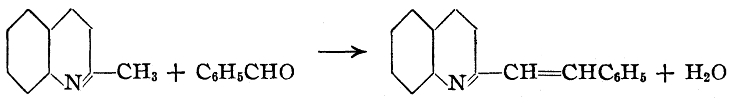
[1] Presented at the Berkeley, California, meeting of the National Academy of Sciences, September, 1930, and at the Eugene, Oregon, meeting of the A. A. A. S., June, 1930. Abstract in *Science*, **72, 402** (1930).

[2] This is not strictly true, since nitrogen is trivalent, while oxygen is divalent. The third valence of the nitrogen in the —CH=N— group may be attached to an alkyl or aryl radical, giving all of the ammono aldehydes the dual character of aldehyde-acetals [Strain, THIS JOURNAL, 49, 1559 (1927)].

[3] Bergstrom and McAllister, *ibid.*, **52**, **2845** (1930)

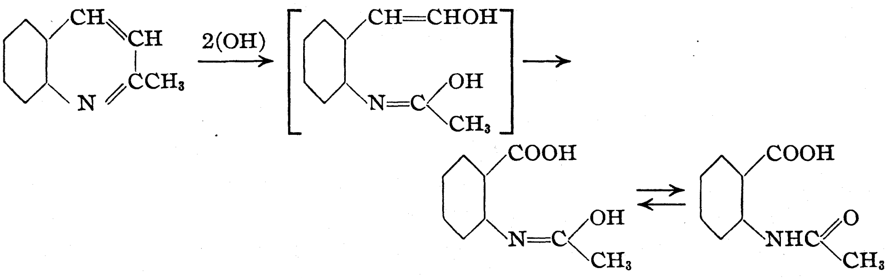
shown that the lithium alkyls and aryls, in ethereal solution, add very readily to the —CH=N— bond of these cyclic aldehyde acetals at ordinary temperatures[4] Quinoxaline, in distinction from pyridine, quinoline and isoquinoline, reacts with ethereal solutions of the Grignard reagent under ordinary conditions.[5] Quinoxaline therefore more closely resembles the familiar aquo aldehydes in its behavior.

If quinoline be regarded as a cyclic ammono aldehyde (-acetal) it follows that 2-methylquinoline (quinaldine) is a cyclic ammono ketone (-acetal) because it contains the grouping —N=C(CH_3)—.[6] In harmony with this view, quinaldine has been found to condense readily with benzaldehyde in the presence of zinc chloride to form benzylidene-quinaldine[7] in accordance with the equation



Clearly this type of reaction, which is by no means restricted to benzaldehyde and quinaldine, can be compared to the union of benzaldehyde with acetone to form dibenzalacetone. Reactions of this nature have led Mills and Smith[8] to compare quinaldine with the ketones of the water system.

The oxidation of quinaldine with potassium permanganate[9] yields N-acetylanthranilic acid, perhaps in accordance with the equation



The rupture of the carbon chain has occurred between the carbon of the ammono carbonyl group, =C=N—, and an adjacent carbon of the ring. The aliphatic aquo ketones on oxidation are similarly broken apart on one side or the other of the carbonyl group.

Many ketones of the water system are tautomeric, in that they exist

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[4] Ziegler, *Ber.*, 63, 1847 (1930); Ziegler and Zeiser, *Ann.*, 485, 174 (1931).

[5] Bergstrom and Ogg, This Journal, 53,245 (1931).

[6] Compare the O=C(CH_3)— group of the aquo ketones.

[7] Wallach and Wiisten, *Ber.*, 16, 2008, 2832 (1883); Jacobsen and Reimer, ibid., 2606.

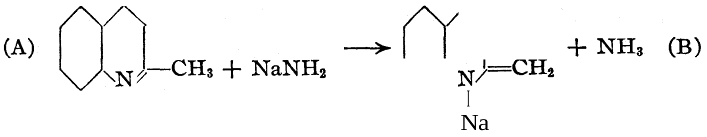
[8] Mills and Smith, *J. Chem. Soc.*, **121**, 2724 (1922).

[9] Doebner and v. Miller, *Ber.*, 15, 3077 (1882); Drewsen, *ibid.*, 16, 1955 (1883).

in a ketonic and an enolic modification, both of which are often capable of independent existence. In cases where both modifications cannot be isolated as such, derivatives of both forms may be known. This is true of quinaldine, since the ammono-keto form is the only one that has been obtained, although many reactions are best explained by the ammono-enolic formula, No. B below, in which Na is replaced by H.[8,10] The N-alkyl derivatives of this form (B) represent a rather reactive but definitely known class of compounds, the N-alkyl-2-methylene-1,2-dihydroquinolines.[11] The replacement of the N-hydrogen atom of formula B by potassium, sodium or other metals should likewise give fairly stable derivatives of the ammono-enol (enamic)[12] modification. It was for the purpose of preparing some of these compounds that the present investigation was undertaken. Ziegler and Zeiser[13] have already announced the preparation of the N-lithium salt of quinaldine ammono-enol (compare formula B) which was effected by the action of lithium phenyl upon quinaldine in ethereal solution. In the present work it is desired to bring to completion the study of the action of the alkali amides upon quinaldine in liquid ammonia, as reported in part last year by the author.'

Preparation of Salts of the Ammono-enolic Modification of Quinaldine.—In a preliminary fashion, it was found that the amides of potassium, sodium and lithium reacted readily with a solution of quinaldine in liquid ammonia at *+20* or −33° to form opaque rich red solutions of the ammono-enolic (enamic) modification of quinaldine. Thus sodium amide and quinaldine react in accordance with the equation

(I)



The isolation of the sodium salt in a state of fair purity is illustrated by the following typical experiment.

In one limb of a two-legged reaction tube[14] was placed 0.36 g. of metallic sodium, together with a coil of iron wire to serve as a catalyst for the reaction of sodium with the solvent to form sodium amide. The other leg contained 1.0 cc. of quinaldine, that is, approximately half the amount required by the above equation. After the disappearance of the blue color of the sodium solution, the quinaldine was washed into the leg containing the resultant sodium amide, whereupon an opaque red solution formed at once with a slight evolution of heat. To insure the completeness of reaction, the solu-

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[10] Chichibabin, *Ber.*, 60, 1607 (1927).

[11] Rosenhauer, Hoffmann and Unger, *ibid.*, 59, 946 (1926); cf. Mumm and co-workers, *Ann.*, 443, 272 (1925); Konigs, Köhler and Blindow, *Ber.*, 58B, 933–940 (1925).

[12] Short and Watt, *J. Chem. Soc.*, 2293 (1930).

[13] Ziegler and Zeiser, *Ann.*, 485, 179 (1931).

[14] Franklin and co-workers, THIS JOURNAL, 27, 831 (1905); 29, 1694 (1907); 35, 1460 (1913); *J. Phys. Chem.*, 15, 510 (1911); 16, 694 (1912).

tion above the remaining sodium amide was concentrated to a small volume and the tube set aside for a day. The concentrated red solution was carefully decanted into the clean leg of the reaction tube and evaporated to dryness by permitting the liquid ammonia to evaporate from the tube, since it proved impossible to induce crystallization of the salt even at −78°. The ammono-enol salt so prepared unavoidably contained the sodium amide that was simultaneously transferred in solution. Since the solubility of sodium amide in ammonia is of the order of a gram a liter at 20°, this error is not serious. The reaction tube, prepared in the customary manner for analysis, was evacuated at 20° and at 100–150°. The reddish-brown ammono-enolate solidified to a voluminous froth at the lower temperature. The loss of ammonia at the higher temperature is evidently attended with a slight ammonolysis of the salt, since a few very small droplets of liquid (quinaldine) condensed on the cooler portions of the tube. The specimen, after heating, was hydrolyzed overnight with water vapor, a yellowish very viscous liquid of somewhat sharp odor being formed. This was dissolved in dilute hydrochloric acid and analyzed for sodium.[15] A second aliquot was made alkaline with sodium hydroxide, the liberated base extracted with ether, the ether evaporated and the residue taken up in alcohol. From this alcoholic solution a picrate was prepared which could not be obtained in a pure state. Obviously quinaldine was not formed in any quantity by the hydrolysis of its heated potassium salt. This was not unexpected, since the heated salt was insoluble in ether, while the unheated material was readily soluble.

Quinaldine could be isolated when unheated specimens of the potassium and sodium salts of the ammono-enol were hydrolyzed. Apparently, the free ammono-enol first liberated in the hydrolysis is only partially converted to the ammono-keto form (ordinary quinaldine), the rest perhaps being polymerized to products of indefinite nature.

The lithium and barium salts of quinaldine ammono-enol were prepared in the same manner from quinaldine and the amides of lithium and barium, which were made by the catalytic action of iron wire upon liquid ammonia solutions of these metals. In neither of these cases does the reaction appear to be quite complete, since small amounts of quinaldine were always unattacked. Calcium amide reacts only to a very slight extent with quinaldine.

The potassium salt of the ammono-enol, prepared by the action of potassium amide upon quinaldine, could not be crystallized from ammonia solution at −78°.[16] Therefore, in order to accomplish its isolation, the product of the action of an excess of potassium amide solution upon quinaldine was freed from solvent ammonia (the liquid ammonia was evaporated from the tube and the latter evacuated) and extracted in the reaction tube with anhydrous ether.[17] The salt remaining after evapora-

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[15] One aliquot portion ($^{1}/_{4}$) was evaporated dry and gently ignited to carbonize the organic matter. Then sulfuric acid was added and after ignition the precipitate was weighed as sodium sulfate.

[16] Potassium amide is soluble in liquid ammonia to about the same extent.

[17] The stopcock of the evacuated reaction tube was immersed in ether and opened to allow the introduction of the required amount of ether. The stopcock was then closed. The ether in the tube, under its own vapor pressure, could be evaporated from one leg to the other in the same manner as liquid ammonia (procedure of E C. Franklin, unpublished work).

tion of the ether retained a small amount of both ether and ammonia at 20° in a vacuum. This was given off at 100°, but the salt simultaneously suffered some decomposition.

In duplicate experiments, in which the loss of weight occasioned (cf. Equation I) by the reaction of weighed quantities of potassium amide and quinaldine was determined,[18] it was found that the potassium salt of the ammono enol retained less than 0.1 mole of ammonia in a vacuum at 20°. Conversely, it was found that the sodium salt of quinaldine retained 0.561 mole of ammonia after intermittent evacuation at room temperatures for a period of two days. Ammonia in excess of half a molecule, at least, cannot be held by the salt as true solvent of "Crystallization."

TABLE I

ANALYSES OF QUINALDINE SALTS

Salt	Metal, % At 20°	Metal, % At 100–50°	Calculated for Anammonous salt	Calculated for Salt xNH$_3$	x
K	20.3, 20.2[b]	22.4, 21.5	21.6		
Na	12.3	13.9	13.9	12.6	0.5
Li[a]	3.74	3.80	4.66	3.80	2
Ba[a]	27.2	27.9	32.6	28.1	4
Ca	Reaction very slow and incomplete				

[a] These figures merely represent the maximum amount of lithium amide or barium amide dissolved by quinaldine, and do not quite correspond to definite compounds, since a little quinaldine was unattacked.

[b] Both ammonia and ether retained by salt. Two specimens analyzed.

An attempt to prepare the zinc and silver salts of the ammono-enol of quinaldine by metathesis in liquid ammonia resulted in failure. The precipitates obtained by adding a solution of the sodium salt of the ammono-enol to a solution of zinc cyanide or to silver iodide when washed proved to be, respectively, an impure zinc amide and a slightly impure metallic silver. Evidently the ammono-enolic modification of quinaldine is a very weak acid, since its zinc and silver salts are so completely ammonolyzed. The appearance of metallic silver instead of silver amide in the above reaction is probably due to a reduction of the latter to metal and the equivalent nitridation of the ammono-enol.

Preparation of Salts of Quinaldine in Other Solvents

Since the use of liquid ammonia is inconvenient for many laboratories, attempts were made to prepare the potassium and sodium salts of quinaldine in other solvents. It was found that quinaldine was unaffected by a solution of sodium ethylate in absolute alcohol at 20°, since the characteristic red color of the enolate failed to develop. The potassium and sodium salts of quinaldine were very slightly soluble in benzene and toluene but readily soluble in anhydrous ethyl ether and in quinaldine

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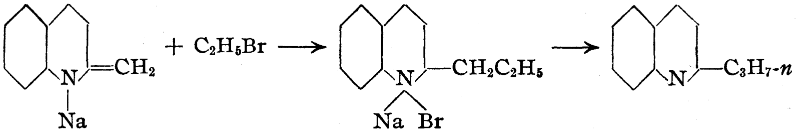
[18] *Cf.* Kraus and Greer, THIS JOURNAL, 45, 3079 (1923).

itself. Preliminary experiments indicated the feasibility of preparing these salts from sodium or potassium amide and quinaldine in absolute ether, but not in benzene or in toluene. The products must necessarily contain ammonia since a molecule of ammonia is liberated in the reaction. (Equation I.)

The Action of Alkyl and Aryl Halides upon Ether and Liquid Ammonia Solutions of the Salts of Quinaldine Ammono-Enol.—Since the sodium salt of the enolic modification of acetoacetic ester reacts with alkyl halides to form alkylated homologs of the keto form, it seemed probable that the related potassium and sodium salts of the ammono-enolic modification of quinaldine would behave similarly—and yield homologs of quinaldine with a lengthened side chain, in accordance with the type equation[19]

(II)



2-Ethyl, 2-n-propyl, 2-n-butyl and 2-ω-phenylethylquinolines were thus prepared by the action of methyl idodide, ethyl bromide, n-propyl bromide or benzyl bromide, respectively, on liquid ammonia or absolute ethereal solutions of the potassium salt of quinaldine. These reactions were conveniently carried out in a preliminary fashion in liquid ammonia reaction tubes. For the preparation of larger quantities of these homologs of quinaldine, it was necessary to adopt a different procedure, which may be illustrated by describing the preparation of 2-n-propylquinoline.

A Pyrex tube, 32 cm. long, 4.5 cm. in diameter and closed at one end was placed inside of a Dewar vessel of slightly larger internal dimensions. The top of the Dewar tube vessel was closed by a rubber stopper through which passed (1) a tube reaching to the bottom of the Pyrex tube lining the Dewar, (2) a short tube bent at right angles for introducing liquid from a tank of commercial anhydrous ammonia, (3) a similar bent tube for venting the ammonia that evaporates within the Dewar to the waste and (4) the tip of a 20-cc. buret, the latter passing through a hole in the center of the stopper. This arrangement is similar to that described by Wooster and Mitchell,[20] but differs from it in the use of a removable Pyrex tube to line the Dewar and in the use of a current of ammonia, introduced through tube (1), for stirring the reaction mixture. The use of a mechanical stirrer in these reactions was found to be unnecessary.

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[19] Since Rosenhauer, Hoffmann and Unger[11] have found that ethyl iodide and N-methyl-2-methylene-1,2-dihydroquinoline react to form 2-n-propylquinoline methiodide, the addition represented by the above equation has been assumed to proceed in a like manner. (A primary 1,3-addition to the enonium conjugated system of Decker,  $CH_2{=}C{-}\underset{|}{N}{-}$ [*Helv. Chim. Acta*, 13, 666 (1930).] Ziegler and Zeiser (Ref. 13) have discussed reactions of this type, and have prepared, among other compounds, 2-n-butyl- and 2-w-phenylethylquinoline by the action of *n*-propyl bromide and benzyl chloride, respectively, on the lithium salt of quinaldine.

[20] Wooster and Mitchell, THIS JOURNAL, 52, 691 (1930).

The Pyrex inner tube fitting the Dcwar having been filled approximately half full of liquid ammonia from the tank, the stopper was removed for a short while and 6.2 g. of metallic potassium introduced together with 0.1 g. of ignited ferric oxide to serve as a catalyst for the conversion of the liquid ammonia solution of potassium to potassium amide. When the conversion of the potassium to potassium amide was complete—as shown by the disappearance of the blue color of the metal solution—19.5 cc. (21.5) g. of quinaldine (0.9 equivalent) was slowly introduced from the buret, while ammonia gas was passed through tube (1) to stir the solution.[21] After standing for two or three hours to make sure that all of the quinaldine had been converted to the potassium salt, ethyl bromide was slowly run into the solution from the buret with stirring until the deep red color of the solution had disappeared. The reaction was fairly vigorous. The reaction product, 2-n-propylquinoline, partly separated as a liquid phase denser than the solvent. The Pyrex tube lining the Dewsr was now removed, the mouth loosely plugged with cotton, and the ammonia allowed to evaporate off under the hood (tube wrapped with toweling to prevent too rapid volatilization of the ammonia). The residue was treated with water to dissolve the potassium bromide and extracted twice with ether to remove the n-propylquinoline. The liquid remaining after evaporation of the ether was distilled in a vacuum, the fraction boiling at 124.5–126° (uncorr.) at 6 mm. being saved as the product; yield, 19.3 g. or 75% of the theoretical.[22]

Picrate, yellow crystals from alcohol, m. p. 162–163° (corr.);[23] mixed melting point with the picrate of 2-n-propylquinoline, prepared by the method of Meisenheimer and Schütze (m. p. 162–163°) is 162–163°, proving their identity.[24]

Methiodide, m. p. 181.7–182.7° (corr.):[24] Analysis of the dried picrate (Dumas): 0.1223 g. gave 13.70 cc. of nitrogen under standard conditions. Calcd. for $C_{18}H_{16}N_4O_7$: N, 14.0. Found: N, 14.0. Analysis of the free base: 0.2823 and 0.2580 g. gave 18.78 and 16.78 cc. of nitrogen under standard conditions. 0.1654 g. gave 0.5111 g. CO_2 and 0.1174 g. H_2O. Calcd. for $C_{12}H_{13}N$: C, 84.16; H, 7.66; N, 8.19. Found: C, 84.28; H, 7.94; N, 8.30, 8.13.

The results of the reactions of other alkyl and aryl halides with the potassium salt of quinaldine are summarized in Table II.

Experiments 1–6, inclusive, and 9 and 12 were carried out in the manner described under the larger scale preparation of 2-*n*-propylquinoline. About 10 g. of quinaldine

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[21] In order that the quinaldine may flow into the reaction cell, it was necessary to connect the top of the buret with the waste ammonia line, which, of course, was directly attached to one of the tubes (3) leading into the cell.

[22] It appears that 2-ethyl-, 2-n-propyl- and 2-n-amylquinolines undergo a slow change (absorption of small amounts of oxygen from the air?) over long periods of time, since analyses of old preparations of these substances (after redistillation in a vacuum) are invariably low in carbon (*cf.* analysis of 2-ethylquinoline). Therefore freshly prepared specimens of 2-n-propyl- and 2-n-amylquinolines were analyzed with the result that the percentages of carbon rose almost to the theoretical. (These analyses are included in the present article.)

The purity of all of the alkylated quinolines prepared in the present article was markedly lowered by using potassium amide much in excess of the amount required by Equation I. The excess of potassium amide appears to react with some of the alkylated quinoline produced in the reaction to form a potassium salt, which in turn is alkylated by treatment with an alkyl halide (*cf.* Ziegler and Zeiser, Ref. 13).

[23] 163–164° according to Meisenheimer and Schiitze, Ber., **56B**, 1356 (1923).

[24] M. p. 180°, Meisenheimer;[23] 184° Freund and Kessler, J. *prakt. Chem.*, ***98***, 243 (1918).

TABLE II

RESULTS WITH OTHER COMPOUNDS

	Halide	Chief organic product identified	B. p. (uncorr.), °C.	*P*, mm.	Solvent used	Yield, %
1	CH_3I	2-Ethylquinoline	123–126	5	NH_3, ether	46
2	C_2H_5Br	2-n-Propylquinoline	128–130	9	NH_3, ether	75
3	*n*-C_3H_7Br	Mixture, chiefly butylquinolines	146–165	10	Ether[a]	26
4	*n*-C_3H_7Br	n-Butylquinoline	139–143	5	NH_3	71
5	*n*-C_4H_9Br	*n*-Amylquinoline	140–142.5	4	Ether[a]	32
6	*n*-$C_5H_{11}Br$	Mixture of bases chiefly hexylquinolies	165–170	12	NH_3	38
7	C_6H_5Br	No reaction, even at 100°				
8	C_6H_5I	No reaction at 100° in toluene				
9	$C_6H_5CH_2Br$	2-Phenylethylquinoline	205–210	9	NH_3	34
10	$CHCl_3$	Quinaldine			NH_3	
11	CH_2Cl_2	Quinaldine			NH_3	
12	$Br(CH_2)_2Br$	Quinaldine			NH_3, ether"	
13	CH_2I_2	Quinaldine			NH_3	
14	$C_6H_5CH_2CH_2Br$	Reaction very slow, even at 50°			Ether[a]	
15	$Br(CH_2)_3Br$	Quinaldine			NH_3	
16	$C_6H_{11}Br$	Quinaldine + a little cyclohexylmethylquinoline(?)			Ether"	

[a] Some gaseous NH_3 always remained dissolved in the ether.

was used in each experiment, together with 1.1 equivalents of potassium. All other experiments were performed on a smaller scale in ammonia tubes. Where ether was used as a solvent, the potassium salt of quinaldine was first prepared in liquid ammonia, the latter evaporated and absolute ether added. The desired alkyl halide was introduced into this solution.

Notes on Identification

(1) **2-Ethylquinoline.**—Picrate, yellow needles from alcohol, m. p. 149–151°, (corr.).[25] Analysis of free base: 0.2537 g. gave 18.02 cc. of nitrogen under standard conditions. 0.1697 g. gave 0.5203 g. CO_2 and 0.1082 g. H_2O. Calcd. for $C_{11}H_{11}N$: C, 84.02; H, 7.06; N, 8.92. Found: C, 83.62; H, 7.13; N, 8.89.

(4) ***n*-Butylquinoline.**—Picrate, separating slowly from alc. soln., m. p. 163–165°, (corr.). The picrate of 2-n-butylquinoline melts at 162–163°.[26] Analysis of base: 0.3132 g. gave 19.62 cc. of nitrogen under standard conditions. 0.1692 g. gave 0.5224 CO_2 and 0.1266 H_2O. Calcd. for $C_{13}H_{15}N$: C, 84.26; H, 8.17; N, 7.57. Found: C, 84.25; H, 8.37; N, 7.84.

(5) ***n*-Amylquinoline.**—Picrate, yellow needles separating slowly from alcohol, m. p. 108.5–109.5° (corr.). Analysis of this picrate: 0.1240 g. gave 13.18 cc. of nitrogen under standard conditions. Calcd. for $C_{20}H_{21}N_4O_7$: N, 13.1. Found: N, 13.30. Analysis of the free base: 0.2935 and 0.3105 g. gave 16.18 and 17.53 cc. of nitrogen under standard conditions. 0.1536 g. gave 0.4748 g. CO_2 and 0.1201 g. H_2O. Calcd. for $C_{14}H_{17}N$: C, 84.36; H, 8.61; N, 7.04. Found: C, 84.31; H, 8.76; N, 6.89, 7.06.

For purposes of comparison, an independent synthesis of 2-n-amylquinoline was carried out by Mr. P. S. Winnek, who followed the method of Spath and Pikl[27] with a slight

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[25] Mulliken, Vol. II, p. 155, gives 146–147° (148°) as the melting point.

[26] Ziegler and Zeiser, Ann., 485, 184 (1931).

[27] Spath and Pikl, Ber., 62B, 2249 (1929).

modification. Butylidene quinaldine was prepared, in accordance with the directions of these authors, by condensing *n*-butyraldehyde with quinaldine; b. p. 162–165° at 5 mm.; 11.5 g. of this product was dissolved in absolute alcohol and reduced with gaseous hydrogen in the presence of platinum oxide according to the directions of Adams.[28] The calculated amount of hydrogen (one mole per mole of butylidene quinaldine) was absorbed in half an hour; b. p. of product saved, 150–151° at 5–7 mm.; yield, 5 g. or 43% of the theoretical. Analysis showed this fraction to have the composition of a slightly impure amylquinoline; picrate, m. p. 107.5–109.0' (corr.); mixed melting point with the picrate of n-amylquinoline prepared in liquid ammonia (m. p. 108.5–109.5") is 108.2–109.0°, showing their identity. The cause of the difference between the preparation of Spath and Pikl and the two specimens of amylquinoline prepared in the present work has not been determined.

(9) **2-ω-Phenylethylquinoline.**—Pale yellow liquid as first distilled, almost all boiling at 210" (uncorr.) (9 mm.). Most of the liquid solidified on standing. The crystals were freed from mother liquor by pressing on a porous plate, m. p. 28.5–29.5°, corr.[29] *Anal.* 0.1408 and 0.1652 g. gave 7.13 and 7.84 cc. of nitrogen under standard conditions. 0.1098 g. gave 0.3520 g. CO_2 and 0.0663 g. H_2O. Calcd. for $C_{17}H_{16}N$: C, 87.50; H, 6.49; N, 6.01. Found: C, 87.43; H, 6.69; N, 6.33, 5.93. Picrate, yellow needles, m. p. 131–132°, (corr.).[30] Analysis of this picrate: 0.1684 g. gave 16.41 cc. of nitrogen under standard conditions. Calcd. for $C_{23}H_{19}N_4O_7$: N, 12.1. Found: N, 12.2. In addition to this picrate there was obtained another picrate in smaller amount, melting at 120.5–121.5". Analysis of this picrate: 0.0538 g. gave 5.30 cc. of nitrogen under standard conditions. Calcd. for $C_{23}H_{19}N_4O_7$: N, 12.1. Found: N, 12.3. Therefore the two picrates have the same composition.

(10)–(16) Quinaldine, if reported as a product of the reactions summarized in the above table, was always identified as the picrate (m. p. 194–195°) and the identification confirmed by determining the mixed melting point of this with some known quinaldine picrate, m. p. 194–195°. The mixed melting points in no cases were changed. Quinaldine in these experiments did not appear to be formed quantitatively.

(16) **Cyclohexylmethylquinoline** (?).—The chief basic product of the action of cyclohexyl bromide on the potassium salt of quinaldine in liquid ammonia was quinaldine itself. A picrate, prepared from the higher boiling fraction (above 140° at 10 mm.) melted at 146.5–147.8° (corr.) after several crystallizations. *Anal.* 0.2679 g. gave 27.36 cc. of nitrogen under standard conditions. Calcd. for $C_{22}H_{23}N_4O_7$: N, 12.3. Found: N, 12.8. Perhaps this was the picrate of the expected 2-w-cyclohexylmethylquinoline. It was obtained in very poor yield.

Discussion

The reactions enumerated in Table II are evidently complicated to some extent by the ammonia retained by the potassium salt of quinaldine, this perhaps accounting for the partial regeneration of quinaldine in experiments (10) to (15) inclusive. If we assume that the potassium salt of quinaldine is slightly ammonolyzed in solution to potassium amide and quinaldine, the observed reactions may be due to the combination of potassium amide with the paraffin polyhalide. The alkyl mono halides

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[28] Adams and others, "Organic Syntheses," John Wiley and Sons, New York, 1928, Vol. VIII, p. 92. Spath and Pikl used a slower-acting palladium catalyst.

[29] M. p. according to Ziegler and Zeiser,[26] 28°.

[30] M. p. of the picrate of 2-ω-phenylethylquinoline according to Ziegler and Zeiser,[26] is 132°.

on the other hand must preferentially add to the enonium conjugated system, $CH_2{=}C{-}NK{-}$[19] in the manner of Equation II.

In this connection it is of interest to find that the potassium salt of the enol of acetophenone, prepared in liquid ammonia according to the directions of Strain,[31] reacts with ethyl bromide (the ammonia tube was cooled to −40° to permit the introduction of the ethyl bromide)[32] to form some acetophenone, but none of the expected butyrophenone. In the absence of liquid ammonia, alkylated acetophenones are formed in excellent yield.[33]

The Action of Heat upon the Salts of Quinaldine.—It has been previously recorded in this article that quinaldine may be recovered in fair yield from the products of hydrolysis of the unheated sodium and potassium salts of quinaldine. The failure to find quinaldine (except in two cases) in the mixture resulting from the hydrolysis of the heated potassium, sodium and lithium salts of the ammono-enol strongly suggests that these salts are thermally unstable.

In order to test this supposition, 5.2 g. of quinaldine was heated in a bomb tube with the potassium amide from 1.5 g. of potassium (1.0 equivalent) for six hours at 150°.[34] At the end of this time, the ammonia in the bomb was distilled off and the Pyrex tube containing the heated potassium salt immersed in a bath of liquid ammonia. Fresh ammonia was distilled into the tube, but the enolate was not completely soluble. Furthermore, ethyl bromide in excess of the calculated amount did not react vigorously with the opaque red solution, nor did it cause the complete decolorization of some reddish mud in the bottom of the reaction tube. The material remaining after evaporation of the ammonia was extracted with ether and the extract distilled. No picrate of 2-n-propylquinoline could be isolated in a pure state from any of the fractions. It is clear then that heating destroyed most of the potassium salt.

Attempt to Prepare the Ammono-enolic Form of Quinaldine.—A solution of the potassium salt of quinaldine ammono-enol, prepared in an ammonia reaction tube at ordinary temperatures, was decanted into a solution of an excess of ammonium bromide. The red color of the enolate did not completely disappear for a few seconds. This would indicate that the ammono-enol form of quinaldine or its ammonium salt has a transitory existence in ammonia solution at room temperatures. Ordinary quinaldine was recovered after evaporation of the solvent am-

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[31] Strain, THIS JOURNAL, 52, 3383 (1930).

[32] Compare Schurman and Fernelius, *ibid.*, 52, 2428 (1930).

[33] Haller, Bull. *soc. chim.*, [4] 31, 1973 (1922).

[34] Blair, THIS JOURNAL, 48, 91 (1926). The interior of the bomb was lined with a Pyrex tube closed at one end only. The formation of potassium amide and of the potassium salt of quinaldine in this tube was accomplished in the same manner as in the larger scale preparation of 2-n-propylquinoline, described above. The ammonia was evaporated from this reaction tube, which was allowed to warm up to room temperature before introduction into the bomb. Then, with the head of the bomb tightened, the desired amount of ammonia was distilled in and the bomb heated in an upright electric

monia and identified as the picrate, m. p. 194–195°, mixed melting point with authentic quinaldine picrate (m. p. 194–195°), 194–195°.

Nitridation of the Potassium Salt.—It was hoped that the addition of iodine to a liquid ammonia or absolute ethereal solution of the potassium salt of quinaldine would produce either 1,4-diquinolylbutane, or 2-o-iodoquinaldine. Neither of these compounds could be isolated as a product of the reaction. Large quantities of a reddish-black tar were formed, together with smaller amounts of quinaldine, irrespective of whether the reaction was carried out in ammonia or in ether. Bromine reacted in a similar fashion with a solution of potassium quinaldine ammono-enolate in ether with the formation of the same products.

Attempted Preparation of Quinaldine-2-acetic Acid.—It was hoped that this compound would be formed by passing dry carbon dioxide through a solution of the potassium salt of quinaldine in absolute ether.[35] The only organic product isolated in any quantity was quinaldine, while the potassium appeared to be converted to potassium aquocarbonate. No cyanamide (ammonocarbonic acid) or cyanate (mixed aquo-ammonocarbonic acid) was formed in the reaction. Ziegler and Zeiser[4b] obtained only quinaldine by the action of carbon dioxide on the lithium salt.

The Action of Acetophenone on the Potassium Salt of Quinaldine.—Acetophenone reacts with a liquid ammonia solution of potassium quinaldine ammono-enolate to form a precipitate of the sparingly soluble potassium acetophenone enolate[31] and quinaldine (the latter identified as picrate). The solution becomes colorless, indicating the complete disappearance of the quinaldine salt.

Notes on the Use of Iron and Cobalt Oxides as Catalysts in the Reaction between Potassium and Ammonia.—In one of the preceding experiments, a liquid ammonia solution of several grams of potassium was converted within a few minutes to potassium amide by the catalytic action of 0.1 *g.* ignited ferric oxide.[36] The latter is therefore a much more effective catalyst for this reaction than either metallic iron or platinum. The use of oxide catalysts in small quantity for the preparation of potassium amide at −33° is perfectly justified, provided the reaction is not influenced by the iron oxide or by traces of potassium oxide in solution. As a catalyst in ammonia tube experiments where one desires a potassium amide of highest purity, ferric oxide is not to be recommended. The following experiments illustrate the point in mind.

Three-tenths gram of freshly ignited ferric oxide was brought into contact with the potassium amide from 0.44 g. of potassium in an ammonia reaction tube at room temperatures. At the end of a day, the oxide, originally red, was coated with a thin black

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[35] The potassium salt still retained a small amount of ammonia.

[36] C. A. Kraus and students have long used ferric oxide as a catalyst for this reaction.

layer which slowly increased in depth during the next three and a half months. After this time had elapsed, the mixture of unchanged ferric oxide and the iron–nitrogen–potassium compound was washed with ammonia dried in a vacuum and dissolved in dilute sulfuric acid. *Anal.* Fe (in solution), 35.9; N, 9.1; K, 28.7; Fe_2O_3 (not dissolved by the dilute acid), 17.0. The precipitate reacted vigorously with water, and therefore resembled the iron–nitrogen–potassium compounds previously described.[37] Nearly all of the potassium oxide (or hydroxide) formed in this reaction was transferred to the other leg as a result of washing the black precipitate. This is to be expected only if the action of potassium amide on ferric oxide yields potassium monoxide, which Kraus and Whyte[38] have shown to be slightly soluble in ammonia.

Potassium hydroxide, if formed, would be slightly soluble in potassium amide solution, as the following experiment indicates: a strong solution of potassium amide, which had been in contact with a stick of potassium hydroxide in one leg of an ammonia reaction tube at room temperatures, was decanted into a much larger volume of pure ammonia in the other leg of the tube. There resulted immediately a precipitate of fine white needles. These were washed with ammonia and analyzed. Calcd. for KOH: K, 69.7. Found: K, 69.6; N, a trace. Apparently the reaction of Kraus and Whyte, expressed by the top arrow in the following equation, is reversible

$$K_2O + NH_3 \rightleftharpoons KNH_2 + KOH$$

Ignited cobalt oxide (Co_3O_4) also proved to be an excellent catalyst for the potassium–ammonia reaction. Like ferric oxide, the oxide of cobalt was very slowly attacked by the potassium amide solution that resulted.

Summary

1. Quinaldine reacts readily with the amides of sodium, potassium and lithium and more slowly with barium amide to form salts of the ammono-enolic form. In this respect quinaldine behaves as a cyclic ammono ketone (ketone-acetal).

2. The potassium salt of quinaldine reacts with methyl iodide, ethyl bromide, n-propyl bromide and benzyl bromide to form, respectively, 2-ethyl-, 2-n-propyl-, 2-n-butyl- and 2-o-phenylethylquinoline. With n-butyl bromide, a base having the composition of an amylquinoline is formed in poor yield. Polyhalides of methane and ethane, in so far as investigated, react with the potassium salt in the presence of ammonia to regenerate quinaldine. Iodine and bromine convert the potassium salt largely to a tar.

3. The potassium salt of quinaldine has been shown to decompose in liquid ammonia solution at 150°. Decomposition likewise takes place in the absence of solvent at 100–150°.

4. Potassium amide in liquid ammonia solution reacts slowly with ferric and cobalto-cobaltic oxide to form potassium oxide or hydroxide and iron- or cobalt–potassium–nitrogen compounds. Potassium amide dissolves potassium hydroxide in small quantities, probably to form potassium oxide.

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[37] Bergstrom, THIS JOURNAL, 46,2635 (1924).

[38] Kraus and Whyte, *ibid.*, 48,1781 (1926).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, CHEMISTRY DEPARTMENT,
UNIVERSITY OF THE PHILIPPINES]

CERTAIN AMINO DERIVATIVES OF LAURIC ACID

BY D. M. BIROSEL

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The literature records a few amino derivatives of lauric acid. By coupling lauryl chloride with certain amino acids, Bondi[1] prepared lauryl-glycine and lauryl-alanine. By the same procedure, Guerin[2] obtained lauryl-toluidines. Condensing a-bromolauryl chloride with certain amino acids in the presence of sodium hydroxide and displacing the halogen atom with an amino group through the action of ammonia, Hopwood[3] and Weizmann prepared certain dipeptides. A search in the literature reveals the lack of reference on the preparation of a-aminolauric acid. This paper describes the preparation, characteristics of a-aminolauric acid and other amino derivatives of this long chain fatty acid.

Experimental Part

Source and Preparation of Lauric Acid.—Lauryl glyceride is the principal constituent of coconut oil, a Philippine produce of great importance. The mixed methyl esters of the fatty acids in the oil were prepared and fractionated under reduced pressure. The portion distilling at 148–155" under 18 mm. pressure was collected. This fraction was redistilled and the water-white liquid ester was preserved for use. The acid obtained from the ester melted at 43–44°.[4]

Preparation of α-Aminolauric Acid.—The method adopted by Adams and Marvel[5] in preparing α-amino-*n*-caproic acid was found applicable in the synthesis of α-aminolauric acid. To fifty grams of melted lauric acid were added 7.5 cc. of phosphorus trichloride and 11 cc. of bromine. The solution was refluxed in an all-glass apparatus provided with a trap to dispose of the escaping hydrobromic acid. Digestion was continued for eight hours, increasing the temperature of the bath to 100° toward the end. The yellow precipitate of phosphorous acid was allowed to settle and the clear liquid product was decanted gently.

Ten grams of the brominated acid chloride was hydrolyzed to obtain the free α-bromolauric acid. The acid was extracted with ether and after evaporating the solvent. a liquid residue was obtained. When cooled the product solidified but at room temperature it became liquid; 9.2 g. of this liquid product was treated with ammonia at 58° for several hours. A white precipitate separated. It was filtered by suction, washed with distilled water and afterward with methyl alcohol. The colorless powder was dried in the oven at 100" and about a 51% yield was obtained.

Acetyl-α-aminolauric Acid.—A trial experiment was undertaken to see whether acetic anhydride has any effect on α-aminolauric acid. A solid was obtained which melted

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[1] Bondi, *Biochem. Z.*, 17,543 (1909).

[2] Guerin, Bull. *soc. chim.*, 29, 1121 (1903).

[3] Hopwood and Weizmann, *J. Chem. Soc.*, 99,571–576 (1911).

[4] Taylor and Clark, THIS JOURNAL, 49,2829 (1927), recorded 43–44° as the melting point of lauric acid. Guerin[2] reported 44° as its melting point.

[5] Adams and Marvel, *ibid.*, 42, 319 (1920); Fischer, *Ber.*, 36, 2982 (1903); *ibid.*, 33,2381 (1900); Abderhalden, Ref. 1; Auwers and Benhardi, *Ber.*, 24,2222 (1891).

very much lower than the original compound. The experiment was repeated using 2 g. of the amino acid. It was digested for a few minutes with an excess of acetic anhydride. When all the solid amino acid had dissolved, the volume of solution was doubled by adding water. An oil separated which solidified. The solid was filtered, washed with water, crystallized from alcohol and dried.

Picrate of α-Aminolauric Acid.—Two grams of a-aminolauric acid was treated with 10 cc. of a concentrated alcoholic solution of picric acid. After digestion for a few minutes, the solid amino acid was completely dissolved. After diluting the alcoholic solution to twice its volume with water, a solid compound precipitated. It was filtered and washed with dilute alcohol. It was crystallized from 50% alcohol, giving pale yellowish crystals.

TABLE I

CONSTANTS AND ANALYTICAL DATA[a]

Compound	M. p., °C.	Formula	Nitrogen analyses, % Calcd.	Nitrogen analyses, % Found
a-Aminolauric acid	263 (dec.)	$C_{12}H_{25}O_2N$	6.50	6.60 6.66
Acetyl-a-aminolauric acid	93-94	$C_{14}H_{27}O_3N$	5.44	5.46 5.50
α-Aminolauric acid picrate	255–256 (dec.)	$C_{18}H_{27}O_9N_4$	12.60	12.20
Methyl a-aminolaurate	241–242 (dec.)	$C_{13}H_{27}O_2N$	6.11	6.27
Isopropyl a-aminolaurate	250–252 (dec.)	$C_{15}H_{31}O_2N$	5.38	5.39
n-Propyl a-aminolaurate	246 (dec.)	$C_{15}H_{31}O_2N$	5.38	5.23
Isobutyl α-aminolaurate	248–249 (dec.)	$C_{16}H_{33}O_2N$	5.16	5.17
Lauryl *p*-nitranilide	80	$C_{18}H_{28}O_3N$	8.75	8.55
Lauryl m-nitranilide	78	$C_{18}H_{28}O_3N$	8.75	8.74

[a] The writer is indebted to Professor Alfredo Santos of the School of Pharmacy, University of the Philippines, for the determination of nitrogen by micro analysis for the last six compounds.

Lauramide.—The amides of lower fatty acids have been prepared by treating their methyl esters with concentrated ammonium hydroxide and it was expected that lauramide could be obtained in this way. It was found, however, that ammonia had no effect on methyl laurate either at room temperature or at 60°. The compound was finally obtained by condensing the acid chloride with ammonia. Ten grams of lauryl chloride was added in small streams to a concentrated solution of ammonium hydroxide which was continually stirred. Methyl alcohol was added to the semi-gelatinous mass. A white solid separated from the alcoholic solution and from the filtrate two more crops of crystals were obtained when the volume of solution was reduced. Recrystallization from alcohol gave a product which was found to melt at 99–100°.[6]

When the residual filtrate was evaporated, a gelatinous mass was obtained. It was dissolved in alcohol and a compound was obtained which melted at 74–75°.[7] When the mixed melting point of this compound was taken with ammonium laurate obtained by passing ammonia into an absolute alcoholic solution of lauric acid, no depression in the melting point was noted. From the filtrate a very small amount of oily substances was obtained.

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[6] Blaise and Guérin, *Bull. soc. chim.*, **29**, 1209 (1903). reported lauramide as melting at 98–99°. The literature records from 97 to 103°.

[7] Falicola, *Gazz. chim. ital.*, **40**, II, 425 (1910), reported 75° as the melting point of ammonium laurate.

[8] Blaise and Guérin, Ref. 6, obtained a small quantity of oily substance when they prepared lauramide by condensing lauryl chloride and ammonia. They characterize it as lauronitrile.

Esters of α-Aminolauric Acid

Methyl a-hinolawate.— Methyl α-bromolaurate was prepared first by condensing 5 g. of a-bromolauryl chloride with methyl alcohol. The ester was purified by washing its ethereal solution with dilute sodium hydroxide. After evaporating the solvent, a liquid residue was obtained. The ester was acted upon by concentrated ammonium hydroxide for several hours at 58°. The white solid compound which separated was filtered, washed with methyl alcohol and dried in the oven at 100°.

Isopropyl **α-Aminolaurate.**—The a-bromolaurate of isopropyl alcohol was prepared by starting with 5 g. of a-bromolauryl chloride and excess alcohol. The purified liquid ester was treated with concentrated ammonium hydroxide at 58° for several hours. The white solid that separated was filtered, washed with methyl alcohol and dried in the oven at 100".

***n*-Propyl α-Aminolaurate.**—Five grams of the a-bromolauryl chloride prepared above was treated with excess propyl alcohol. The purified liquid ester was treated with ammonia at 58° for several hours. The white solid compound was filtered, washed with methyl alcohol and dried.

Isobutyl α-Aminolaurate.—Five grams of the a-bromo acid chloride was condensed with excess isobutyl alcohol. The liquid ester was purified by washing its ethereal solution with dilute sodium hydroxide. The halogen of the ester was displaced by an amino group when the ester was acted upon by ammonia at 58° for several hours. The amino compound separated as white precipitate from the solution. It was filtered, washed with methyl alcohol and dried.

Nitranilides

Lauryl-*p*-nitranilide.—One gram of *p*-nitraniline was condensed with a little excess of lauryl chloride. Upon warming the mixture, the solid nitraniline dissolved. The product was extracted with ether and washed with dilute alkali, afterward with distilled water. When the solvent was evaporated, a solid residue was obtained. The solid was crystallized from alcohol, giving fine short white needle crystals.

Lauryl-*m*-nitranilide.—Two grams of m-nitraniline was condensed with a little excess of lauryl chloride. The solid m-nitraniline dissolved when the mixture was warmed. The ethereal solution of the compound was washed with dilute sodium hydroxide and afterward with water. A solid residue was left when the solvent was evaporated. Crystallization from alcohol gave fine short needle crystals.

Summary

1. The preparation of a-aminolauric acid has been described.
2. Nine amino derivatives of lauric acid have been prepared.

MANILA, PHILIPPINE ISLANDS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

THE NUMBER OF STRUCTURALLY ISOMERIC ALCOHOLS OF THE METHANOL SERIES

BY HENRY R. HENZE AND CHARLES M. BLAIR

RECEIVED APRIL 13, 1931 PUBLISHED AUGUST 5, 1931

Although several attempts have been made by Cayley and others[1] to calculate the number of isomeric hydrocarbons of the methane series, little attention has been given to the similar problem of calculating the number of isomeric alcohols of the methanol series. This limited treatment[1g] undoubtedly depended upon the fact that the methanol homologs were considered as typical mono-substitution products of the paraffins; hence, it was logical to assume that the number of isomeric alcohols should be conditioned by the number of hydrocarbons from which, theoretically, the former might be derived. Such formulas as have been advanced for determining the number of isomeric alcohols of any given carbon content actually prove to be inadequate and erroneous. Hence, it seemed desirable to derive a formula which would estimate accurately the number of isomeric alcohols.

Our initial attempt sought to establish a simple mathematical relationship between the total number of isomers and their carbon content. It was soon realized that no such simple relationship exists, and the problem was solved only by recognition of the fact that the alcohols might be classified according to simple types, for each of which the number of isomers could be computed. The types into which the alcohols were divided were those commonly recognized in organic chemistry, namely, (1) primary, (2) secondary and (3) tertiary. The scheme for calculating the number of isomers of each type depends upon the method of forming their structural formulas.

(1) The structural formulas of the primary alcohols, RCH_2OH, of n total carbon atom content, may be formed from those of the alcohols of $n - 1$ carbon atoms, ROH, by removing the OH group from each and attaching the resulting alkyl radical, R—, to the —CH_2OH group. Obviously, the number of primary alcohols that may be formed in this way will equal the total number of alcohols of all types containing $n - 1$ carbon atoms. This may be expressed as

$$p_n = T_{(n-1)} \qquad \text{(I)}$$

where p_n is the number of primary alcohols of n carbon atoms, and T_{n-1} is the total number of alcohols of all types containing $n - 1$ carbon atoms.

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[1] (a) Cayley, *Ber.*, 8, 1056 (1875); (b) Schiff, *ibid.*, 8, 1542 (1875); (c) Hermann, *ibid.*, 13, 792 (1880): 30, 2423 (1897); 31, 91 (1898); (d) Tiemann, *ibid.*, 26, 1605 (1893); (e) Delannoy, *Bull. soc. chim.*, [3] 11, 239 (1894); (f) Losanitsch, *Ber.*, 30, 1917, 3059 (1897); (g) Goldberg, *Chem.-Ztg.*, 22, 395 (1898); (h) David, *Rev. gen. Sci.*, 39, 142 (1928); (i) Trautz, "Lehrbuch der Chemie," Berlin, 1924, Vol. III, p. 23.

(2) The structural formulas of the secondary alcohols, RR′ >CHOH, of n total carbon atom content, may be formed from those of the alcohols ROH and R′OH (the carbon content of R— plus R′— always equaling $n - 1$) by removing the OH group from each and attaching the resulting alkyl radicals, R— and R′—, to the >CHOH group. The number of secondary alcohols that may be thus formed will equal the total number of possibilities, without exception or repetition, of combining simultaneously with the >CHOH group every value of R— taken one at a time and every complementary value of R′— also taken one at a time. These possibilities are theoretically of two types: (a) in which the two alkyl radicals, R— and R′—, are of unequal carbon content; and (b) in which these are of equal carbon content. Type (b) is actually impossible with an alcohol of an even number of carbon atoms for in that type $n - 1$ should be divisible by two. The number of isomeric secondary alcohols may be calculated by the following (finite) recursion formulas according to whether the carbon content is even or odd.

Even $$s_n = T_1 \cdot T_{(n-2)} + T_2 \cdot T_{(n-3)} + \ldots + T_{(n-2)/2} \cdot T_{(n/2)} \qquad \text{(IIa)}$$

Odd

$$s_n = T_1 \cdot T_{(n-2)} + T_2 \cdot T_{(n-3)} + \ldots + T_{(n-3)/2} \cdot T_{(n+1)/2} + \frac{T_{(n-1)/2} \cdot (1 + T_{(n-1)/2})}{2} \qquad \text{(IIa}'\text{)}$$

where T is the total number of alcohols of all types containing the number of carbon atoms represented by its subscript. Note that the subscripts in each term add up to $n - 1$, and that the number of terms is $(n - 1)/2$ for odd carbon atom content and $(n - 2)/2$ for even.

(3) The structural formulas of the tertiary alcohols, RR′ >C<OHR″, of n total carbon atom content, may be formed from those of the alcohols ROH, R′OH and R″OH (the carbon content of R— plus R′— plus R″— always equaling $n - 1$) by removing the OH group from each and attaching the resulting alkyl radicals, R—, R′— and R″—, to the >C<OH group. The number of tertiary alcohols that may be thus formed will equal the total number of possibilities, without exception or repetition, of combining simultaneously with the >C<OH group every value of R— taken one at a time and all complementary values[2] of R′— and R″— also taken one at a time. These possibilities are theoretically of three types: (a) in which the three alkyl radicals are of different carbon content; (b) in which two of the alkyl radicals are of equal carbon content and different from that of the third; and (c) in which the three alkyl radicals are of equal carbon content. Type (c) is actually possible only when $n - 1$ is divisible by three. The number of alcohols of each type may be calculated by the following (finite) recursion formulas for that particular type:

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[2] The values of R′— and R″— complementary to R— satisfy the relationship that the total carbon content of R— plus R′— plus R″— equal $n - 1$.

The number of isomeric tertiary alcohols of type (a) equals

$$\Sigma T_i \cdot T_j \cdot T_k \qquad \text{(IIIa)}$$

where i, j and k are integers, distinct, and greater than zero; $i + j + k = n - 1$; $i > j > k$.

The number of terms of type (a) depends on whether n is even or odd. Even: if $n/6$ or $(n - 2)/6$ is an integer, the number of terms of type (a) is $(n - 2)(n - 6)/12$; and if $(n + 2)/6$ is an integer the number of terms is $(n - 4)^2/12$.

Odd: if $(n + 1)/6$ or $(n + 3)/6$ is an integer, the number of terms is $(n - 3)(n - 5)/12$; and if $(n - 1)/6$ is an integer the number of terms is $(n^2 - 8n + 19)/12$.

The number of isomeric tertiary alcohols of type (b) equals

$${}^1/_2 \Sigma T_i \cdot (1 + T_i) \cdot T_j \qquad \text{(IIIb)}$$

where i and j are integers, distinct, and greater than zero, and $2i + j = n - 1$.

The number of terms of type (b) also depends on whether n is even or odd. Even: if $n/6$ or $(n - 2)/6$ is an integer, the number of terms of type (b) is $(n - 2)/2$; and if $(n + 2)/6$ is an integer, the number of terms is $(n - 4)/2$.

Odd: if $(n + 1)/6$ or $(n + 3)/6$ is an integer, the number of terms is $(n - 3)/2$; and if $(n - 1)/6$ is an integer, the number of terms is $(n - 5)/2$.

The number of isomeric tertiary alcohols of type (c) equals

$$\frac{T_i(1 + T_i)(2 + T_i)}{6} \qquad \text{(IIIc)}$$

where i is an integer, greater than zero, and $3i = n - 1$.

Obviously, there will never be more than one term of type (c) for any given value of n.

Grateful acknowledgment is made to Dr. Leo Zippin[3] and to Professor Orrin Fink, Jr., of Pennsylvania State College for their aid in checking the recursion formulas.

The actual use of these formulas may be illustrated in the calculation of the number of isomeric heptyl alcohols, $C_7H_{15}OH$.[4] Primary alcohols: $n = 7$

$$p_7 = T_6 = 17$$

Secondary alcohols: number of terms equals $(n - 1)/2 = 3$

$$s_7 = T_1T_5 + T_2T_4 + T_3(1 + T_3)/2$$
$$= 1.8 + 1 \cdot 4 + 2 \cdot 3/2 = 15$$

Tertiary alcohols: type (a), number of terms (for $(n - 1)/6$ = an integer) equals $[(n - 4)^2 + 31/12 = 1$

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[3] National Research Fellow in Mathematics.

[4] It is of interest to note that the total number of heptyl alcohols is erroneously stated as being 38 in Richter's "Organic Chemistry" (Spielmann), second edition, Vol. I, p. 121.

$$T_3 \cdot T_2 \cdot T_1 = 2 \cdot 1 \cdot 1 = 2$$

Type (b), number of terms (for (n − 1)6 = an integer) equals (n − 5)/2 = 1

$$T_1(1 + T_1)T_4/2 = 1(1 + 1)4/2 = 4$$

Type (c), number of terms (for (n − 1)/3 = an integer) equals 1

$$T_2(1 + T_2)(2 + T_2)/6 = 1(1 + 1)(2 + 1)/6 = 1$$

$$t_7 = 2 + 4 + 1 = 7$$

$$T_7 = p_7 + s_7 + t_7 = 17 + 15 + 7 = 39$$

The following table indicates the number of isomeric alcohols of the methanol series as calculated by the use of the recursion formulas.[5]

TABLE I

NUMBER OF ISOMERIC ALCOHOLS

Carbon content	Primary	Secondary	Tertiary	Total
1	1	0	0	1
2	1	0	0	1
3	1	1	0	2
4	2	1	1	4
5	4	3	1	8
6	8	6	3	17
7	17	15	7	39
8	39	33	17	89
9	89	82	40	211
10	211	194	102	507
11	507	482	249	1,238
12	1,238	1,188	631	3,057
13	3,057	2,988	1,594	7,639
14	7,639	7,528	4,074	19,241
15	19,241	19,181	10,443	48.865
16	48,865	49,060	26,981	124,906
17	124,906	126,369	69,923	321,198
18	321,198	326,863	182,158	830,219
19	830,219	849.650	476,141	2,156,010
20	2,156,010	2,216,862	1,249,237	5,622,109

Summary

1. No direct or simple relationship appears to exist between the total number of isomeric alcohols of the methanol series and their carbon content.

2. Formulas of the (finite) recursion type are advanced which permit the calculation from their carbon content of the number of primary, secondary and tertiary alcoholic isomers. In using these recursion formulas to calculate the total number of such alcohols of any given carbon content, the total number of isomers of every lesser carbon content must be known.

3. The totals so obtained agree exactly through the dodecyl alcohols

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[5] The structural formulas of the homologs of methanol, inclusive of the dodecyl alcohols, were written in connection with the derivation of these recursion formulas. The totals obtained from actual count of these structural formulas agreed exactly with those derived from the use of the recursion formulas.

with the numbers required by theory as tested by actually writing all the possible structural formulas.

4. The usefulness of the formulas advanced is not limited to the calculation of the number of structurally isomeric alcohols. Since the latter are typical mono-substituted derivatives of the paraffins, the figures recorded in Table I more generally represent the number of structurally isomeric mono-substitution products of the saturated hydrocarbons inclusive of the eicosanes.

AUSTIN, TEXAS

[CONTRIBUTION NO. 106 FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

SOME ORGANIC ACIDS IN BARLEY, MAIZE, OATS AND RYE PLANTS

BY E. K. NELSON AND H. H. MOTTERN

RECEIVED APRIL 23, 1931 PUBLISHED AUGUST 5, 1931

In continuation of the work on the organic acids of cereal plants, which began with a study of the acids of wheat plants,[1] an investigation has been made of the non-volatile acids in the green parts of the growing plants of barley, maize, oats and rye. The maize was raised in the field. The barley, oats and rye plants were grown in the greenhouse. All plants were beginning to head when cut. As in the case of wheat plants the investigation was confined to the non-volatile acids, extracted by boiling water from the dried, ground plants. These have not been previously reported in the literature.

Aconitic acid, previously reported as present in sugar cane[2] and in sorghum[3] and found in the wheat plant,[1] is present also in these plants of the grass family. Other acids in some of these plants which have not been found in numerous investigations of the acids of fruits are tricarballylic acid and malonic acid.

The Acids of Barley Plants.—The acids were separated from one hundred pounds of barley plants and converted into the ethyl esters, yielding 84 g. of crude esters. Fractionation at 10 mm. yielded: 1, 80–95°, 0.4 g.; 2, 95–105°, 0.6 g.; 3, 105–115°, 1.5 g.; 4, 115–125°, 5.2 g.; 5, 125–135°, 42.2 *g.*; 6, 135–150°, 1.1 g.; 7, 150–165°, 2.8 g.; 8, 165–173°, 21.9 g.; residue, 8 g.

Fraction 1 yielded oxalic dihydrazide, melting at 235° and further identified by optical crystallographic data.[4] The filtrate, seeded with malonic hydrazide, yielded a second crop of crystals, melting at 148–149° and further identified as malonic hydrazide by optical data.

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[1] Nelson and Hasselbring, This Journal, 53, 1040–1043 (1931).

[2] Behr, *Ber.*, 10, 35 (1877).

[3] Parsons, Jahresb., 1444 (1882).

[4] Optical crystallographic examinations were made by G. L. Keenan of the Food and Drug Administration.

Fractions 4 and 5 yielded malic hydrazide melting at 179°.

Fraction 7 was seeded with tricarballylic hydrazide, but the result was negative. Malic hydrazide was obtained instead, and was identified as such by its melting point.

Fraction 8 yielded a small quantity of hydrazide melting at 186°. When this was mixed with tricarballylic trihydrazide, the melting point was between that of tricarballylic trihydrazide and 186°. Optical crystallographic data showed it to be slightly impure tricarballylic trihydrazide.

The filtrate from tricarballylic hydrazide was seeded with citric hydrazide. On standing, citric trihydrazide separated. It melted at 108°, and was identified by the optical method. The yield of tricarballylic hydrazide was small as compared with that of the citric hydrazide, showing the fraction to consist mainly of ethyl citrate.

Aconitic acid was obtained from the ether extraction of the acids previous to esterification. The ether extraction afforded about 2 g. of crystals contaminated with an oily material. On purification the crystals melted at 180–181° and were further identified as aconitic acid by optical crystallographic examination.

Oxalic acid was determined by the method of Arbenz[5] and 0.019% was found on the basis of the green plants.

The Acids of Maize Plants.—The acids, separated as lead salts from ninety-six pounds of fresh maize plants in the roasting-ear stage of maturity, were converted into the ethyl esters, yielding 83 g. of crude esters.

Fractionated four times at 10 mm. the following fractions were obtained: 1, 85–95°, 2.1 g.; 2, 95–105°, 3.6 g.; 3, 105–115°, 2.8 g.; 4, 115–125°, 3.5 g.; 5, 125–135°, 20.2 g.; α_D −10.5"; 6, 135–145°, 1.8 g.; 7, 145–155°, 3.3 g.; 8, 155–165°, 11.1 g.; 9, 165–179°, 6.2 g.; residue, 28.0 g.

The hydrazides were prepared from these fractions. Fraction 1 yielded an immediate precipitate of oxalic dihydrazide, melting at 235° and further identified by optical crystallographic examination. The filtrate from oxalic dihydrazide was seeded with malonic dihydrazide, but with a negative result.

Fraction 2 yielded a mixture of oxalic and malic hydrazides; fraction 3, impure malic hydrazide; and fractions 4 and 5, pure malic hydrazide melting at 179°. From fraction 6 a few crystals of malic hydrazide were obtained. Fraction 8 afforded an oily hydrazide. The acid, isolated from the ester after saponification, melted at 180–181°, and was unsaturated. It was identified as aconitic acid by optical aystallographic data.

Fraction 9 gave an immediate precipitate of a crystalline hydrazide which after recrystallization from 75% alcohol melted at 182°, and which by optical crystallographic data was further identified as tricarballylic trihydrazide.

Citric acid was identified in this fraction by the Stahre[6] reaction, in which pentabromoacetone was formed. Oxalic acid, which was determined by the Arbenz method, amounted to 0.029% on the fresh basis.

The Acids of Oat Plants.—The acids, isolated as lead salts from one hundred pounds of oat plants, were brought into a rather concentrated water solution and extracted with ether in a continuous extraction outfit. The ether solution was washed three times with 5-cc. portions of water, and the washings were added to the aqueous solution of acids.

On evaporation, 9.42 g. of yellow, crystalline acids was obtained. This was recrystallized from ethyl acetate. It was mainly aconitic acid, as shown by optical crystallographic data and by the color reaction given by aconitic acid on heating with acetic anhydride.

The acids left after ether extraction were esterified, affording 13.5 g. of crude esters,

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[5] Arbenz, Mitt. *Lebensm. Hyg.*, 8, 98 (1917).

[6] Stahre, *Nord. Farm. Tidskrift.*, 2, 41 (1895).

which, on fractionating at 10 mm., yielded the following fractions: 1, 95–125°, 2.0 g.: 2, 125–130°, 8.7 g.; 3, 130–150°, 0.6 g.; 4, 150–160°, 0.5 g.

Fraction 1, on refractionating, gave fraction 1a, 90–110°; 1b, 110–120°; 1c, 120–125°. Hydrazides were prepared from these fractions.

From fraction 1a, a small quantity of malonic hydrazide was separated. There was not enough for a melting point determination, but it was identified by optical crystallographic data.

Fractions 1b, 1c and 2 yielded malic hydrazide. Fraction 3 yielded a mixture of malic and an oily hydrazide, and from fraction 4 a few crystals, identified by the usual methods as citric hydrazide, were obtained. These were associated with the oily hydrazide resulting, no doubt, from aconitic acid which had remained unextracted by ether. The content of oxalic acid, determined by the Arbenz method, was found to be 0.04% on the basis of the fresh material.

The Acids of Rye Plants.—The acids from one hundred pounds of rye plants, separated as lead salts and esterified, yielded 43 g. of crude esters.

Fractionation at 10 mm. afforded the following fractions: 1, 90–100°, 1.4 g.; 2, 125–135°, 14.9 g., α_D −9.75°; 3, 135–145°, 2.5 g.; 4, 145–155°, 0.9 g.; 5, 155–165°, 8.8 g.; 6, 165–175°, 4.0 g.; residue, 3.7 g.

The hydrazides were prepared from these fractions.

Fraction 1 afforded an immediate precipitate of a hydrazide, crystallizing in needles and melting at 235°, which corresponds to the hydrazide of oxalic acid. The filtrate from oxalic hydrazide was examined for malonic hydrazide, but none was found.

Fractions 2, 3 and 4 yielded malic hydrazide, melting at 178–179°.

Fraction 5 did not yield a pure crystalline hydrazide. It was, therefore, saponified and the acid separated. The acid was not completely soluble in water. Aconitic acid was identified in the water-soluble portion by optical crystallographic data and the color reaction with hot acetic anhydride. The water-insoluble fraction, a sirupy acid, was not identified.

Fraction 6 afforded an impure hydrazide. This fraction was then redistilled, and the hydrazide obtained from the redistilled fraction, melting at 104–105°, was further shown to be citric trihydrazide by optical crystallographic data. A determination of oxalic acid gave 0.048% on the basis of the fresh material.

Summary

Barley plants were found to contain aconitic, malic, citric, malonic, tricarballylic and oxalic acids. A determination of oxalic acid showed that it contained 0.019% on the basis of the fresh material.

Maize plants were found to contain aconitic, malic, citric, tricarballylic and oxalic acids. The percentage of oxalic acid in the fresh material was found to be 0.029.

Oat plants were found to contain aconitic, malic, citric, malonic and oxalic acids. 0.04% of oxalic acid was found in the fresh plants.

Aconitic, malic, citric and oxalic acids were found in rye plants. The undried plants contained 0.048% of oxalic acid.

The occurrence of aconitic acid in these members of the grass family, as well as in sugar cane and sorghum, is noteworthy.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH CHEMICAL LABORATORY, PURDUE UNIVERSITY AGRICULTURAL EXPERIMENT STATION]

THE VAN SLYKE METHOD FOR PROTEIN ANALYSIS AS AFFECTED BY FATS[1]

BY SIGFRED M. HAUGE

RECEIVED APRIL 29, 1931 PUBLISHED AUGUST 5, 1931

The Van Slyke method[2] for protein analysis was designed for the differentiation of pure proteins by the determination of chemical groups characteristic of certain amino acids. Wishing to investigate the distribution of amino acids in naturally occurring protein materials, numerous investigators attempted to use this method for the determination of the nitrogen distribution of various materials containing not only proteins but carbohydrates, fibers, fats and various other constituents present in plant and animal substances. The confusion arising from this work led Van Slyke[3] in 1915 to call attention again to the fact that his method was devised to be used with pure proteins, not accompanied by other substances.

The effect of carbohydrates and fiber on the Van Slyke method has been thoroughly investigated, especially by Gortner and his co-workers.[4] They have shown that these substances materially affect the nitrogen distribution of this method and have ascribed the effect to the action of the aldehyde group.

Although considerable work has been done on the effect of carbohydrates, a survey of the literature has failed to disclose any similar work having been conducted on the effect of fats and related compounds on the Van Slyke method. However, Morrow[5] stated: "The Van Slyke method of analysis for the determination of certain amino acids is limited in its application to pure proteins, to solutions of practically pure proteins, or to protein substances comparatively free from carbohydrates, fibers, fats, etc."

It therefore seemed desirable to make a critical study of the effect of the presence of fat and related compounds on the nitrogen distribution of proteins as determined by the Van Slyke method.

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[1] Presented before the Division of Agricultural and Food Chemistry at the Indianapolis Meeting of the American Chemical Society, March 31, 1931. Published with the approval of the Director of the Purdue University Agricultural Experiment Station.

[2] D. D. Van Slyke, J. *Biol. Chem.*, 10, 15–55 (1911).

[3] D. D. Van Slyke, *ibid.*, 22, 281–285 (1915).

[4] (a) Gortner and Blish, THIS JOURNAL, 37, 1630–1636 (1915); (b) Gortner and Holm, *ibid.*, 39, 2477–2501 (1917); (c) Gortner, *J. Biol. Chem.*, 26, 177–204 (1916); (d) Holm and Gortner, THIS JOURNAL, 42, 632–640 (1920).

[5] C. A. Morrow, "Biochemical Laboratory Methods," John Wiley and *Sons*, Inc., New York, 1927, p. 161.

Experimental

Throughout this investigation, the technique for the Van Slyke method as summarized in Morrow's text, "Biochemical Laboratory Methods,"[5] was used. A description of the materials hydrolyzed as well as the results of the analyses are given in tables. The figures for each individual treatment represent the average of two, three or more determinations made from individual hydrolyses.

In the first series of experiments, the protein used was casein (Hammersten). Three grams of casein was hydrolyzed alone; in the presence of butter fat; in the presence of individual representative constituents of fat, such as glycerol, stearic acid, representing the saturated group of fatty acids, and oleic acid representing the unsaturated groups; and, finally, in presence of carnauba wax, which is not a triglyceride. The amounts of materials used and the results of the analyses obtained from these hydrolysates are given in Table I.

TABLE I

THE EFFECT OF THE PRESENCE OF FAT, GLYCEROL, STEARIC ACID, OLEIC ACID AND CARNAUBA WAX ON THE VAN SLYKE ANALYSIS OF CASEIN (AVERAGE RESULTS)

Material hydrolyzed, 3 g. of casein +	Ammonia nitrogen, mg.	Humin nitrogen			Basic nitrogen			Non-basic nitrogen		Nitrogen recovered, mg.
		Acid insol., mg.	Acid sol., mg.	P. T. A., mg.	Amino, mg.	Non-amino, mg.	Arginine, mg.	Amino, mg.	Non-amino, mg.	
	41.02	3.01	6.65	2.10	66.76	35.16	33.42	243.15	16.95	414.80
2 g. butter fat	41.42	2.59	10.34	3.54	61.62	36.64	29.96	230.72	20.28	407.15
2 g. glycerol	41.23	2.48	10.36	4.87	58.55	43.72	24.52	186.10	58.82	406.13
3 g. glycerol	41.46	2.79	19.39	5.60	54.95	53.43	21.68	174.66	60.54	412.82
3 g. stearic acid	41.20	2.73	6.58	2.14	68.92	35.24	33.08	240.96	13.84	411.61
3 g. oleicacid	41.37	3.23	6.36	2.00	66.38	34.42	33.32	237.42	15.92	407.10
3 g. carnauba wax	41.20	2.57	5.32	2.10	64.29	33.71	30.80	234.10	19.40	402.69

It will be noted that the ammonia nitrogen remained about constant in all cases. This was true also of the acid-insoluble humin. In the samples hydrolyzed in the presence of butter fat, there was an increase in the acid-soluble humin, the phosphotungstic acid humin and a decrease in the amino nitrogen of both the basic and non-basic fractions. As a consequence of the decrease in amino nitrogen, there is an increase in the non-amino nitrogen of these fractions because these values are obtained by the difference between the total nitrogen and the amino nitrogen. There is also a significant decrease in the arginine nitrogen value. The values for the other amino acids found in the basic nitrogen fraction are omitted because cystine is present only in small amounts and any values calculated for histidine and lysine which were based on such decreased amino and arginine values as obtained in the presence of fat, would be of no significance.

Since the Van Slyke method was found to be affected by fat, the next step was to determine the constituent responsible for this action. In the tests with glycerol, stearic acid and oleic acid, it was found that the fatty acids were without effect, while glycerol affected the same groups that were affected by the butter fat but to a greater extent. Thus it appears that glycerol is the reactive agent responsible for the effects produced.

The tests with carnauba wax were conducted for the purpose of determining the effect of wax, and especially of a material which is not a triglyceride, upon the Van Slyke method. The results show that carnauba wax had little, if any, effect on the nitrogen distribution.

These effects produced by fats and glycerol on the results of the Van Slyke analyses are in some respects similar and in others unlike that produced by carbohydrate material. Unlike the action of carbohydrates, glycerol or fats do not cause the formation of acid-insoluble humin, but in respect to the other fractions, the effects are similar. Gortner[4c] observed that in addition to the formation of acid-insoluble humin, carbohydrate material caused an increase in the acid-soluble humin, phosphotungstic acid humin and non-amino nitrogen, and a decrease in the arginine nitrogen and amino nitrogen, similar to that obtained in these experiments with fat and glycerol.

In the second series of experiments, gelatin (Bacto-Gelatine, Difco Standardized) was used as the protein. Since gelatin contains little or no tyrosine, tryptophane, cystine and histidine, it was thought that analyses of this protein with and without additions of glycerol might give an insight into the amino acid involved in the formation of the acid-soluble and phosphotungstic acid humins, as well as show what effect the absence of a number of amino acids might have on the other fractions. The results are given in Table II. It is to be observed that the results are quite different from those obtained with casein. There is no increase in the acid-soluble humin and phosphotungstic acid humin nitrogen. However, the amino nitrogen and arginine fractions are decreased in a similar manner as before.

TABLE II

THE EFFECT OF THE PRESENCE OF GLYCEROL ON THE VAN SLYKE ANALYSIS OF GELATIN (AVERAGE RESULTS)

		Humin nitrogen			Basic nitrogen			Non-basic nitrogen		
Material hydrolyzed	Ammonia nitrogen, mg.	Acid insol. mg.	Acid sol., mg.	P.T.A., mg.	Amino, mg.	Non-amino, mg.	Arginine, mg.	Amino, mg.	Non-amino, mg.	Nitrogen recovered, mg.
3 g. gelatin	18.18	0.29	1.48	5.38	110.80	61.53	67.76	209.21	53.37	459.24
3 g. gelatin + 3 g. glycerol	18.35	.31	1.38	5.20	80.90	88.90	56.4	190.22	71.48	455.74

The third series of experiments were performed to determine the effect of glycerol on arginine, tyrosine and tryptophane. These amino acids were Pfanstiehl products used without further purification. The results of these analyses are given in Table III. In the case of arginine, the arginine value and amino nitrogen were decreased by the presence of glycerol, Concerning the ammonia and humin nitrogen fractions, the differences were not large enough to be significant. For the unexpected presence of nitrogen in the non-basic fraction, no explanation is offered.

TABLE III

THE EFFECT OF GLYCEROL ON THE NITROGEN DISTRIBUTION OF SOME AMINO ACIDS (AVERAGE RESULTS)

Material hydrolyzed	Ammonia nitrogen, mg.	Humin nitrogen Acid insol., mg.	Acid sol., mg.	P.T.A., mg.	Basic nitrogen Amino, mg.	Non-amino, mg.	Arginine, mg.	Non-basic nitrogen Amino, mg.	Non amino, mg.	Nitrogen recovered, mg.
3 g. arginine	0.07	0.07	0.07	1.26	21.11	55.19	77.44	5.46	2.26	86.49
3 g. arginine + 3 g. glycerol	.14	.21	.21	1.94	17.28	57.76	61.04	3.98	4.67	86.19
2 g. tyrosine	.0	.0	.0					23.44	.0	23.44
2 g. tyrosine + 3 g. glycerol	.16	.0	4.52					14.30	4.22	23.20
3 g. tryptophane	.07	.70	0.42					20.69	19.35	41.21
3 g. tryptophane + 3 g. glycerol	.12	.80	1.12					17.95	22.26	42.25

The experiments with tyrosine clearly indicate that tyrosine hydrolyzed in the presence of glycerol tends to form acid-soluble humin. It is interesting to note that tyrosine has also been found to be responsible for the formation of acid-soluble humin when hydrolyzed in the presence of aldehyde~. There was a definite decrease in amino nitrogen.

Unlike the action of aldehydes on tryptophane,[4c] glycerol does not cause the formation of acid-insoluble humin. However, there is some indication that it does contribute some nitrogen to the acid-soluble humin. Again, it will be observed that glycerol caused a decrease in amino nitrogen.

Summary

1. The Van Slyke method for protein analysis is affected by the presence of fat.

2. The reactive constituent of the fat molecule is glycerol; the fatty acids such as stearic acid, representing the saturated group, and oleic acid representing the unsaturated groups, are without effect.

3. The significant effects produced by fat or glycerol are: an increase in the acid-soluble humin, in the phosphotungstic acid humin, and in the non-amino nitrogen, and a decrease in the amino nitrogen and arginine values.

4. Carnauba wax, which is not a glyceride, had little, if any, effect on the Van Slyke method.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE NATIONAL INSTITUTE OF HEALTH OF THE UNITED STATES PUBLIC HEALTH SERVICE]

THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. III. DIRECT INTRODUCTION OF GOLD INTO THE AROMATIC NUCLEUS

(PRELIMINARY COMMUNICATION)[1,2]

BY M. S. KHARASCH AND HORACE S. ISBELL

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Introduction

In previous papers by Kharasch and Isbell[3] the applicability of the Grignard reagent in the preparation of gold carbon compounds is discussed. The authors point out that in their experience the use of the Grignard reagent is definitely limited to the preparation of gold compounds of the ethyl radical and radicals that lie below the ethyl radical in the Table of Electronegativity of Radicals.[4] This limitation of the Grignard reagent, as well as the inapplicability of other indirect methods, to the preparation of aromatic gold compounds forced us to investigate the direct action of anhydrous gold chloride on aromatic compounds.

Fortunately, the direct action, whenever possible, of anhydrous auric chloride upon aromatic substances leads to the introduction of the gold into the aromatic nucleus and the formation of a compound $RAuX_2$. Our preliminary results indicate that direct "auration" is as general a reaction as nitration, halogenation or mercuration, except that it is a much faster reaction and the products of the reaction are much less stable.

Previous Work.—The action of aqueous solutions of auric chloride upon organic substances has been studied exhaustively.[5] The results of these studies may be summarized as follows: first, the reduction of a water solution of gold chloride by organic substances is a function of the hydrogen-ion concentration and in general the reduction is more rapid in alkaline solution. Second, organic substances may be divided into three classes based upon their behavior toward a water solution of gold chloride: (1) a class of substances which neither reduce nor extract gold chloride from a water solution (the saturated hydrocarbons belong in this class); (2) organic substances which are oxidized by a water solution of gold chloride

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[1] Published by permission of the Surgeon-General.

[2] This work is being continued by M. S. Kharasch and T. M. Beck.

[3] Kharasch and Isbell, THIS JOURNAL, 52,2919 (1930); *ibid.*, 53, 2701 (1931).

[4] Kharasch and Marker, *ibid.*, 48, 3131 (1926); Kharasch and Flenner (unpublished work).

[5] Lenher, *ibid.*, 24, 357, 918 (1902); 35, 550 (1913). See also Mellor. "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, 1923, Vol. III, pages 600–603, for numerous references.

with the consequent precipitation of metallic gold; (3) a class of substances which extract the gold chloride from a water solution.

Behavior of Anhydrous Gold Chloride toward Organic Reagents.—Our studies of the behavior of anhydrous gold chloride toward organic substances make it quite evident that the solvents belonging in Class 3, cited above, in reality do not extract gold chloride from water but a hydrated complex. Furthermore, our experience indicates that aromatic substances, as well as oxygen-containing aliphatic compounds, either react with anhydrous gold chloride to give, at least as intermediates, gold carbon compounds or combine with that reagent to form complexes. Saturated hydrocarbons and alkyl halides in the aliphatic series, and nitrobenzene in the aromatic series, appear to be the only compounds unaffected by anhydrous gold chloride. Nitrobenzene, incidentally, in spite of the appreciable solubility of anhydrous gold chloride in it, is thus far the only aromatic compound which we have found not to interact or form very stable complexes with that reagent.

The above conclusions are based upon the following considerations: (1) the behavior of anhydrous auric chloride toward benzene and other substances; (2) the behavior toward benzene and other aromatic substances of hydrated auric chloride or anhydrous auric chloride previously treated with small quantities of ether, alcohol, glacial acetic acid, etc.

The Reaction of Anhydrous Auric Chloride and Benzene,—When dry benzene is added slowly to anhydrous auric chloride, a vigorous reaction ensues—hydrogen chloride is evolved and 1,2,4,5-tetrachlorobenzene and aurous chloride may be isolated from the mixture. On the other hand, if finely divided anhydrous auric chloride is added to a large quantity of dry benzene (thiophene free), an immediate evolution of hydrogen chloride takes place and the solution acquires a red color which in a few minutes turns brown. If allowed to stand for a few moments longer, a bright yellow precipitate is formed. The precipitate thus formed is aurous chloride and the solution contains phenyl chloride.[6] The yield is 97.7% of the calculated amount.

However, if the reaction given above is stopped at the point where the brown precipitate is formed, a different result is obtained. This may be accomplished by the addition of ether, a few cc. of acetic acid, alcohol, ethyl acetate or other reagents containing oxygen. If an equal volume of ether is added a yellow solution results, without the formation of any aurous chloride. Upon evaporation of the ether–benzene mixture yellow crystals are obtained. These may be separated from the adhering gold chloride by

[6] In this connection the statement of Lenher, This Journal, 35, 552 (1913), is quite pertinent: "It has not been possible to produce aurous type of compounds (inorganic) by the use of an organic reducing agent." Under anhydrous conditions the formation of aurous chloride is quite the usual occurrence.

thorough washing with water and crystallization from alcohol. Beautiful, long, narrow crystals, which are almost colorless, are thus obtained. The analysis and behavior of the compound indicate that it is phenyl auric dichloride. The yield is 0.41 g. from 2 g. of auric chloride.

Anal. Subs. (dried over P_2O_5), 0.0597: Au, 0.0342. Calcd. for $Au(C_6H_5)Cl_2$: Au, 57.14. Pound: Au, 57.17.

The compound is difficultly soluble in water, readily soluble in salt solution, very soluble in alcohol, difficultly soluble in ether, insoluble in benzene and petroleum ether. It decomposes at 73–75" or upon long standing.

The first step of the reaction may therefore be postulated as follows

$$C_6H_6 + AuCl_3 \longrightarrow C_6H_5AuCl_2 + HCl \qquad (1)$$

It is quite likely that the molecule of phenyl auric dichloride reacts then with another molecule of benzene to give diphenyl auric chloride and hydrogen chloride.

$$C_6H_5AuCl_2 + C_6H_6 \longrightarrow (C_6H_5)_2AuCl + HCl \qquad (2)$$

The compound diphenyl auric chloride is evidently an exceedingly unstable substance and in the presence of hydrogen chloride the following decomposition takes place

$$(C_6H_5)_2AuCl + HCl \longrightarrow C_6H_5Cl + AuCl + C_6H_6 \qquad (3)$$

Our assumption of the instability of diphenyl auric chloride is based upon our attempts to prepare this substance directly from auric chloride and the Grignard reagent, and some rather extensive experiments to prepare the compound from phenyl auric dichloride and phenyl magnesium bromide. In all of the above experiments we were unable to isolate the compound diphenyl auric chloride.

The evidence adduced points to the conclusion that the addition of ether to the mixture of anhydrous auric chloride and benzene, at a point where the brown color is formed, effectively blocks the interaction of the phenyl auric dichloride with benzene by forming a stable complex between the ether and the phenyl auric dichloride.

Additional evidence regarding the combination of ether with anhydrous auric chloride lies in the fact that when we add ether to the benzene solution prior to the addition of gold chloride, no phenyl auric dichloride is formed. Furthermore, neither chloroauric acid nor hydrated gold chloride gives any gold organic compound when treated with benzene, as in the formation of phenyl auric dichloride. That this inhibiting effect of the ether is not due to a dilution effect is shown in a most striking manner by the fact that one drop of benzene in 10 ec. of petroleum ether reacts vigorously with dry auric chloride, while pure benzene will not react with anhydrous auric chloride which is simply moistened with ether.

Effect of Substituents upon Reactivity of Aromatic Substances and Anhydrous Auric Chloride.—Thus far the following gold–carbon compounds have been prepared by direct auration: phenyl auric dichloride, tolyl auric dichloride, diphenyl auric dichloride, methylsalicylate auric dichloride and o-nitroanisole auric dichloride. The latter substance has not been analyzed as yet. Only a preliminary study has been made of the action of gold chloride and of different types of radicals, their rates of reaction and the stability of the products. The time interval before the addition of the ether depends upon the particular compound into which gold is being introduced. If a reaction takes place with a high speed, obviously it is extremely difficult to stop that reaction at one of the intermediate stages.

Very negative radicals react very vigorously with auric chloride. Thus in a qualitative way we might arrange the aromatic hydrocarbons in the following order according to the vigor of their reaction with auric chloride: naphthalene, diphenyl, toluene and benzene. This arrangement of the substances is the same as that found for the electronegativity of the radical~. The instability of these organo-auric dichlorides is also in perfect accord with the hypothesis developed in the preceding section, that slightly electronegative radicals should form more stable compounds toward hydrolytic agents than the compounds of the more electronegative radicals.

The influence of different substituents in the benzene nucleus on the rate of reactions with anhydrous gold chloride is quite marked. Strongly electronegative groups, *i. e.*, NH_2, $-N(CH_3)_2$, OH, increase the speed of reaction and decrease the stability of the products. Weakly electronegative groups have the opposite effect. Thus the reaction between phenol and auric chloride is almost instantaneous, while the reaction with nitrobenzene is extremely slow, at ordinary temperature. Combinations of the two types of effects, for example, methyl salicylate and *o*-nitroanisole react to give fairly stable products. Between the substances which react extremely rapidly with auric chloride and lead to very unstable substances and those that react slowly are a large number of compounds which in the future will form the foundation for a chemistry of organic gold compounds.[7]

Gold Chloride as a Halogen Carrier.—If benzene is added dropwise to anhydrous gold chloride, a vigorous reaction takes place and 1,2,4,5-tetrachlorobenzene may be isolated from the residue. On the other hand, if a large quantity of benzene is added at one time, phenyl chloride is formed. We have shown previously that an intermediate compound, phenyl auric dichloride, is formed. This compound, similar to other

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[7] Not only do the aromatic compounds undergo direct auration but aliphatic compounds containing active hydrogen atoms undergo a similiar reaction. Thus, malonic acid reacts with anhydrous auric chloride with the liberation of hydrogen chloride and the formation of a gold organic compound. The latter resembles in properties phenyl auric dichloride. These reactions are being investigated.

organo-metallic compounds, reacts with chlorine gas to give auric chloride and phenyl chloride. In the presence of chlorine gas auric chloride can thus function as a halogen carrier. In actual experiments benzene was rapidly chlorinated when auric chloride was used as a catalyst. The chlorine was practically completely absorbed and one or more chlorine atoms easily introduced into benzene. Phenylauric dichloride reacted equally well as a catalyst.

This definite mechanism of the catalytic effect of auric chloride is of interest particularly when one bears in mind similar catalytic activity on the part of other metal catalysts where no such intermediates have been isolated, *i.* e., iron and aluminum. It is hard to see, however, in view of the difference in position of these metals in the electromotive series, how the isolation of the intermediate gold organic substances helps the theory of intermediate compound formation as applied to the other catalysts.

The gold halides may also be employed as condensing agents in the Friedel and Craft syntheses in place of the aluminum halides.

Properties of Aryl Gold Dichlorides.—Upon heating, the aryl gold dichlorides decompose at their melting points. They are instantly acted upon by strong reducing agents, such as stannous chloride or hydroquinone, and metallic gold is formed. This behavior of the aryl gold dichlorides is similar to that of the alkyl gold dichlorides and strikingly different from that of the dialkyl gold chlorides, which are very stable to reducing agents.

With thiosalicylic acid the aryl gold dichlorides react like auric chloride, namely, the auro-thiosalicylic acid is formed. The aryl gold dichlorides are also insoluble in water but quite soluble in sodium chloride solution, probably forming the chloroaurate complexes $Na^+(RAuCl_3)^-$.

In the case of phenyl gold dichloride the complex with sodium chloride, while stable toward heat in 0.4 M concentration, is rapidly decomposed in alkaline solution with the separation of metallic gold.

The analyses of the aryl gold dichloride offered some difficulty. Since they had to be washed with water to extract the unchanged gold chloride, they most likely combined with that reagent to form the complex $H^+(RAuCl_2OH^-)$, an assumption suggested by the ready solubility of the aryl gold dichlorides in sodium chloride. In view of the fact also that the substances were rather unstable, they had to be analyzed rapidly. The phenyl gold dichloride, which is the most stable of the aryl gold dichlorides we had prepared thus far, could be dried in *vacuo* to constant weight over phosphorus pentoxide. In the case of the other compounds, we had to work much more rapidly and thereby dry the materials less thoroughly. The analyses therefore indicate that while all solvents of crystallization had been completely removed from them, they all still contained a molecule of water of hydration. With better facilities, however, than we had available at the time, the water of hydration undoubtedly could be removed readily.

Experimental Part

The Reaction between Phenyl Auric Dichloride and Phenylmagnesium Chloride.—To 1.726 g. of phenylauric chloride dissolved in 200 cc. of anhydrous ether at −10°, the Grignard reagent from 1.044 g. (1.25 equivalents) of phenyl bromide was added drop by drop. During the addition of the reagent a small amount of gold precipitated. When the reaction seemed to be complete, 200 cc. of petroleum ether was added. The excess of Grignard reagent was then decomposed and the ether extract washed repeatedly with water and finally dried with sodium sulfate. The ether extract contained considerable gold. Upon evaporation of the ether, gold was precipitated. The product of the reaction was unstable and we were unable to isolate a gold–carbon compound.

The Preparation of Tolyl Auric Dichloride.—Tolyl auric dichloride is obtained by the action of auric chloride on toluene. Finely divided auric chloride is mixed with a small amount of toluene, whereupon hydrogen chloride is evolved, a brown precipitate separates, and the solution acquires a deep red color. After a few minutes ether is added, as in the case of benzene. Upon evaporation of the solvent the residue is washed with petroleum ether and then water. It is then crystallized from ether.

Anal. Subs., 0.0688: Au, 0.0364. Calcd. for $C_7H_7AuCl_2H_2O$: Au, 52.30. Found: Au, 52.91.

The compound is yellow and crystalline. It is soluble in alcohol, ether and benzene, and insoluble in carbon tetrachloride and petroleum ether. It darkens very quickly on exposure to strong light.

The addition of toluene to a nitrobenzene solution of auric chloride at −15° gave light yellow crystals whose properties were the same as those of tolyl auric dichloride.

An ethyl acetate solution of auric chloride did not react with toluene.

The Preparation of Diphenyl Auric Chloride.—Diphenyl auric dichloride, $C_{12}H_9AuCl_2$, was prepared from a petroleum ether solution of diphenyl and anhydrous auric chloride by essentially the same method that was used for the preparation of phenyl auric dichloride. The yield from two grams of auric chloride was 0.127 g. of diphenyl auric dichloride.

Anal. Subs., 0.0430: Au, 0.0192. Calcd. for $C_{12}H_9AuCl_2H_2O$: Au, 44.91. Found: Au, 44.95.

The compound is yellow and crystalline. It decomposes at about 65°. It is soluble in alcohol and ether, insoluble in petroleum ether and water. It is soluble in sodium chloride solution.

The Preparation of Methyl Salicylate Auric Dichloride.—Methyl salicylate auric dichloride was prepared by dissolving one gram of methyl salicylate in 50 cc. of petroleum ether. After the addition of 4 g. of auric chloride, the method for the preparation of gold compounds by direct "auration" as previously given was used.

Anal. Subs., 0.0993: Au, 0.0455. Calcd. for $C_8H_7O_3AuCl_2H_2O$: Au, 45.11. Found: Au, 45.82.

The compound is light yellow and crystalline. It is quite stable and melts and decomposes at 107°. It is soluble in alcohol and ether, insoluble in petroleum ether and water. It is soluble in sodium chloride solution. An alcoholic solution of the compound is decomposed very rapidly when treated with an alkali or sodium bicarbonate solution. Metallic gold separates in all cases.

o-Nitroanisole Auric Dichloride.—*o*-Nitroanisole when treated in cyclohexane solution with auric chloride reacted to give a crystalline compound. This was worked up in the usual manner. The compound was insoluble in petroleum ether, cyclohexane and water; it dissolved readily in alcohol.

Summary

1. It is pointed out that anhydrous auric chloride reacts rapidly, at ordinary temperatures, with aromatic compounds except nitrobenzene, with the liberation of hydrogen chloride and the formation of compounds $RAuCl_2$.

2. It is shown that anhydrous auric chloride reacts with most oxygen-containing substances, forming complexes.

3. Nitrobenzene is shown to be the only solvent, thus far discovered, which dissolves gold chloride without undergoing a reaction with that reagent.

4. The effect of substituents in the benzene ring on the speed of reaction of the compounds with gold chloride is discussed.

5. The behavior of aryl gold dichlorides toward reducing reagents is discussed.

6. It is shown that the aryl gold dichlorides, while insoluble in water, dissolve in sodium chloride solution probably forming complexes of the chloroaurate type.

7. The effect of gold chloride as a halogen carrier is discussed from the standpoint of the intermediate compounds that have been isolated, and the further reaction of those substances and chlorine.

8. The preparation and properties of the following aryl gold dichlorides are described: phenyl auric dichloride, tolyl auric dichloride, diphenyl auric dichloride, methyl salicylate auric dichloride and o-nitroanisole auric dichloride.

CHICAGO. ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE NATIONAL INSTITUTE OF HEALTH OF THE UNITED STATES PUBLIC HEALTH SERVICE]

THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. IV. GOLD IMIDE COMPOUNDS[1]

BY M. S. KHARASCH AND HORACE S. ISBELL

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Introduction

The elements of the first sub-group in the periodic system, *i.* e., copper, silver and gold, form two distinct classes of imide salts. Thus, copper in alkaline solution gives the well-known "biuret"[2] reaction with biuret and reacts readily also with other compounds which contain an imide group. Specifically, with succinimide, a complex salt,[3] $K_2Cu(C_2H_2O_2N)_4$

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[1] Published by permission of the Surgeon-General.

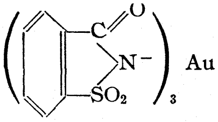
[2] Schiff, *Ber.*, 29, 298 (1896); *Ann.*, 352, 73 (1907); Rising and Johnson, J. *Biol. Chem.*, 80,709 (1928); Rising, Hicks and Moerke, *ibid.*, 89, 1 (1930).

[3] Tschugaeff, *J. Russ. Phys.-Chem. Soc.*, 7, 1083 (1906); *Ber.*, 40, 1973 (1907).

is formed. However, silver forms a normal salt with succinimide ($Ag(C_2H_4O_2N)$).[4]

The tendency of gold to form compounds of the chloroaurate type[5] is clearly shown by a new class of gold imide compounds which we have prepared.

Previous Work.—There are no gold carbonyl imides described in the literature. The sulfinimides, which are more acidic, form metallic salts more readily and a process has been described for the preparation of gold sulfinimides.[6] The method consists in treating the alkali salt of the sulfinimide with auric hydroxide. In the case of saccharin a compound of the following type is claimed



According to the disclosure in the patents, these gold sulfinimides give "the well-known gold reactions with stannous chloride or oxalic acid." Obviously these gold sulfinimides furnish an appreciable concentration of auric ions in solution. The patents further state that "the formation of these compounds is surprising, since by the use of aromatic carbonyl imides as for example, phthalimide, this reaction does not take place."

Our experience differs fundamentally from that of the above authors in the following respects: (1) we have been able to prepare gold carbonyl imide complexes. (2) The structures of the gold imide complexes are different from those assumed in the German patents. *(3)* The stability of our gold imide complexes is very great, for they do not give, at ordinary temperatures, tests for gold when treated with such reagents as stannous chloride or oxalic acid.

Properties of Imido-auric Acids.—The compounds of gold imides which we have prepared may be represented by the general formula $H^+[Au(imide)_4]^-$. We have designated them as imido-auric acids because their structures are similar to the structure of chloroauric acid. They give colorless solutions which are characterized by great stability toward both heat and reducing agents. Thus, neutral solutions of these compounds may be warmed without reduction with hydroquinone, stannous chloride or other powerful reducing agents, while strongly acid or alkaline solutions of the substances are only reduced upon warming. This great stability of the gold compounds toward reducing agents indicates that they do not ionize to give an appreciable quantity of gold ions.

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[4] Bunge, Ann. *Suppl.*, 7, 119 (1870); Ley and Werner, *Ber.*, 38, 2199 (1905); 40, 705 (1907)

[5] This tendency has been stressed in our previous papers, THIS JOURNAL, 53, 2701 (1931); 53, 3053 (1931).

[6] German Patents 347,139 and 348,070.

These complex salts of gold imides are also very stable toward mineral acids at ordinary temperatures. The addition of a mineral acid to a salt of the gold imides usually leads to the separation of the imido-auric acids. This behavior of the salts of gold imides is in striking contrast to the behavior of the salts of copper imides, which are decomposed instantly even by such weak acids as acetic.

The imido-auric acids are definitely acidic, forming well-characterized salts and reacting acid to indicators. In particular succinimido-auric acid is a relatively strong acid. It decomposes carbonates and turns Congo red blue Even more remarkable is the fact that ammonium succinimido-aurate may be crystallized from hot glacial acetic acid without decomposition. The acid properties of this succinimido-auric acid cannot be attributed to succinimide, for the latter is a very weak acid.

The alkali and alkaline earth salts of the imido-auric acids are extremely soluble in water, but insoluble in alcohol. On the other hand, ammonium succinimido-aurate is crystalline and difficultly soluble in water but more soluble in alcohol than the corresponding alkali salts. The presence of other salts, particularly salts of halides, such as sodium chloride, produces a great change in the solubility of some of these compounds. Thus, the difficultly soluble ammonium succinimido-aurate dissolves easily in dilute aqueous salt solutions of chlorides and bromides. The desirability of avoiding the presence of large quantities of salts in the preparation and crystallization of these compounds is obvious.

Some of the free acids are very soluble in water, for example succinimido-auric acid; others are difficultly soluble, such as the phthalimido-auric acid.

The Preparation of Imido-auric Acids.—The imido-auric acids are best prepared by the direct combination of gold hydroxide and the desired imide. In some cases the reaction takes place by simply heating an aqueous mixture of auric hydroxide and the imide. Usually, however, the reaction takes place more readily in the presence of a small quantity of a halogen salt or a mineral acid. The halogen salt or acid serves as a means of obtaining an appreciable quantity of auric ions in solution. This is particularly desirable since auric hydroxide is practically insoluble in water. In general, any substance which increases the concentration of auric ions in solution would increase the rate at which the imido-auric acids are formed. An excess of auric hydroxide is also employed and serves as a buffer to regulate the acidity. In some cases, due to the insolubility of the imide, it is necessary to use other solvents besides water, *i. e.*, a mixture of alcohol and water. A soluble salt of the imide may be used, but this increases the difficulty in the separation of the products of the reaction.

The Structure of Ammonium Succinimido-aurate.—Since the reaction between auric hydroxide and imides takes place slowly, the solution must be kept warm for a considerable period. This long heating may result in the hydrolysis of a portion of the imide, liberating ammonia, which may lead to the production of the ammonium salt of the imido-auric acid. Its formation in the presence of succinic acid indicates that the imido-auric acid is a relatively strong acid; otherwise it would not deprive succinic acid of the ammonium radical.

In order to establish the structure of ammonium succinimido-aurate, it was converted into the corresponding barium salt. This was accomplished by heating a solution of the ammonium salt with barium hydroxide, when ammonia was liberated and upon concentration of the solvent pure barium succinimido-aurate separated. Subsequently the barium salt was decomposed with the calculated quantity of sulfuric acid and the crystalline free acid was obtained. This crystalline free acid was then changed back into the ammonium salt by treating it with ammonium hydroxide. Furthermore, succinimide was recovered, practically quantitatively, by the reduction of ammonium succinimido-aurate with zinc.

Experimental Part

1. Ammonium **Succinimido-aurate, $NH_4Au(C_4H_4O_2N)_4 \cdot 4H_2O$.—To** 117 g. of succinimide and one gram of auric chloride dissolved in 500 cc. of water, moist auric hydroxide (equivalent to 40 g. of auric oxide) was added. The mixture was warmed on the steam-bath for forty-eight hours. Most of the auric hydroxide dissolved and a colorless product formed. Sufficient boiling water was then added to dissolve the crystals which had formed and the hot solution filtered. Upon cooling the filtrate, colorless crystals of ammonium succinimide-aurate separated. Sixty-six grams of solid was thus obtained. The product was crystallized from hot water and subsequently air dried at room temperature.

Anal. Subs., 0.1022: Au, 0.0296. Calcd. for $AuC_{16}H_{20}O_8N_5 \cdot 4H_2O$: **Au,** 29.02. Found: **Au,** 28.96.

Crystalline ammonium succinimido-aurate became anhydrous after drying for several months in *vacuo* over phosphoric anhydride. Samples were also dehydrated by drying for eight hours at 80° in *vacuo*.

Anal. Subs., 0.3624: Au, 0.1373; N, 29.5 cc. of $N/10$ acid. Calcd. for $AuC_{16}H_{20}O_8N_5$: Au, 32.47; N, 11.51. Found: Au, 32.51; N, 11.40.

The salt separates from water in transparent prismatic crystals, frequently in the form of almost regular hexagons but sometimes elongated; when viewed from the ends they are rectangular and from the sides trapezoidal.

An 0.1-g. quantity of the substance heated in a crucible, detonated violently. In a melting point tube, it decomposed at 270 to 280°, gradually turning purple and finally black, without melting.

The compound is difficultly soluble in water or dilute alcohol, insoluble in ether, benzene, chloroform and most organic solvents. It is fairly soluble in hot glacial acetic acid, crystallizing upon cooling. It gives colorless solutions in concentrated sulfuric acid which decompose when heated, with the precipitation of metallic gold. It is soluble in sodium carbonate solution or in alkalies, forming the corresponding alkali salts.

Two grams of ammonium suecinimido-aurate was dissolved in **50** cc. of hot glacial acetic acid. Upon cooling the filtrate **1.3** g. of crystalline ammonium succinimido-aurate separated, This was washed with ether and dried at 70° *in vacuo.*

Anal. Subs., **0.1062;** Au, **0.0345.** Calcd. for $AuC_{16}H_{20}O_8N_5$: Au, **32.47;** Found: Au, **32.49.**

A second lot of crystalline succinimido-aurate was obtained by the addition of ether to the mother liquor. The crystals weighed **0.6** g.

Barium Succinimido-aurate, $Ba[Au(C_4H_4O_2N)_4]_2$.—Two grams of ammonium succinimido-aurate was dissolved in **29** cc. of cold *N*/10 barium hydroxide. After solution the odor of ammonia was observed. The solution was concentrated in vacuo to about **5** *cc.,* when a small quantity of unchanged ammonium succinimido-aurate had separated. The clear filtrate was diluted with methyl alcohol until it turned slightly turbid, when crystallization of the substance occurred. After several hours the crystals were collected on a filter. It was crystallized from a mixture of alcohol and water. The pure product was dried at 70° *in vacuo* to the constant weight of **0.7514** g.

Anal. Subs., **0.0712:** Au, **0.0212;** $BaSO_4$, **0.0126.** Calcd. for $BaAu_2C_{32}H_{32}O_{16}N_8$: Au, **29.97;** Ba, **10.44.** Found: Au, **29.93;** Ba, **10.40.**

The crystals separated from dilute alcohol or water in long slender needles which formed in fan-like clusters. They were very soluble in water but insoluble in organic solvents. In a melting point tube the compound decomposed at 268–270°. **A** water solution was not reduced by aqueous solutions of hydroquinone or stannous chloride.

Succinimido-auric Acid, $HAu(C_4H_4O_2N)_4$.—To **0.5** g. of barium succinimido-aurate dissolved in **15** cc. of water, **7.6** cc. of *N*/10 sulfuric acid was added slowly while the solution was shaken vigorously. The barium sulfate which precipitated was collected on a **filter.** The clear filtrate was evaporated *in vacuo* to a sirup, which was brought to crystallization by the addition of a small quantity of alcohol. The crystals were collected on a filter, washed with alcohol, followed by ether, and finally dried at 80° in *vacuo.* The weight of material was **0.35** g.

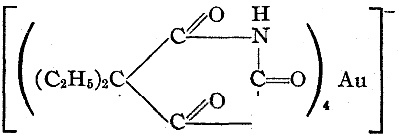
Anal. Subs., **0.0464: Au, 0.0154.** Calcd. for $HAuC_{16}H_{16}O_8N_4$: **Au, 33.19. Found:** Au, **33.19.**

When crystallized from dilute alcohol or water, succinimido-auric acid is obtained in the form of very fine needles. These needles are easily soluble in water, difficultly soluble in alcohol and insoluble in ether and ethyl acetate. In a melting point tube this compound decomposed at **210–240°,** depending upon the rate of heating.

A water solution of succinimido-auric acid was neutralized with a solution of ammonium hydroxide. **A** precipitate of ammonium succinimido aurate formed immediately. The crystals were collected on a filter and dried in *vacuo.*

Anal. Subs., **0.1056:** Au, **0.0342.** Calcd. for $NH_4AuC_{16}H_{16}O_8N_4$: Au, 32.47. Found: Au, **32.38.**

Separation of **Succinimide** from Ammonium **Succinimido-aurate.**—One gram of anhydrous ammonium succinimido-aurate, $(NH_4)Au(C_4H_4O_2N)_4$, was partially dissolved at room temperature in **25** cc. of water which contained **0.2** g. of sodium chloride, and one gram of granulated zinc was added. The mixture was allowed to stand at room temperature. After twenty-four hours considerable gold had been deposited and the solution had become distinctly alkaline. Dilute acetic acid was then added until the solution was neutral. Then the mixture was set aside for another twenty-four hours, when the hydrogen-ion concentration was adjusted again. After standing for about ten days all the gold had been reduced to the metal. The succinimide was then isolated in the usual manner. The weight of material was **0.6** g. and the melting point **116°.** After a single crystallization the melting point rose to 124°.

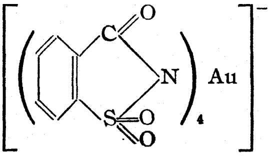
Barbital **Imido Auric** Acid  $\overset{+}{H}\cdot 3H_2O$.—Barbital (di-ethylbarbituric acid) in water solution reacts with auric hydroxide very slowly to give a silky precipitate. A water solution of barbital on standing for two months with four grams of auric hydroxide formed less than 0.5 g. of this silky precipitate. Even on warming on a steam-bath the rate of formation was very slow. The addition of a small amount of auric chloride or a drop of hydrochloric acid, however, greatly accelerated the rate of formation; other chlorides had the same effect.

0.01 mole of auric hydroxide was mixed with 0.04 mole of barbital and 50 cc. of water and two drops of concentrated hydrochloric acid was added. After digestion on the steam-bath for forty-eight hours, practically all the gold hydroxide had been changed to a white silky precipitate. Upon crystallization from 50% alcohol a pure compound resulted.

Anal. Subs., 0.1122, 0.1164, 0.1449, 0.0466, 0.0916: Au, 0.0232, 0.0236, 0.0294, 0.0096, 0.0188. Calcd. for $HAuC_{32}H_{44}O_{12}N_8\cdot 3H_2O$. Au, 20.41; N, 11.59. Found: Au, 20.68, 20.27, 20.29, 20.60, 20.52; average 20.47; N, 11.74, 11.42; average 11.57.

The compound is white and crystalline. It is soluble in dilute alcohol, very difficultly soluble in water and 95% alcohol, insoluble in ether, benzene and petroleum ether. It is not readily reduced by hydroquinone or sodium hydrosulfite. It decomposes at 200° to a black liquid.

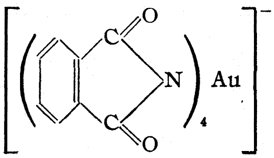
Sodium Salt of Barbital **Imido** Auric Acid.—Barbital imido auric acid dissolves in sodium hydroxide solution forming a sodium salt which may be precipitated by the addition of alcohol. This salt is very soluble in water. It is very stable toward reducing agents. A water solution of this salt, after careful acidification with hydrochloric acid, gives a precipitate of barbital imido auric acid.

Benzoic Sulfinimido-auric Acid $\overset{+}{H}$  $\cdot 3H_2O$.—Auric hydroxide reacts much more readily with saccharin than with any other compound which we tried, to form a complex imide. Due to the greater acidity of this group it is not necessary to add gold chloride or other substances in order to accelerate the reaction.

0.01 mole of auric hydroxide was digested with 0.04 mole of saccharin in water solution. A yellow crystalline compound resulted. After crystallization from 50% alcohol and drying for eighteen hours over phosphoric anhydride, the following analyses were obtained.

Anal. Calcd. for $HAuC_{28}H_{16}O_{12}N_4S_4\cdot 3H_2O$. Au, 20.41; N, 5.69. Found: Au, 20.14; N, 5.41.

The compound is difficultly soluble in dilute alcohol, almost insoluble in water and 95% alcohol, insoluble in organic solvents, slightly soluble in salt solutions but soluble in alkalies. It decomposes gradually without melting at 135°.

Sodium Phthalimido-aurate $\overset{+}{Na}$  $\cdot 3H_2O$.—The **reac-**

tion with phthalimide proceeds slowly and the addition of gold chloride or other salts is necessary. The separation from the reaction product of any unchanged phthalimide is difficult, due to the low solubility of the latter.

The sodium salt was prepared by the reaction between sodium carbonate, auric hydroxide and phthalimide. It was crystallized several times from alcohol–water mixtures.

Anal. Subs., 0.0938: Au, 0.0220; Na_2SO_4, 0.0094. Calcd. for $NaAuC_{32}H_{16}O_8N_4\cdot 3H_2O$: Au, 22.95; Na, 2.70. Found: Au, 23.45; Na, 3.24.

The compound is difficultly soluble in water, insoluble in alcohol, acetone, ether and slightly soluble in dilute alcohol. It was not reduced by hydroquinone or sodium hydrosulfide. It begins to decompose at 185°, gradually becoming black as the temperature rises.

This product was not quite pure, and it probably contained a small amount of sodium phthalimide, which resulted in a high sodium content. However, there is no doubt as to the identity of this compound, as its physical and chemical properties indicate that the compound is sodium phthalimido-aurate.

The authors wish to acknowledge their indebtedness to Dr. Carl Voegtlin of the National Institute of Health of the United States Public Health Service for his interest and the encouragement he has given them throughout the work on gold compounds.

Summary

1. It is shown that gold hydroxide reacts with carbonvlimides as well as with sulfinimides to give compounds of the chloro-aurate type. These compounds have been designated as imido-auric acids and are represented by the general formula $^{+}H[Au(imide)_4]^{-}$.

2. The great stability of the imido auric acids, as well as their salts, toward powerful reducing agents is discussed.

3. The acid character of succinimido auric acid $\overset{+}{H}[Au(succinimide)_4]^{-}$ is emphasized. It is shown that this acid is a stronger acid than carbonic acid.

4. The following representatives of a new class of gold carbonyl imides are described: succinimido-auric acid, ammonium succinimido-aurate, barium succinimido-aurate, barbitalimido-auri acid and sodium phthalimido-aurate.

5. A sulfinimide derivative, saccharinimido-auric acid, is described.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRY INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE MECHANISM OF SULFUR LABILITY IN CYSTEINE AND ITS DERIVATIVES. I. SOME THIO ETHERS READILY SPLIT BY ALKALI

BY BEN H. NICOLET

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It is the purpose of the present paper, first, to describe the behavior of certain ketonic derivatives of thio ethers which are somewhat remarkably labile toward alkali, and, afterward, to point out a probable relation between the behavior of these compounds and the problem of "labile sulfur" in materials of biological interest.

Generally speaking, the thio ethers, RSR', are very stable toward all hydrolytic agents. Even the mercaptans of hydrocarbon radicals are quite stable toward acids and alkalies. Recently Billheimer and Reid[1] have shown that certain aliphatic mercaptans, when heated for two hours at 260° with 3 N alkali, are only partially hydrolyzed, and these results may perhaps be taken as typical. Vorlander[2] found, not unexpectedly, that triphenylmethyl mercaptan was rather readily hydrolyzed.

Really striking lability of the single bond[3] between carbon and divalent sulfur, however, is to be found only in derivatives containing other substituents, suitably located, and of these the most effective appears to be the keto group.

The α-keto derivatives, $RCOCH_2SR'$, show in some cases considerable instability of the sulfur–carbon bond, particularly toward alkaline and reducing reagents, and it is of interest that no compound of the type $RCOCH_2SH$ appears to have been isolated in a state of purity. The hydrolytic splitting of such compounds seems, however, to have little relation to the common reactions of biological sulfur compounds, as it is frequently, if not generally, attended by the oxidation of the sulfur[4] and its replacement by hydrogen.

Particular attention must be paid, however, to the β-keto sulfides, $RCH(SR')CH_2COR''$. A number of these compounds have been made, chiefly by Ruhemann[5] (see also Posner[6]). The reaction involved is the

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[1] Billheimer and Reid, THIS JOURNAL, 52, 4338 (1930).

[2] Vorlander and Mittag, *Ber.*, 46, 3450 (1913).

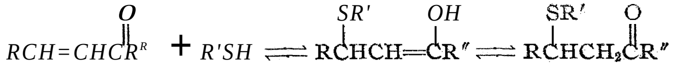
[3] The thio acids and their esters, as well as thiourea derivatives, are substances, the hydrolysis of which is well known and fairly well understood. They are expressly omitted from the present discussion.

[4] The compound $C_6H_5COCH(SCH_2COOH)C_6H_5$ (desylthioglycolic acid), for instance, deposits desoxybenzoin when dissolved in cold dilute alkali. This reaction is being studied and the results will be reported later.

[5] Ruhemann, J. Chem. *Soc.*, 87, 461 (1905).

[6] Posner, *Ber.*, 35, 809 (1902).

addition of a mercaptan to an a,@-unsaturatedketone, preferably with the aid of an alkaline catalyst, as in Equation A and is doubtless to be considered as a 1,4-addition to the conjugated series of double bonds.



$$RCH{=}CH\overset{O}{\overset{\|}{C}}R + R'SH \rightleftharpoons R\overset{SR'}{C}HCH{=}\overset{OH}{C}R'' \rightleftharpoons R\overset{SR'}{C}HCH_2\overset{O}{\overset{\|}{C}}R'' \qquad (A)$$

Ruhemann and Posner were both primarily interested in the sulfones to be obtained by the oxidation of their products, and neither appears to have noticed that, in the presence of alkali, the reaction represented in Equation A is quite easily reversed, and the initial products regenerated.[7]

Reading from right to left, Equation A represents this reversal as a 1,4-elimination from the enol form, with regeneration of the original conjugated unsaturated system. Easy reaction would accordingly be expected also for a substance of the type $RCH(SR')CH{=}CHCH_2COR''$, from the enol form of which 1,6-elimination of H and SR' should take place. But this latter case seems to have no present biochemical significance.

In the Experimental Part the preparation of certain of these β-keto sulfides and their behavior when treated with alkalies are described. Two examples may be discussed briefly at this point.

From benzalacetophenone and thioglycolic acid, the sulfide acid C_6H_5-$CH(SCH_2COOH)CH_2COC_6H_5$(I) was prepared. It does not dissolve in dilute caustic alkalies to give a clear solution, because of the ease with which benzalacetophenone is liberated. In 0.1 *N* sodium carbonate solution at room temperature it is more than one-third decomposed in one hour, as measured by the weight of crystalline benzalacetophenone of correct melting point obtained when the solution is filtered. The reaction goes to completion on longer standing. The ease of splitting is here very strikingly greater than that of the "labile sulfur" of, for instance, insulin, as determined by Abel and Geiling.[8]

In the case of β-*p*-tolylmercapto-benzylacetophenone, $C_6H_5CH(SC_6H_4CH_3)CH_2COC_6H_5$ (11), and similar compounds, the lack of a carboxyl group makes experiments in water difficult, as the substances dissolve appreciably neither in water nor in alkali. When, however, the substance II is dissolved in alcohol together with an excess of lead acetate (no reaction occurs at this stage) and treated with sufficient sodium hydroxide solution to make the final alkali concentration 0.1 molar, the yellow lead salt of *p*-tolylmercaptan is rapidly precipitated at room temperature. If the reaction is stopped after one minute by the addition of an excess of acetic acid, the decomposition is found to have been nearly quantitative,

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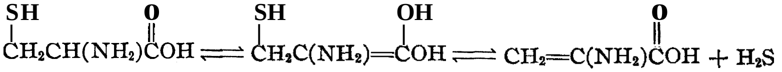
[7] Kohler and Reimer [Am. *Chem.* J., 31, 163 (1904)] have, however, made brief mention of the fact that the analogous sulfones are readily split by alkali to give sulfinates and unsaturated ketones.

[8] Abel and Geiling, *J. Pharmacol.*, 25,423 (1925).

as measured by the weight of the pure lead salt obtained. Other analogous derivatives were correspondingly reactive. Moreover, the substance II, when warmed on a steam-bath with a slight excess of phenylhydrazine in acetic acid, readily gives the sulfur-free 1,3,5-triphenylpyrazoline.

It should, perhaps, be emphasized here that the combined work of Ruhemann,[5] Kohler[7] and Posner[6] leaves no reasonable doubt as to the structures of thio ether derivatives of the type described.

Suggested Mechanism of the Reaction of Cysteine with Alkali.—In the previous section the action of alkalies on certain β-keto thio ethers has been discussed, but inspection of the formula of cysteine shows that it also has its —SH group attached in the β-position with reference to a —CO— group, and although the latter forms part of a carboxyl group, there is at least a formal analogy between the two types of compounds. Equation B is thus analogous to Equation A, above, reversed.



$$\overset{\text{SH}}{\overset{|}{\text{C}}}\text{H}_2\text{CH(NH}_2)\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OH} \rightleftharpoons \overset{\text{SH}}{\overset{|}{\text{C}}}\text{H}_2\text{C(NH}_2)\!=\!\overset{\text{OH}}{\overset{|}{\text{C}}}\text{OH} \rightleftharpoons \text{CH}_2\!=\!\text{C(NH}_2)\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OH} + \text{H}_2\text{S} \quad \text{(B)}$$

Equation B thus represents the idea that the removal of sulfur from cysteine by alkalies is due primarily to the presence of the sulfur in the position β- to the carboxyl group, and suggests that it takes place as a 1,4-elimination of hydrogen sulfide[9] from an intermediate enolized form. Various reasons for such a view will now be given.

That alkaline decomposition of cysteine (or cystine) involves the removal of H_2S (or H_2S_2) from the molecule, rather than simple hydrolysis (replacement of —SH by —OH), seems fairly certain and, incidentally, constitutes a striking analogy to the reaction of the β-keto sulfides. Clarke and Inouye[10] have recently given additional reasons for believing that aminoacrylic acid is one of the early products of the reaction. Baumann[11] long ago stated that S-phenylcysteine loses phenylmercaptan when heated with alkali, at least as rapidly as cysteine loses hydrogen sulfide under similar conditions.

It is, on the other hand, a well-known fact that the tendency to enolization of a carboxyl group is likely to be very small indeed compared to that of a keto group. Is the tendency in this particular case sufficient to justify the theory presented? Fortunately, evidence is available to test this point. There is very little doubt that the racemization of an optically active α-amino acid by alkali, when it occurs, is due to just this enolization process. Most of the common amino acids of biochemical interest show very little tendency to racemize except under quite extreme conditions. But serine (Daft and Coghill[12]) is apparently very readily

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[9] From cystine, RSSH, or eventually H_2S_2, would be split out.

[10] Clarke and Inouye, *J. Biol. Chem.*, 89, 399 (1930).

[11] Baumann, Ber., 15, 1733 (1882).

[12] Daft and Coghill, *J. Biol. Chem.*, 90, 341 (1931).

racemized by surprisingly dilute alkali, and the careful measurements of Andrews[13] on its analog, cystine, show that the latter is slowly racemized even by cold alkali, and at a rate several times (but not many times) more rapid than the rate of sulfur loss under the same conditions. This is as it should be, for enolization must cause racemization, but need not necessarily lead, in any given instance, to the loss of sulfur,

The loss of sulfur in alkaline cystine solutions is a relatively slow reaction. With boiling normal alkali, in the presence of excess lead oxide, it is about half complete in an hour (Clarke and Inouye[10]). The decomposition of the β-keto sulfides is so enormously more rapid than this that there seems to be no difficulty on this ground in accepting the suggested mechanism, as represented by Equation B.

But certain derivatives of cysteine and of cystine are known in which the sulfur is very much more labile than in the amino acids themselves. Referring only to substances of known constitution, glutathione shows very strikingly greater sulfur lability than does cysteine (Hopkins[14]). Dialanylcystine loses hydrogen sulfide (and sulfur) somewhat more readily than cystine, but very much less readily than does its anhydride.[15,16] Derivatives of cystinehydantoin[17,18] also show conspicuous reactivity. These results are of interest in relation with the fact that many proteins (and, of course, insulin) contain a portion of their sulfur in a form conspicuously more labile than that of cystine itself.

In this connection, attention must be called to the fact that modifications of the carboxyl group such as ester or amide formation are well known to increase the tendency toward enol formation with the hydrogen of the a-carbon atom. Applications of this fact in the biochemical field may be seen in the work of Dakin[19] and Levene[20] on the racemization of peptides and diketopiperazine derivatives. A detailed discussion of this point does not seem to be called for here, but it has already been pointed out that increased ease of racemization (of a cysteine or cystine residue) and increased ease of desulfurization should be expected to go together.

The conclusion to be drawn is that, on the basis of the theory presented in this paper, it would be expected that certain cystine derivatives should be more sensitive to desulfurization by alkali than cystine itself; and this expectation of increased sensitivity would apply specifically to those

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[13] Andrews, *J. Biol. Chem.*, 80, 191 (1928).

[14] Ropkins, *ibid.*, 84, 276 (1929).

[15] Bergmann and Stather, *Z physiol, Chem.*, 152, 193, 198 (1925).

[16] Brand and Sandberg, *J. Biol. Chem.*, *70,381* (1926).

[17] Bergmann and Delis, ***Ann.***, 458, 76 (1927).

[18] Nicolet, *J. Biol. Chem.*, 88, 403 (1930).

[19] Dakin, *ibid.*, 13, 357 (1912); Dakin and Dudley, *ibid* , 15, 263 (1913).

[20] Levene and Pfaltz, *ibid.*, 63, 661 (1925); 68, 277 (1926).

derivatives in which the carboxyl group of cystine is in peptide or analogous combination. Cystine peptides in which the carboxyl group remains free should, on the whole, be distinctly less reactive, not necessarily than cystine itself, but than somewhat similar peptides in the formation of which the cystine carboxyl takes part.[21] As glutathione (the reduced form) is known[22] to be γ-glutamyl-cysteyl-glycine, its special sensitivity is in accord with this expectation.

The existence of decidedly "labile" sulfur in many biological products has suggested to a number of workers in the past that these products must contain a portion of their sulfur in some unknown form, certainly different from cysteine. It should be pointed out that, as cysteine derivatives are known which show greatly increased sulfur lability, and as their behavior is only what would be expected on the basis of the ideas here presented, "labile sulfur" is scarcely to be considered as an indication of the presence of novel types of sulfur compounds.

Experimental

Benzylacetophenone-β-thioglycolic Acid, $C_6H_5CH(SCH_2COOH)CH_2COC_6H_5$, (I).—**Thioglycolic** acid (2.0 cc.) was dissolved in 25 cc. of absolute alcohol, and 2 N sodium ethylate (in absolute alcohol) added until 0.5 cc. more was present than necessary for neutralization to phenolphthalein. One mole of benzalacetophenone (5.2 g.) was then added, and the solution allowed to stand overnight. It was then just neutralized with acetic acid, poured into 100 cc. of 3% sodium carbonate solution and filtered promptly with suction from a gelatinous precipitate into a flask containing an excess of acetic acid. A crystalline precipitate formed, which melted at 120° and after two recrystallizations from five parts of alcohol melted constantly at 129°. The yield was about 40%.

Anal. Calcd. for $C_{17}H_{16}O_3S$: S, 10.67. Found: S, 10.72, 11.12 (Parr bomb).

If more alkali is used in the condensation, the amount of the precipitate is larger, and the acid cannot readily be obtained crystalline. The gelatinous precipitate dissolved with some difficulty in hot alcohol and after five recrystallizations melted at 199–200°. It was tentatively identified as the low-melting form of 1,3,5-tribenzoyl-2,4-diphenylpentane.

Hydrolysis of the Acid, I.—Half a gram of the pure acid was added to 25 cc. of normal sodium hydroxide. The solution was turbid from the beginning and soon deposited a heavy precipitate of crystalline material. On filtration after fifteen minutes a good yield of benzalacetophenone, melting at 55.5°, was obtained.

Even in 0.1 N sodium carbonate, a really clear solution of the acid could not be obtained. On standing at room temperature, the turbidity of the solution gradually increased, and after one and one-half hours filtration separated more than half of the calculated amount of benzalacetophenone. On longer standing, a further quantity separated. The solution contained thioglycolic acid. It is thus apparent that even under

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[21] It is almost obvious that the adjacent amino group would also exert an influence on the firmness of the sulfur bond. Modification of the amino group would therefore have its effect. It is, however. believed that the effect of the carboxyl, and particularly of the carboxamido group, is of decidedly greater importance.

[22] Nicolet, *J. Biol. Chem.*, 88, 389 (1930); Kendall, Mason and McKenzie, *ibid.*, 88, 409 (1930); Grassmann, Uyckerhoff and Eibler, *Z. physiol. Chem.*, 189, 112 (1930).

these very mild conditions the material breaks down to give the substances from which it was formed. It was to prevent, in so far as possible, a similar decomposition, that the crude solution of the sodium salt, in the preparation of the acid, was filtered directly into acetic acid

Benzylacetone-β-thioglycolic Acid, $C_6H_5CH(SCH_2COOH)CH_2COCH_3$.—This acid nas prepared essentially as described above, but from benzalacetone. It has not yet been obtained in crystalline condition, and its detailed description is therefore postponed

Benzylacetophenone - β - p - tolylsulfide, $C_6H_5CH(SC_6H_4CH_3)CH_2COC_6H_5$ (**II**)[5].—Molar proportions of benzalacetophenone (8 4 g.) and *p*-tolylmercaptan (5.0 g.) were dissolved in 40 cc of benzene, and a little 2 N sodium ethylate solution added (0.5 cc more than required to give a pink color with phenolphthalein). After standing overnight, 2 cc. of acetic acid and 25 cc. of alcohol were added. The product (crude yield 86%) was best purified by solution in its own weight of warm chloroform and addition of warm alcohol. It is soluble in hot alcohol to the extent of 7–8%, but quite difficultly soluble in cold alcohol. It melts at 113°.

Anal. Calcd. for $C_{22}H_{20}OS$: S, 9.64. Found: S, 9.72, 9.72 (Parr bomb).

When this sulfide was dissolved in acetic acid and warmed on the steam-bath with a slight excess of phenylhydrazine, p-tolylmercaptan was split out and 1,3,5-triphenylpyrazoline was easily formed in good yield. The product was identical with that formed from benzalacetophenone and phenylhydrazine.

Benzylacetone - β - *p* - tolylsulfide, $C_6H_5CH(SC_6H_4CH_3)CH_2COCH_3$ (**III**).—The preparation from benzalacetone followed closely that for its analog, II. The reaction was stopped by the addition of acetic acid without alcohol, the benzene solution evaporated, and the quite soluble residue crystallized from a small volume of alcohol. The pure substance melts at 64°.

Anal. Calcd. for $C_{17}H_{18}OS$: S, 11.85. Found: S, 11.96, 11.81 (Parr bomb)

Alkaline Hydrolysis of the Sulfides II and 111.—Due to the insolubility of these substances in water and in alkali, it was necessary to use alcoholic solutions, but since the reaction with alkali is reversible, an idea of its rate can only be got when one of the products is removed as it is formed. Accordingly, the following procedure was used.

One gram of the sulfide II was dissolved in 86 cc. of warm alcohol, and the solution rapidly cooled to 30–35° (it is then supersaturated). Twice the calculated amount of 20% lead acetate solution was then added (no coloration or precipitate was produced) followed by sufficient 6 *N* alkali to neutralize the acetic acid from the acetate and leave the solution 0 5 N with regard to alkali. A yellow precipitate began to form at once and after ten minutes an excess of acetic acid was added to stop the reaction. The orange precipitate soon became yellow and crystalline. It weighed 0.6 g. and was practically pure $Pb(SC_6H_4CH_3)_2$, melting at 205–208° to an orange-red oil. On treatment of the lead salt with potassium iodide and iodine, di-p-tolyl disulfide was obtained in good yield (m. p. 45.5") and fully identified.

When alkali concentrations as low as 0.1 N were used, an equally good yield of the lead mercaptide was obtained, and this was still true when the time of action of the alkali was reduced to one minute. Control experiment3 showed that reaction occurred only while the solution was alkaline.

The behavior of the sulfide III was similar in all respects.

Summary

Certain @-ketonicsulfides have been described which are split by alkali with rather extreme ease to give mercaptans and a,@-unsaturatedketones.

A structural analogy between these compounds and cysteine or cystine has been pointed out, and some of the reasons have been given for considering the action of alkali on the two classes of compounds as analogous. From these considerations, a mechanism for the alkaline decomposition of cysteine has been developed and reasons have been indicated for the anticipation of greatly increased reactivity in certain specified types of cysteine and cystine derivatives.

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[CONTRIBUTION RROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. XIII. OXIDATION OF METHYLDERRITOLIC ACID AND THE SYNTHESIS OF 2,3,5- AND 2,3,6-TRIMETHOXYBENZOIC ACIDS AND THEIR DERIVATIVES

BY L. E. SMITH AND F. B. LAFORGE

RECEIVED MAY 9, 1931 PUBLISHED AUGUST 5, 1931

As reported in previous articles,[1] derritol methyl ether is converted by catalytic hydrogenation into methylderritolic acid, which is oxidized by hydrogen peroxide in alkaline solution to a compound of the formula of a trimethoxyphenylacetic acid. We have also reported that this trimethoxyphenylacetic acid is oxidized by permanganate to a trimethoxybenzoic acid melting at 78–80.'

Four of the six trimethoxybenzoic acids have been definitely described in the literature, but since the properties of none of the known acids agree with those of the oxidation product of the trimethoxyphenylacetic acid from derritol methyl ether, it seemed necessary to prepare the two missing members, that is, the 2,3,5- and 2,3,6-trimethoxybenzoic acids.

Orthovanillin was used as the starting material, the methylation of which was carried out according to the method of Spath and Mosettig.[2] The methyl ether was nitrated by the method of Perkin and Robinson[3] and the isomeric 2,3-dimethoxy-5-nitro and 2,3-dimethoxy-6-nitrobenzaldehydes were separated by means of their *p*-toluidides.[4]

The first-mentioned compound was converted into 2,3-dimethoxy-5-hydroxybenzaldehyde, which was then methylated and oxidized to the 2,3,5-trimethoxybenzoic acid, which melted at 105'.

The 2,3,5-trimethoxyphenylacetic acid was prepared from the corresponding aldehyde by the Mauthner synthesis.

The 2,3,6-trimethoxybenzoic acid was prepared by first oxidizing the 2,3-dimethoxy-6-nitrobenzaldehyde and then replacing the nitro group

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[1] LaForge and Smith, THIS JOURNAL, 52, 1088, 4597 (1930).

[2] Späth and Mosettig, Ann., 433, 144 (1923).

[3] Perkin and Robinson, J. Chem. *Soc.*, 105, 2389 (1914).

[4] Perkin, Robinson and Stoyle, ibid., 125, 235 (1924).

by the hydroxyl group with subsequent methylation to the trimethoxy derivative.

The melting points of the six theoretically possible trimethoxybenzoic acids are given in the following table:

Trimethoxybenzoic acid	Melting point, °C.	Trimethoxybenzoic acid	Melting point, °C.
2,3,4	97-99	2,4,5	144
2,3,5	105[a]	2,4,6	142–144 (decomposition)
2,3,6	145–146	3,4,5	168–170

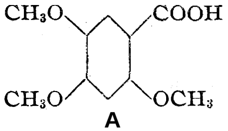
[a] For a compound which they assume to have this formula, Faltis and Neumann, *Monatsh.*, 42, 372 (1921), report a melting point of 141–143°.

As the properties of none of these acids agreed with those of the oxidation product of the trimethoxyphenylacetic acid from derritol methyl ether, it seemed probable that our supposed trimethoxybenzoic acid was an impure substance. Therefore, we have repeated our oxidation experiments and found that the product obtained under the conditions employed was in fact a mixture containing considerable quantities of unchanged starting material from which we were unable to isolate the oxidation product.

We have now, by an indirect method, obtained the trimethoxybenzoic acid corresponding to the natural trimethoxyphenylacetic acid in a pure condition and found it to melt at 145°.

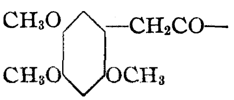
The procedure followed was to convert the trimethoxyphenylacetic acid into its ethyl ester, from which the trimethoxybenzyldiphenylcarbinol was prepared by the Grignard reaction. The carbinol was then dehydrated to the corresponding alkene, which yielded the trimethoxybenzoic acid by permanganate oxidation.

This acid is identical with the trimethoxybenzoic acid recently prepared by Clark[6] by the methylation of the dimethoxyhydroxybenzoic acid obtained by the oxidation of dehydrodeguelin and identified as asaronic acid of formula (A), melting at 145°. When mixed with this acid the trimethoxybenzoic acid from derritol methyl ether showed no depression of the melting point, but it showed a very marked depression when mixed with 2,3,6-trimethoxybenzoic acid, which also melts at 145°. Dihydroderritol methyl ether also gave asaronic acid when oxidized in acetone solution with permanganate and from derritol a small yield of the dimethoxyhydroxybenzoic acid was obtained which was identical with the oxidation product of dehydrodeguelin.[5]



A

It is established, therefore, that the three methoxyl groups in derritol methyl ether occupy the 2,4,5-positions, and that this compound contains the grouping (B).



B

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[5] E. P. Clark, This journal, 53, 2007 (1931).

Experimental

2,3-Dimethoxy-5-hydroxybenzaldehyde.[6]—Three grams of 5-nitro-o-vanillin methyl ether was dissolved in 5.25 cc. of 30% sodium bisulfite and the solution diluted with 25 cc. of water. This solution was slowly added to a boiling mixture of 22.5 g. of calcium carbonate (from 23 5 g. of calcium chloride and 37.5 g. of potassium carbonate) and 60 g. of ferrous sulfate in 150 cc. of water. The mixture froths considerably especially in the early stages of the reaction. The boiling was continued for one and one-half hours, after which the dissolved amino aldehyde, which proved to be unstable in the free state, was filtered into 12 cc. of concentrated hydrochloric acid diluted with two or three parts of water. This solution was cooled to 3° and 0.93 g. of sodium nitrite in 75 cc. of water was added. The solution of the diazo compound was warmed to room temperature and then left on the steam-bath for two hours. After boiling for ten minutes with decolorizing carbon the solution was filtered and extracted with ether. The ether extracts after drying over anhydrous sodium sulfate were evaporated. The crystalline residue of 2,3-methoxy-5-hydroxybenzaldehyde was recrystallized from water; m. p. 152". The yield varied somewhat but was usually about 0.5 g.

Anal. Subs., 0.0569: CO_2, 0.1240; H_2O, 0.0283. Calcd. for $C_9H_{10}O_4$: C, 59.34; H, 5.49. Found: C, 59.43; H, 5.52.

Methylation of **2,3-Methoxy-5-hydroxybenzaldehyde.**—Two grams of the aldehyde was dissolved in 4 cc. of 33% sodium hydroxide and 12 cc. of water in a three-necked flask fitted with a mechanical stirrer. Four cc. of methyl sulfate was slowly added, followed by 2 cc. of 33% sodium hydroxide. After stirring for three hours on a water-bath, the mixture was filtered, and the separated crystals were washed with water. The 2,3,5-trimethoxybenzaldehyde was recrystallized from 50% ethyl alcohol; m. p. 71°; yield, 1.2 g.

Anal. Subs., 0.0209: AgI, 0.0763. Calcd. for $C_{10}H_{12}O_4$: $3CH_3O$, 47.44. Found: CH_3O, 47.58.

Oxidation of **2,3,5-Trimethoxybenzaldehyde.**—Thirty-five hundredths gram of the aldehyde was suspended in 50 cc of water containing 0.1 g. of potassium hydroxide. The mixture was oxidized on the steam-bath with 8 cc. of 3% potassium permanganate. The solution was filtered from the manganese dioxide, acidified with dilute hydrochloric acid and extracted with ether. The ether extracts after drying over anhydrous sodium sulfate were evaporated, leaving the crystalline 2,3,5-trimethoxybenzoic acid, which was then recrystallized from water; m. p. 105"; yield, 0.15 g.

Anal. Subs., 0.0735: CO_2, 0.1521; H_3O, 0.0367. Calcd. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.66. Found: C, 56.43; H, 5.54.

Azlactone of **2,3,5-Trimethoxybenzaldehyde.**—One and two-tenths grams of the aldehyde, 1.5 g. of hippuric acid and 0.6 g. of anhydrous sodium acetate were intimately mixed in a mortar. The mixture was placed in a 50-cc. Erlenmeyer flask, 3.5 cc. of acetic anhydride added, and the mixture heated on the steam-bath for two hours. After cooling, 5 cc. of water was added, the mixture allowed to stand for an hour, filtered and the product washed with water and then with ethyl alcohol. The azlactone was recrystallized from ethyl alcohol; m. p. 181–183°. The yield was nearly quantitative.

Anal.[7] Subs., 3.892 mg.: CO_2, 9.625 mg.; H_2O, 1.737 mg. Subs., 7.099 mg.; N, 0.260 cc. Calcd. for $C_{19}H_{17}O_5N$: C, 67.25; H, 5.01: N, 4.13. Found: C, 67.56; H, 4.96; N, 4.16.

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[6] German Patent 62,950.

[7] We are indebted to Mr. J. R. Spies of this division for carrying out the micro analyses reported in this paper.

2,3,5-Trimethoxyphenylacetic Acid.—One and eight-tenths grams of We azlactone was boiled for one and one-half hours with 14 cc. of water containing 2.8 g. of potassium hydroxide. After cooling. 1.3 cc. of 30% hydrogen peroxide was added, the solution was allowed to stand for one and one-fourth hours and then warmed for fifteen minutes on the steam-bath. After acidifying with hydrochloric acid, the solution was extracted with ether. The ether extracts after drying over anhydrous sodium sulfate were evaporated, and the products were kept in an oven at 105° overnight to remove benzoic acid. The remaining substance was recrystallized from water, m. p. 83°. When mixed with the trimethoxyphenylacetic acid from methylderritolic acid, the melting point was depressed to 60–65°

Anal. Subs., 4.130 mg.: CO_2, 8.873 mg.; H_2O, 2.296 mg. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.15. Found: C, 58.46; H, 6.13.

Reduction of **2,3-Dimethoxy-6-nitrobenzoic** Acid.—Nine grams of ferrous sulfate was dissolved in 25 cc. of water and an excess of concentrated ammonium hydroxide was added. The mixture was heated to 92° and 1 g. of the acid dissolved in ammonium hydroxide was added in small portions. The solution was boiled for one hour, then filtered and cooled. As the resulting amino acid proved to be unstable, the solution was cooled to 5°, made acid with an 8 cc. excess of concentrated hydrochloric acid, and 0.66 g. of sodium nitrite dissolved in 25 cc. of water was added in small portions with constant stirring. The solution was allowed to warm to room temperature and then boiled for ten minutes with decolorizing carbon. After filtering, the solution was cooled and extracted with ether. The ether extract, after drying over anhydrous sodium sulfate, was evaporated and the resulting 2,3-methoxy-6-hydroxybenzoic acid was recrystallized from water. It consists of long needles of m. p. 82°; yield, 0.25 g.

Anal. Subs., 0.0683: CO_2, 0.1365; H_2O, 0.0311. Subs., 0.0206: AgI, 0.0487. Calcd. for $C_9H_{10}O_5$: C, 54.54; H, 5.05; $2CH_3O$, 31.31. Found: C, 54.49; H, 5.06; CH_3O, 31.23.

Methylation of **2,3-Methoxy-6-hydroxybenzoic** Acid.—One gram of the acid was dissolved in 40 cc. of 5% potassium hydroxide and to this solution 2 cc. of methyl sulfate was added with mechanical stirring. The stirring was continued for three hours, after which the solution was made acid with hydrochloric acid and extracted with ether. After drying over anhydrous sodium sulfate, the ether extracts were evaporated. The 2,3,6-trimethoxybenzoic acid was recrystallized from water, m. p. 145–146°.

Anal. Subs., 0.0580: CO_2, 0.1208; H_2O, 0.0297. Subs., 0.0194: AgI, 0.0647. Calcd. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.66; $3CH_3O$, 43.86. Found: C, 56.78; H, 5.69; CH_3O, 44.05.

Amide of **2,4,5-Trimethoxyphenylacetic** Acid from Methylderritolic Acid.—Five-tenths gram of the acid was dissolved in 10 cc. of benzene and to this solution 0.5 g. of phosphorus pentachloride was added. After boiling off the hydrogen chloride, the solution was cooled in an ice-bath and saturated with dry ammonia. Water was then added and the benzene removed by boiling. The amide was recrystallized from water; m. p. 169°; yield, 0.4 g.

Anal.[7] Subs., 3.481 mg.; CO_2 7.498 mg.; H_2O, 2.050 mg. Subs., 3.396 mg.; N, 0.186 cc. Calcd. for $C_{11}H_{15}O_4N$: C, 58.67; H, 6.67; N, 6.22. Found: C, 58.74; H, 6.54; N, 6.22.

Ethyl Ester of the **2,4,5-Trimethoxyphenylacetic** Acid from Methylderritolic Acid.—Two and two-tenths grams of the acid, 5 cc. of absolute ethyl alcohol and 0.5 cc. of concentrated sulfuric acid was refluxed for three hours. After dilution with two volumes of water, the solution was made alkaline with solid potassium carbonate and extracted with ether. The ether solution was extracted with water and after drying over anhydrous sodium sulfate was evaporated. The crude ester was not purified further but was treated directly with the Grignard reagent.

2,4,5-Trimethoxybenzyldiphenylcarbinol.—The phenylmagnesium bromide was prepared in the usual manner, with 1.34 g. of magnesium turnings and 8.34 g. of bromobenzene. Four and one-half grams of the crude trimethoxyphenylacetic ester in ether solution was added to the Grignard reagent over a period of forty-five minutes, with constant stirring. The mixture was then refluxed for an hour and, after cooling, hydrolyzed with dilute sulfuric acid with slight warming to complete the reaction. The ether layer was separated and after drying over anhydrous sodium sulfate was evaporated. The resulting carbinol was recrystallized from ethyl alcohol, m. p. 130–131°.

Anal. Subs., 0.0700: CO_2, 0.1942; H_2O, 0.0419. Calcd. for $C_{23}H_{24}O_4$: C, 75.82; H, 6.59. Found: C, 75.65; H, 6.65.

α-2,4,5-Trimethoxyphenyl-β-diphenylethylene.—One-half gram of 2,4,5-trimethoxybenzyldiphenylcarbinol was heated with a trace of iodine in an Abderhalden drier at 138° until the evolution of water ceased. On cooling, the oily residue became crystalline and was recrystallized from dilute ethyl alcohol; m. p. 101–103°; yield, 0.35 g.

Anal. Subs., 0.0667: CO_2, 0.1951; H_2O, 0.0386. Calcd. for $C_{23}H_{22}O_3$: C. 79.76; H, 6.35. Found: C, 79.77; H, 6.43.

2,4,5-Trimethoxybenzoic Acid.—Three-tenths gram of α-2,4,5-trimethoxyphenyl-β-diphenylethylene was dissolved in 25 cc. of acetone and small amounts of finely ground potassium permanganate were added over a period of several days until a permanent purple color was obtained. The solution was filtered, the precipitate washed with acetone and after drying digested with boiling water. After filtering from the manganese dioxide, the solution was made acid with dilute hydrochloric acid and extracted with ether. The ether extracts after drying over anhydrous sodium sulfate were evaporated. The resulting 2,4,5-trimethoxybenzoic acid was recrystallized from water, m. p. 145–146°. A mixed melting point with 2,4,5-trimethoxybenzoic acid prepared by Dr. E. P. Clark of this Laboratory gave no depression.

Anal.[7] Subs., 3.356, 4.572 mg.: CO_2, 6.959, 9.447 mg.; H_2O, 1.658, 2.252 mg. Calcd. for $C_{10}H_{12}O_5$: C. 56.6; H, 5.66. Found: C, 56.55, 56.35; H. 5.49, 5.47.

Oxidation of Dihydroderritol Methyl Ether.—Five grams of dihydroderritol methyl ether was dissolved in 200 cc. of anhydrous acetone neutral to permanganate. The solution was cooled in an ice-bath, and 16 g. of finely powdered potassium permanganate was added in small portions with mechanical stirring. Several days were required to complete the reaction. The mixture was filtered and the precipitate digested with 300 cc. of water and filtered from manganese dioxide. The filtrate, after concentrating to a small volume under reduced pressure, was made acid and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated. The residue was recrystallized from water, m. p. 145°. The yield was 0.4 g. A mixed melting point with asaronic acid showed no depression.

Oxidation of Derritol.—Five grams of derritol was oxidized and the reaction product isolated in the manner described above. The reaction was complete in about five hours. The product was washed with a small amount of dilute methyl alcohol and then recrystallized from water, m. p. 211–212° with decomposition. When mixed with the hydroxydimethoxybenzoic acid, which Clark obtained from dehydrodeguelin, the melting point showed no depression.

Summary

The preparation and properties of 2,3,5 and 2,3,6-trimethoxybenzoic acids are described. The addition of these two missing members completes the series of six possible acids of this type.

The 2,3,5-trimethoxyphenylacetic acid was prepared from the corresponding 2,3,5-trimethoxybenzaldehyde.

The trimethoxyphenylacetic acid obtained from derritol methyl ether was converted into its ethyl ester, which yielded the diphenylcarbinol by the Grignard reaction. This carbinol was dehydrated to the corresponding trimethoxyphenyldiphenylethylene, which was oxidized to a trimethoxybenzoic acid. This acid proved to be identical with 2,4,5-trimethoxybenzoic acid (asaronic acid).

The same acid was obtained by direct oxidation of derritol methyl ether and derritol itself yielded a dimethoxyhydroxybenzoic acid.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

THE NUMBER OF ISOMERIC HYDROCARBONS OF THE METHANE SERIES

BY HENRY R. HENZE AND CHARLES M. BLAIR

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At various times attempts have been made by both mathematicians and chemists to derive a formula by which the number of isomeric hydrocarbons of the methane series could be calculated.

Apparently the first attempt to derive such a formula was made by the English mathematician Cayley[1] in 1875. He recognized that the number of isomers for a given carbon content was dependent upon the number of those of lesser carbon contents, and thus he obtained successively for every magnitude an expression for the fundamental chains common to all of magnitude N. This function led to the building of "centric and bicentric trees," and with the help of the same he predicted the number of isomeric hydrocarbons inclusive of a carbon content of thirteen. However, his predictions of the number of isomers for the carbon contents of twelve and thirteen were in error.

Almost simultaneously with this attempt of Cayley was that of Schiff.[2] Using a method involving combinations and permutations, he calculated the number of isomeric hydrocarbons through the dodecanes, obtaining for the dodecanes, however, the same erroneous value as that of Cayley.

This error, along with that of Cayley as to the number of tridecanes, was first corrected by Hermann[3] about five years later. The latter divided the structural formulas of the isomers into types, according to the number of branches attached to the fundamental chain of each, and attempted to relate the number of isomers of each type to the total number

[1] Cayley, *Ber.*, 8, 1056 (1875).

[2] Schiff, *ibid.*, 8, 1542 (1875).

[3] Hermann, *ibid.*, 13,792 (1880); 30,2423 (1897); 31, 91 (1898).

of hydrocarbons. His results were limited to the series CH_4 $C_{13}H_{28}$ and the utilization of his method of calculation does not allow one to predict accurately the number of isomers of the hydrocarbons more complex than the tridecanes.

In 1893, Tiemann[4] also recognized the existence of various types of isomers (monomethyl, dimethyl, monoethyl, etc.), and using an abbreviated numerical system of writing these isomers, counted their number. He recorded the results inclusive of the decanes, but his totals for the nonanes and decanes were incorrect.

This problem of calculating the number of isomeric hydrocarbons was attacked by Delannoy[5] at about the same time but from an entirely different angle. He developed an empirical formula in which an additional term was brought into use with each unit increase in the carbon content. This formula served to calculate the number of isomers through the tridecanes, but it does not hold for those of higher carbon contents.

Another effort at solution of this problem by use of combinations, permutations and variations was that of Losanitsch,[6] who attempted to apply these in determining the number of isomers of each of the types into which he divided the hydrocarbons. We tabulated the number of isomers of certain types through $C_{20}H_{42}$ but summed these so as to obtain the total number of isomers only inclusive of $C_{14}H_{30}$. It is to be noted that his results for $C_{12}H_{26}$ and $C_{14}H_{30}$ are in error.

Goldberg,[7] in 1898, observing that the previously advanced formulas were complicated and difficult to apply, attempted to derive a simpler formula for calculating the number of hydrocarbons. He developed such a formula but, unfortunately, it did not hold above $C_{10}H_{22}$, the totals calculated becoming increasingly below the actual number of isomers. Goldberg recognized this drawback, and, desiring to obtain the number of isomers for higher carbon contents, adopted the Geneva system to number the branch chains and wrote, in an abbreviated form, the structural formulas of all isomers inclusive of the undecanes, but made no predictions for any higher homologs.

For the period of twenty-five years following the work of Goldberg no further reference to this problem is to be found recorded in the literature. The next work appearing is that of Trautz,[8] who in 1924 published a rigorous mathematical treatment of this question. However, this work, combinatorial in nature, was centered upon the substituted hydrocarbons rather than upon the paraffins themselves and cannot be used inaccurately predicting the number of isomers except for those of low carbon content.

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[4] Tiemann, Ber., 26, 1605 (1893).

[5] Delannoy, Bull. *soc. chim.*, [3] 11, 239 (1894).

[6] Losanitsch, Ber., 30, 1917, 3059 (1897).

[7] Goldberg, *Chem.-Ztg.*, 22, 395 (1898).

[8] Trautz, "Lehrbuch der Chemie," Berlin, 1924, Vol. III, p. 23.

The most recent attempt recorded in literature is that of David[9] in **1928.** His formula is only a slight modification of that of Delannoy, in which an additional term was added for each unit increase in carbon content, and is of no value in calculating the number of isomers for carbon contents greater than eleven.

It is seen, therefore, that the mathematical formulas which have been advanced for calculating the number of isomeric hydrocarbons, when tested by actual writing and counting of the structural formulas, are found to be correct only inclusive of that carbon content for which they were derived and are in error in predicting the number of isomers for higher carbon contents. The cause for these errors is readily seen, for a formula based upon a "centric" or a "bicentric" center of symmetry will obviously become in error when the carbon content increases so that additional centers of symmetry are introduced. Similarly, formulas so derived that an additional term must be added for each unit increase in the carbon content will also be in error for all carbon contents greater than that for which the additional terms can be definitely established.

It seemed desirable, therefore, to derive a formula which would accurately estimate the number of isomeric hydrocarbons. Attempts to derive such a formula soon showed that no simple mathematical relationship exists between the total number of isomers and their carbon content. The problem was solved only by establishing a relationship between the number of isomeric hydrocarbons of a given carbon content and the previously calculated number of isomeric alcohols of lesser carbon contents. This relationship is in direct contrast to the idea held by previous workers who considered the number of alcohols to be conditioned by the number of hydrocarbons from which, theoretically, the former might be derived.

Theoretical Discussion

In this treatment we find it desirable to separate the hydrocarbons into classes according to whether their carbon content is even or odd. Those hydrocarbons whose carbon content, N, is an even number, are further divided into two groups: A, consisting of those hydrocarbons whose graphic formula may be divided into two parts of $N/2$ carbon atoms each; and B, the remaining isomeric hydrocarbons whose graphic formula cannot be so divided. Division of the graphic formula into two parts signifies breaking the single bond between two adjacent carbon atoms, thus obtaining two alkyl radicals.

Likewise, the hydrocarbons whose carbon content, N, is an odd number, are also divided into two groups: **A,** consisting of those hydrocarbons whose graphic formula can be divided into two parts, one of $(N + 1)/2$ carbon atoms and the other of $(N - 1)/2$ carbon atoms; and B, con-

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[9] **David, *Rev. gén. sci.*, 39, 142 (1928).**

sisting of the remaining hydrocarbons whose graphic formula cannot be so divided.

For the hydrocarbons of even carbon content, in calculating the number of isomers in group **A,** two factors are utilized: **(I)**, the number of possible alkyl radicals of $N/2$ carbon atoms, and (11), the number of possibilities, without exception or repetition, of combining the alkyl radicals of $N/2$ carbon atoms with those of $N/2$ carbon atoms.

(I). The number of paraffin alkyl radicals of a given carbon content is equal to the number of isomeric alcohols of that carbon content. The method of calculating this number has been previously determined.[10]

(II). If two alkyl radicals of $N/2$ carbon atoms each are combined, a hydrocarbon of N carbon atoms is obtained. Therefore, the number of hydrocarbons of N carbon atoms that may be obtained will depend upon the number of alkyl radicals of $N/2$ carbon atoms; and, since each isomeric alkyl radical is a distinct substance, the number of combinations of the $T_{N/2}$ alkyl radicals of $N/2$ carbon atoms, taken one at a time, with the $T_{N/2}$ alkyl radicals of $N/2$ carbon atoms, taken one at a time, may be calculated by the mathematical formula for this type of combination, that is

$$T_{N/2}(1 + T_{N/2})$$

For the hydrocarbons of odd carbon content, in calculating the number of isomers in group **A,** two factors are also utilized: (I), the number of possible alkyl radicals of $(N + 1)/2$ carbon atoms and of $(N - 1)/2$ carbon atoms, and (11), the number of possibilities, without exception or repetition, of combining the alkyl radicals of $(N + 1)/2$ carbon atoms, taken one at a time, with those of $(N - 1)/2$ carbon atoms, also taken one at a time. In order to prevent duplication in determining the number of these combinations, it is necessary to recognize that part of the alkyl radicals of $(N + 1)/2$ carbon atoms may be derived from the alkyl radicals of $(N - 1)/2$ carbon atoms by the addition to the free valence of the latter, of the $—CH_2—$ group. Hence, the hydrocarbons resulting from combining such portion of the alkyls of $(N + 1)/2$ carbon atoms, that may be so derived, with the alkyls of $(N - 1)/2$ carbon atoms are considered as being formed by joining the alkyls of $(N - 1)/2$ carbon atoms to the alkyls of $(N - 1)/2$ carbon atoms through an intermediate carbon atom, and the number of such possible combinations will equal $T_{(N-1)/2}(1 + T_{(N-1)/2})$, where T is the total number of alcohols of all types containing the number of carbon atoms represented by its subscript. The combination of the remaining portion of the alkyls of $(N + 1)/2$ carbon atoms with the alkyls of $(N - 1)/2$ carbon atoms will form the balance of the isomeric hydrocarbons of group **A,** and the calculation of their number will be made by the mathematical formula

$$T_{(N-1)/2}(T_{(N+1)/2} - T_{(N-1)/2})$$

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[10] Henze and Blair, THIS JOURNAL, 53, 3042 (1931).

The total number of hydrocarbons in group A will consist, therefore, of the sum of the number of hydrocarbons obtained in these two ways. Hence, the number of isomers in group A will equal

$$\frac{T_{(N-1)/2}(1 + 2T_{(N+1)/2} - T_{(N-1)/2})}{2} \cdot$$

If the graphic formula of the hydrocarbons of even carbon content cannot be divided into two parts of $N/2$ carbon atoms each there must be in the formula one carbon atom, and only one, to which are attached branches none of which may contain more than $(N/2 - 1)$ carbon atoms. Obviously, there must be at least three branches, and since carbon has only four valences, there cannot be more than four branches.

Similarly, for those hydrocarbons of odd carbon content whose graphic formulas cannot be divided into two parts, one of $(N + 1)/2$ carbon atoms and the other of $(N - 1)/2$ carbon atoms, there must be in each of such formulas one carbon atom, and only one, to which are attached branches none of which may contain more than $(N - 3)/2$ carbon atoms. By a treatment similar to that already utilized in the case of the hydrocarbons of even carbon content, it may be shown that this specified carbon atom must have attached to it either three or four branches.

Hence, the isomeric hydrocarbons of group B, both even and odd, will be of two types: (a), those in which three branches are attached to the specified carbon atom, and (b), those in which four branches are attached to the specified carbon atom. The total number of isomers of group B will be obtained by a summation of types (a) and (b).

Type (a) would seem to consist of three possible cases: (1), in which all three branches were of different carbon content; (2), in which two branches were of the same carbon content and different from the third; (3), in which all three branches were of the same carbon content. All three of these cases are actually possible but all will not necessarily be present with every value of N. The number of isomers in each case may be calculated by the following mathematical formula for that particular case.

Case (1) $\Sigma T_i \cdot T_j \cdot T_k$ (a_1)

where $i + j + k = N - 1$; i, j and k are integers, distinct, and greater than zero; $i > j > k$; i, for even carbon content, is never greater than $(N/2 - 1)$; i, for odd carbon content, is never greater than $(N - 3)/2$.

Case (2) $^1/_2\Sigma T_i \cdot T_j(1 + T_i)$ (a_2)

where $2i + j = N - 1$; i and j are integers, distinct, and greater than zero; for even carbon content, neither i nor j may be greater than $(N/2 - 1)$; for odd carbon content, neither i nor j may be greater than $(N - 3)/2$.

Case (3) $^1/_6T_i(1 + T_i)(2 + T_i)$ (a_3)

where $3i = N - 1$; i is an integer greater than zero.

Type (b) would seem to consist of five possible cases: (1), in which all four branches are of different carbon content: (2). in which two branches are of the same carbon content and each of the others of different content; (3), in which three branches are of the same carbon content and different from the fourth; (4), in which all four branches are of the same carbon content; (5), in which the four branches can be divided into two sets of two branches each, the individual members of each set being of the same carbon content but differing in content from the members of the other set. It will be seen that cases (4) and (5), though theoretically possible for hydrocarbons of both even and odd carbon content, are actually possible only for the latter, for in case (4) $(N - 1)$ should be divisible by four, and in case (5) $(N - 1)$ should be divisible by two. The number of isomers in each case may be calculated by the following mathematical formula for that particular case.

Case (1) $$\Sigma T_h \cdot T_i \cdot T_j \cdot T_k \tag{b$_1$}$$

where $h + i + j + k = N - 1$; h, i, j and k are integers, distinct, and greater than zero; $h > i > j > k$; h, for even carbon content, is never greater than $(N/2 - 1)$; h, for odd carbon content, is never greater than $(N - 3)/2$.

Case (2) $$\tfrac{1}{2}\Sigma T_i \cdot T_j \cdot T_k(1 + T_i) \tag{b$_2$}$$

where $2i + j + k = N - 1$; i, j and k are integers, distinct, and greater than zero.

Case (3) $$\tfrac{1}{6}\Sigma T_i \cdot T_j(1 + T_i)(2 + T_i) \tag{b$_3$}$$

where $3i + j = N - 1$; i and j are integers, distinct, and greater than zero.

Case (4) $$\tfrac{1}{24}T_i(1 + T_i)(2 + T_i)(3 + T_i) \tag{b$_4$}$$

where $4i = N - 1$; i is an integer greater than zero.

Case (5) $$\tfrac{1}{4}\Sigma T_i \cdot T_j(1 + T_i)(1 + T_j) \tag{b$_5$}$$

where $2i + 2j = N - 1$; i and j are integers, distinct, and greater than zero; $i > j$.

The total number of hydrocarbons of N carbon atoms may be determined by adding to the number of isomers calculated in group A the summation of the number calculated in each of the cases of group B.

The actual meaning and use of these recursion type formulas[11] may be illustrated in the calculation of the number of isomeric tetradecanes.[12]

Sample Calculation

Group **A.** $N = 14;\ N/2 = 7$

$T_7 \cdot (1 + T_7)/2 = 39 \cdot (1 + 39)/2 = 780$

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[11] Grateful acknowledgment is made to Dr. Leo Zippin, National Research Fellow in Mathematics, for his aid in checking the recursion formulas.

[12] The number of isomeric tetradecanes erroneously calculated as being 1855, first by Losanitsch and later by Trautz, has been accepted without further substantiation and appears in certain recent textbooks of organic chemistry.

Group B. $N-1 = 13;\ N/2-1 = 6$

Type (a)

Case (1)

$T_6 \cdot T_5 \cdot T_2 = 17 \cdot 8 \cdot 1 = 136$
$T_6 \cdot T_4 \cdot T_3 = 17 \cdot 4 \cdot 2 = 136$

Case (2)

$T_6 \cdot T_1 \cdot (1 + T_6)/2 = 17 \cdot 1 \cdot (1 + 17)/2 = 153$
$T_5 \cdot T_3 \cdot (1 + T_5)/2 = 8 \cdot 2 \cdot (1 + 8)/2 = 72$
$T_4 \cdot T_5 \cdot (1 + T_4)/2 = 4 \cdot 8 \cdot (1 + 4)/2 = 80$

Case (3)

This case is not actually possible for this carbon content

Type (b)

Case (1)

$T_6 \cdot T_4 \cdot T_2 \cdot T_1 = 17 \cdot 4 \cdot 1 \cdot 1 = 68$
$T_5 \cdot T_4 \cdot T_3 \cdot T_1 = 8 \cdot 4 \cdot 2 \cdot 1 = 64$

Case (2)

$T_5 \cdot T_2 \cdot T_1 \cdot (1 + T_5)/2 = 8 \cdot 1 \cdot 1 \cdot (1 + 8)/2 = 36$
$T_4 \cdot T_3 \cdot T_2 \cdot (1 + T_4)/2 = 4 \cdot 2 \cdot 1 \cdot (1 + 4)/2 = 20$
$T_3 \cdot T_6 \cdot T_1 \cdot (1 + T_3)/2 = 2 \cdot 17 \cdot 1 \cdot (1 + 2)/2 = 51$
$T_3 \cdot T_5 \cdot T_2 \cdot (1 + T_3)/2 = 2 \cdot 8 \cdot 1 \cdot (1 + 2)/2 = 24$
$T_2 \cdot T_6 \cdot T_3 \cdot (1 + T_2)/2 = 1 \cdot 17 \cdot 2 \cdot (1 + 1)/2 = 34$
$T_2 \cdot T_5 \cdot T_4 \cdot (1 + T_2)/2 = 1 \cdot 8 \cdot 4 \cdot (1 + 1)/2 = 32$
$T_1 \cdot T_6 \cdot T_5 \cdot (1 + T_1)/2 = 1 \cdot 17 \cdot 8 \cdot (1 + 1)/2 = 136$

Case (3)

$T_4 \cdot T_1 \cdot (1 + T_4)(2 + T_4)/6 = 4 \cdot 1 \cdot (1 + 4)(2 + 4)/6 = 20$
$T_3 \cdot T_4 \cdot (1 + T_3)(2 + T_3)/6 = 2 \cdot 4 \cdot (1 + 2)(2 + 2)/6 = 16$

Thus, the number of isomeric tetradecanes equals 1858.

In Table I is to be found a summary of the number of terms actually present in all theoretically possible cases of types (a) and (b) through a carbon content of forty. Since the number of alkyl groups (*i. e.*, the total number of isomeric alcohols) through C_{20} is recorded in a previous contribution, it is now possible to calculate the number of isomeric hydrocarbons of double this carbon content. Hence, to calculate the total number of isomeric hydrocarbons of the methane series of higher carbon content it would become necessary to make a preliminary calculation of the total number of isomeric alcohols of the methanol series of $N/2$ and lesser carbon contents.

The number of isomeric paraffins, as calculated by the use of these recursion type formulas, for certain selected carbon contents is shown in Table II. It should be noted that the data utilized in deriving these recursion formulas were the totals of the isomers of the series C_4H_{10} to $C_{10}H_{22}$ inclusive as obtained by actual writing of their structural formulas. Since the total number of isomeric tridecanes and tetradecanes, as calculated by

TABLE I

NUMBER OF TERMS IN ALL THEORETICALLY POSSIBLE CASES OF (A) AND (B)

Carbon content	1	3	5	7	9	11	13	15	17	19	21	23	25	27	29	31	33	35	37	39
a_1....	.	.	.	.	.	.	1	1	2	3	4	5	7	8	10	12	14	16	19	21
a_2....	.	.	.	.	1	2	1	3	3	3	4	5	4	6	6	6	7	8	7	9
a_3....	.	.	.	1	.	.	1	.	.	1	.		1	.		1	.	.	1	.
b_1....	.	.	.	.	.	1	1	3	5	8	12	18	24	33	43	55	69	86	104	126
b_2....	.	.	.	.	1	.	4	4	7	10	14	16	23	26	32	38	45	50	60	66
b_3....	.	.	.	.	.	2	.	2	2	2	2	4	2	4	4	4	4	6	4	6
b_4....	.	.	1	.	1	.	1	.	1	.	1	.	1	.	1	.	1	.	1	.
b_5....	.	.	.	1	1	2	2	3	3	4	4	5	5	6	6	7	7	8	8	9
Total.	.	.	1	2	4	7	11	16	23	31	41	53	67	83	102	123	147	174	204	237

Carbon content	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
a_1....	.	.	.	.	1	1	2	3	4	5	7	8	10	12	14	16	19	21	24	27
a_2....	.	.	1	2	1	3	3	3	4	5	4	6	6	6	7	8	7	9	9	9
a_3....	.	1	.	.	1	.	.	1	.	.	1	.	.	1	.	.	1	.	.	1
b_1....	.	.	.	.	.	1	2	4	7	11	16	23	31	41	53	67	83	102	123	147
b_2....	.	.	.	1	3	4	7	10	13	17	22	26	32	38	44	51	59	66	75	84
b_3....	.	.	1	1	1	2	2	2	3	3	3	4	4	4	5	5	5	6	6	6
Total.	.	1	2	4	7	11	16	23	31	41	53	67	83	102	123	147	174	204	237	274

the recursion formulas, differed from the totals previously accepted in the literature, it seemed desirable also to write and count all the structural formulas, as required by theory, of the undecanes, dodecanes, tridecanes and tetradecanes. The numbers so obtained agree exactly with the totals as calculated by the use of the mathematical formulas.

TABLE II

NUMBER OF ISOMERIC HYDROCARBONS OF THE METHANE SERIES

Carbon content	Number of isomers	Carbon content	Number of isomers
1	1	11	159
2	1	12	355
3	1	13	802
4	2	14	1858
5	3	15	4347
6	5	16	10,359
7	9	17	24,894
8	18	18	60,523
9	35	19	147,284
10	75	20	366,319

Carbon content	Number of isomers
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

Summary

1. No direct or simple relationship appears to exist between the total number of isomeric hydrocarbons of the methane series and their carbon content.

2. By means of a separation of the isomeric hydrocarbons of each specified carbon content into types, arbitrarily chosen upon the basis of their structural formulas, a relationship may be established between the number of hydrocarbons and the alkyl groups of which the former may be considered to be composed. Mathematical formulas of the (finite) recursion type are advanced which permit of the calculation, from their carbon content, of the number of isomeric hydrocarbons in each of these structural types. In using these recursion formulas to calculate the total number of such hydrocarbons of any given carbon content, the total number of alkyl groups (*i. e.,* the total number of isomeric alcohols) of $N/2$ and **all** lesser carbon contents must be known.

3. The totals obtained by use of these mathematical formulas agree exactly through the tetradecanes with the numbers required by theory as tested by actually writing all the possible structural formulas.

AUSTIN, TEXAS

[CONTRIBUTION FROM CHEMICAL LABORATORIES OR THE UNIVERSITY OF NEBRASKA AND NORTHWESTERN UNIVERSITY]

THE INFLUENCE OF THE ARSONO GROUP ON THE ACTIVITY OF NUCLEAR CHLORINE

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It has long been known that halogens in the benzene nucleus can neither be removed nor replaced by the ordinary reagents which act upon them in the aliphatic series. Nevertheless, the presence of certain groups such as nitro, cyano, carboxyl, etc., loosens the attachment and promotes substitution. Most of the experimental work in the study of replacement reactions has been done with halogeno-nitro compounds. However, as early as 1892, Heidenreich and Victor Meyer[2] showed that o-bromobenzoic acid and ammonia reacted at 200° to give diphenylamine. Later, Ullmann[3] made a study of the condensation of o-chlorobenzoic acid with aniline and found that a catalyst was necessary, the salts of copper being most effective. The addition of potassium carbonate and the use of nitrobenzene as a solvent were also found to increase the yields.

Since the arsono group is similar in structure to the nitro, carboxyl, and sulfonic acid groups, and is meta directing, halogen in the ortho

[1] Parke. Davis and Company Fellow.

[2] Heidenreich and Meyer, *Ber.*, 25, 2188 (1892).

[3] Ullmann, *Ann.*, 355, 312 (1907).

position, by analogy, should be reactive. In fact, Gibson and his coworkers[4] have successfully applied the method of Ullmann to condensation reactions of o-bromophenylarsonic acid with various aromatic amines.

Thus it was suggested to make a study of the reactivity of the halogen of o-chlorophenylarsonic acid and to determine the value of its application to the synthesis of new arsenicals.

Condensations of the arsonic acid with primary aliphatic and aromatic amines and with ammonia were found to take place readily when they were heated in amyl alcohol with a copper catalyst and potassium carbonate. Secondary amines, benzamide and potassium phthalimide did not condense under like conditions while alcohols or alcoholates were found to replace the chlorine with the formation of the corresponding ethers.

Experimental[5]

General Procedure for the Preparation **of** Alkylamino-phenylarsonic Acids.—Ten grams of o-chlorophenylarsonic acid, 10 g. of anhydrous potassium carbonate, a trace of cuprous iodide, 6 cc. of the primary alkylamine and 25 cc. of amyl alcohol in a 50-cc. Erlenmeyer flask, fitted with a condenser with ground-glass connection, were heated in an oil-bath at 130–135° for fifteen hours, the reaction mixture being well stirred. The excess amine and amyl alcohol were removed by steam distillation, and the resulting solution was treated with decolorizing carbon. On acidification to Congo red paper with dilute hydrochloric acid, a grayish mass separated, which was crystallized from dilute acetic acid. Recrystallization from 75 cc. of hot 3 *N* hydrochloric acid gave a fine white precipitate which was identified as an alkoxyphenylarsonic acid (described later). After filtering, the alkylaminophenylarsonic acid was recovered by almost neutralizing the filtrate to Congo red paper with dilute sodium hydroxide. The portion insoluble in hydrochloric acid solution was treated again with 50 cc. of 3 N hydrochloric acid, and more amino compound recovered. The total yield of the alkylaminophenylarsonic acid obtained varied from 20–49% while the total yield of the ether varied from traces to as much as 7%. For analysis the amino compound was reprecipitated from a smaller amount of 3 N hydrochloric acid and crystallized from dilute acetic acid.

TABLE I

ALKYLAMINOPHENYLARSONIC ACID

-Aminophenylarsonic acids	Yield, %	M p , °C. (corr)	Analyses, % Arsenic Calcd	Analyses, % Arsenic Found	Analyses, % Nitrogen Calcd	Analyses, % Nitrogen Found
o-n-Propyl-	20	128	28 94	28 87	5 41	5 40
o-n-Butyl-	40	126	2745	27.37	513	511
o-n-Amyl-	48	98	2611	2609	488	487
o-Isoamyl-	49	115	2611	26.12	488	477
o-β-Hydroxyethyl-	45	141–143	28 71	28 67	5 37	5 35
Carboxy-methyl-	30	178d	27.25	27 30	5 09	5 05

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[4] Burton and Gibson, *J. Chem. Soc.*, 247 (1927); Gibson and Johnson, *ibid.*, 2499 (1927); 2204 (1928).

[5] The potentiometric method of Cislak and Hamilton, THIS JOURNAL, 52, 638 (1930), was used for the quantitative determination of arsenic in the compounds prepared. The analyses are given in duplicate when the proof of the structures of the compounds hinged upon the arsenic analyses, and the amount of the purified sample permitted.

o-Arsonophenyl-N-butyl-nitrosamine.—To 5 g. of o-n-butylaminophenylarsonic acid in 100 cc. of 3 *N* hydrochloric acid, a solution of 8 g. of sodium nitrite in 25 cc. of water was slowly added, with stirring. The nitrosamine which formed was filtered, washed with water and dried. It was purified by treating with 40 cc. of hot ethyl acetate, cooling, and then crystallizing the residue from 400 cc. of hot water; yield 4.57 g. The cream-colored needle-like crystals melted with decomposition at 147° (corr.).

Anal. Calcd. for $C_{10}H_{15}O_4N_2As$: As, 24.73. Found: As, 24.82, 24.73.

Reaction with Ammonium Carbonate in Sealed Tubes.—Ten grams of *o*-chlorophenylarsonic acid, 10 g. of anhydrous potassium carbonate, 0.5 g. of copper acetate and 25 cc. of amyl alcohol were placed in a bomb tube and thoroughly mixed while heating in a steam-bath. After cooling, 10 g. of ammonium carbonate was mixed with the contents and the tube sealed. The tube was heated in a bomb oven for fifty hours at 135°. The mixtures from three tubes, prepared and treated as above, were combined and steam distilled, and the remaining solution decolorized and strongly acidified. The tarry substance (see below) which formed was removed, and the solution made just alkaline to Congo red paper (acid to litmus), and evaporated to dryness. The solid residue was extracted with portions of hot absolute alcohol which were combined, and the alcohol removed by evaporation. The oily substance which remained was dissolved in a small amount of water, decolorized and the water allowed to evaporate. At first an oil separated, followed by white crystals. By gently warming with a little water, the crystals dissolved, leaving most of the oily substance. By two such extractions a small amount of white needle-like crystals was obtained which melted at 151–152° (corr.). The melting point of o-arsanilic acid given by Jacobs, Heidelberger and Rolf[6] is 153°. A solution of the crystals when diazotized gave an orange dye with R-salt.

Anal. Calcd. for $C_6H_8O_3NAs$ (*o*-arsanilic acid): As, 34.54. Found: As, 34.34.

The. tarry substance (see above), which was insoluble in the acid solution, was treated with boiling 6 N hydrochloric acid. It formed a clear solution from which a small quantity of a non-identified substance slowly separated (from hot solution) as white needles. The substance did not melt below 240°, was soluble in dilute sodium hydroxide, but insoluble in hot 6 N hydrochloric acid. A qualitative test showed the presence of nitrogen and the absence of chlorine. The arsenic content was found to be 27.64%. The filtrate from the acid treatment above was allowed to cool. Long white needles separated which were recrystallized from hot 6 N hydrochloric acid, dissolved in alkali, decolorized and reprecipitated with acid. When air dried, the substance melted at 132–136° with foaming. However, when dried in *vacuo* over sulfuric acid, or in the oven at 100°, the substance melted at 198–200° (corr.). A test for nitrogen was positive, while one for chlorine was negative. The arsenic analysis corresponded to that for diphenylamine-*o*,*o*′-diarsonic acid.

Anal. Calcd. for $C_{12}H_{13}O_6NAs_2$: As, 35.95. Found: As, 36.00, 36.02.

Reaction with **Monomethylaniline.**—A mixture of 10 g. of o-chlorophenylarsonic acid, 12 g. of anhydrous potassium carbonate, copper powder and 30 cc. of monomethylaniline (no solvent) was heated for fifteen hours at 140–150°, with stirring. After removing the methylaniline by steam distillation, the resulting solution was decolorized and acidified. The substance which separated was treated with hot acetone, cooled and filtered. The portion insoluble in acetone was further purified by dissolving in alkali, decolorizing, and reprecipitating with acid. The substance was dried in a desiccator over sulfuric acid and there was no further loss in weight on drying for ten hours in an oven at 100°. The yield was 1.65 g. A qualitative analysis showed the absence of ni-

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[6] Jacobs, Heidelberger and Rolf, THIS JOURNAL, 40, 1583 (1918).

trogen and chlorine. The arsenic analysis corresponded to diphenyl ether *o,o'*-diarsonic acid. The substance softened and darkened at 240°.

Anal. Calcd. for $C_{12}H_{12}O_7As_2$: As, 35.87. Found: As, 35.97, 35.97.

General Procedure for the Preparation of Alkoxyphenylarsonic Acids.—Ten grams of o-chlorophenylarsonic acid, 10 g. of anhydrous potassium carbonate, a little copper powder, and 35 cc. of an alcohol containing 1.6 g. of potassium (or an equivalent amount of sodium) were heated at 130–135° for fifteen hours with stirring. After steam distillation and treatment with activated charcoal the alkoxyphenylarsonic acid was precipitated by acidifying with concd. hydrochloric acid. The yield was 30–49%.[7]

TABLE II

ALKOXYPHENYLARSONIC ACIDS

-Phenylarsonic acid	Yield, %	M. p., °C. (corr.)	Arsenic analyses, % Calcd.	Found
o-n-Butoxy-	30	200	27.55	27.56
o-Isoamoxy-	43	201	26.02	26.00
o-Phenoxy-	49	174	25.49	25.40

Discussion

In beginning a study of the reactions of o-chlorophenylarsonic acid, a series of about sixty condensation reactions with aniline was carried out under different experimental conditions. Specific examples have been chosen from this series to show the various effects. In general, 5 g. of the arsonic acid, 5 g. of anhydrous potassium carbonate, a trace of copper powder, and 20 cc. of aniline (no solvent) were heated in the apparatus described in the Experimental Part for fifteen hours, at 135°. In the tables only the conditions or amounts which differ from the general procedure are given. The yields indicated are based upon the amounts obtained after steam distillation, acidification, and a single crystallization from acetone and water.

Only two catalysts, copper and cuprous iodide, were tried in this series of reactions. Cuprous iodide gave a better yield but the product obtained when using copper was found to be purer. No yield was obtained in the absence of a catalyst. Freshly prepared cuprous iodide was more efficient than that which had been kept for some time.

TABLE III

THE EFFECT OF CHANGES IN TEMPERATURE

Temp., °C.	115	135	160	185
Time, hrs.	10	10	10	10
Yield, %	Trace	56	7	Trace

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[7] In the case of o-phenoxyphenylarsonic, acidification with concd. hydrochloric acid gave an oil. The water layer was removed and the oily substance treated with ether. A white crystalline precipitate formed which was dissolved in the cakd. amount of dilute sodium hydroxide, decolorized with charcoal and reprecipitated by the slow addition of hydrochloric acid. The product was further purified by recrystallization from an acetone–water solution.

As indicated in Table III, the best yields were obtained at a temperature of about 135°.

TABLE IV

THE EFFECT OF CHANGES IN REACTION TIME

Time, hrs.	3	5	10	20
Yield, %	52	58	56	52

From the data in Table IV, apparently the reaction was finished in from three to five hours.

TABLE V

THE EFFECT OF SOLVENTS (Cu_2I_2 WAS USED AS THE CATALYST)

Aniline, cc.	Solvent	Yield, %
15	None	61
25	None	61
15	Amyl alcohol (4 cc.)	69
15	Amyl alcohol (8 cc.)	65
5	Amyl alcohol (25 cc.)	68
15	Nitrobenzene (8 cc.)	56
15	Nitrobenzene (25 cc.)	Small
15	Amyl alcohol (25 cc.) and water (1 cc.)	60
15	Amyl alcohol (25 cc.) and water (5 cc.)	48
15	Water (5 cc)	48

Slightly better yields were obtained using amyl alcohol as the solvent. The action of nitrobenzene was unfavorable. Small amounts of water, which hinder the ordinary Ullmann reaction, did not greatly affect the yield.

Condensations did not take place when sodium carbonate or sodium acetate was substituted for the potassium carbonate. In no case was a triphenylamine-diarsonic acid isolated. Theoretically such a compound could be formed by the reaction of two molecules of o-chlorophenylarsonic acid with one molecule of aniline.

Incidentally, it was found that o-chlorophenylarsonic acid, when heated to boiling with water containing a slight excess of aniline, formed a crystalline aniline salt. Aniline was liberated again on treating with alkali.

A series of condensations was also carried out with primary aliphatic amines. The amines (iso- and n-amyl, n-butyl, and n-propyl) readily condensed with *o*-chlorophenylarsonic acid under the conditions found favorable in the experiments with aniline. The products, after the usual recrystallizations, etc., were found to be mixtures. This was indicated by slight changes in the melting points on recrystallization and also by the fact that nitrogen determinations were consistently low. By crystallizing from hot 3 N hydrochloric acid, a white crystalline substance separated on cooling which did not contain nitrogen and which corresponded in properties to a compound (*o*-amoxyphenylarsonic acid) obtained by treating o-chlorophenylarsonic acid with potassium amylate, under the usual experimental conditions. Smaller yields were obtained with butyl- and propylamines, probably due to their lower boiling points and to the greater solubilities of their condensation products. A sealed tube reaction with ethylamine was carried out and a small quantity of a substance obtained which melted at 126–127°. The melting point given in the literatures for o-ethylaminophenylarsonic acid is 128–129°.

Ethanolamine (b. p. 168°, uncorr.) in the absence of a solvent condensed very readily with o-chlorophenylarsonic acid to form *o*-β-hydroxyethyl-aminophenylarsonic acid. This product has previously been prepared by Rodewald and Adams[9] by treating o-arsanilic acid with β-chloroethyl-chlorocarbonate and hydrolyzing the resulting product with alkali. The nitrosamine was prepared to prove an amino rather than an ether linkage.

Glycine condensed, in the presence of amyl alcohol, to give fair yields of phenylglycine-o-arsonic acid. To avoid steam distilling, the amyl alcohol was removed by extractions with ether.

It was desired to include in this study the reaction of o-chlorophenylarsonic acid with ammonia. This reaction was carried out in sealed tubes using ammonium carbonate as the source of ammonia. Copper acetate was used as the catalyst, since due to its solubility it was easily dispersed throughout the reaction mixture. Theoretically one, two, or three hydrogen atoms of ammonia could be replaced by phenylarsonic acid radicals to give (1) o-arsanilic acid, (2) a diphenylamine-diarsonic acid, and (3) a triphenylamine-triarsonic acid. From the reaction mixture, o-arsanilic acid was identified by means of its melting point, its reaction with R-salt, and by its arsenic analysis. A small amount of a second substance containing nitrogen was obtained which was soluble in hot 6 *N* hydrochloric acid, but crystallized on cooling. Its arsenic analysis corresponded to that calculated for a diphenylamine-diarsonic acid. A third product was isolated which contained nitrogen and arsenic (27.64%) which was insoluble in hot 6 *N* hydrochloric acid, and did not melt below 240°. The nature of this substance was not determined.

All attempts to condense with secondary aliphatic amines (di-isoamyl-, di-*n*-butyl-, and diethylamines) were unsuccessful. The reactions were carried out at various temperatures in the absence of a solvent, but no reaction product was obtained. When amyl alcohol was used as a solvent, amoxyphenylarsonic acid was formed in yields as high as 20%.

Although Gibson and Johnson[10] have found it possible to condense *o*-bromophenylarsonic acid with monomethylaniline, the reaction under similar conditions with *o*-chlorophenylarsonicacid gave no product containing nitrogen. When heated under the usual conditions to 140–150° with monomethylaniline (no solvent), a product was obtained which was insoluble in acetone or dilute hydrochloric acid but was readily soluble in alkali. The arsenic content wss found to correspond to that calculated for a diphenyl ether diarsonic acid. Theoretically this could be formed if part of the *o*-chlorophenylarsonic acid were hydrolyzed to form o-hydroxyphenylarsonic acid, which in turn reacted with some of the remaining o-chlorophenylarsonic acid. The latter reaction would be probable since phenol was found to react readily to form diphenyl ether *o*-arsonic acid. While no evidence has been obtained of the formation of o-hydroxyphenylarsonic acid in any of the reactions studied thus far, still it is possible that certain reagents may bring about the hydrolysis of o-chlorophenylarsonic acid. In fact, Tuttle[11] found that o-chlorobenzoic acid when heated with piperidine yielded salicylic acid, but none was obtained when heated with a potassium hydroxide solution. Since the usual methods of splitting ethers are not applicable to diphenyl ethers, and since no suitable derivative

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[8] Burton and Gibson, *J. Chem. Soc.*, **2387 (1927).**

[9] Rodewald and Adams, THIS JOURNAL, **45,3102 (1923).**

[10] Gibson and Johnson, *J.* Chem. *Soc.*, **2499 (1927).**

[11] Tuttle. THIS JOURNAL, **45, 1906 (1923).**

with known constants could be found, no final proof of the structure of this compound was made.

In the course of this work a few other reactions were attempted which were unsuccessful. The formation of ethers from alcohols or alcoholates, and the work of Hurtley,[12] who, in studying the replacement of halogen in o-bromobenzoic acid, condensed that acid with malonic ester, acetoacetic ester and benzoylacetone, suggested like condensations with o-chlorophenylarsonic acid. However, under similar conditions the corresponding reactions did not take place. Benzamide and potassium phthalimide also failed to react under conditions similar to the amino condensations or at higher temperature.

Summary

1. A study was made of the effects of changes in the reaction conditions, such as temperature, time, catalyst, solvent, etc., on the reaction of *o*-chlorophenylarsonic acid with aniline.

2. o-Chlorophenylarsonic acid was condensed with a series of aliphatic amines and amino compounds, namely, isoamyl-, n-butyl-, n-propyl-, and ethanolamines, and with glycine. The nitrosamine derivatives of n-butyl-, and β-hydroxyethylaminophenylarsonic acids were also prepared.

3. A sealed tube reaction with ammonium carbonate gave a reaction mixture from which o-arsanilic acid, and diphenylamine-*o,o'*-diarsonic acid were isolated.

4. Attempts to condense o-chlorophenylarsonic acid with monomethlyaniline yielded a product which analyzed for diphenyl ether *o,o'*-diarsonic acid.

5. The alcoholates of isoamyl and n-butyl alcohols and also phenol were condensed with o-chlorophenylarsonic acid to give isoamoxy-, n-butoxyphenylarsonic acids, and diphenyl ether *o*-arsonic acid, respectively.

LINCOLN, NEBRASKA

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[12] Hurtley, *J.* Chem. *Soc.*, 1870 (1929).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, STANFORD UNIVERSITY]

THE CHEMICAL REACTIVITY OF THE FUSED BASES. II. THE ACTION OF FUSED POTASSIUM AMIDE UPON ALIPHATIC NITRILES[1]

BY R. A. FULTON AND F. W. BERGSTROM

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Introduction

The preparation of methane may readily be accomplished in the laboratory by heating sodium acetate with sodium hydroxide or, better, with soda lime.[2] Unfortunately, the methane so prepared is never quite pure, since it is generally contaminated with hydrogen and with other gases that may arise from the decomposition of the sodium acetate alone.[2(d-h)] Unsuccessful attempts have been made to generalize this reaction and to prepare the lower hydrocarbons of the methane series by heating the sodium salt of an acid containing one more carbon atom than the desired product with soda lime. The following equation expresses the anticipated reaction

$$\mathrm{R{-}COONa + NaOH = R{-}H + Na_2CO_3} \qquad (A)$$

Although some elementary organic textbooks still give this as a general method for the preparation of aliphatic hydrocarbons, it is now recognized that these reactions are rather complex and yield, besides sodium carbonate and hydrogen, quantities of hydrocarbons containing fewer carbon atoms than would be expected.[3] Nevertheless, by distilling a mixture of sodium ethylate and the sodium salt of stearic, palmitic, elaidic or oleic acid in a vacuum, Mai[4] has been able to obtain fair yields of the hydrocarbons that would be anticipated if the reaction followed the course of Equation **A.**

In the related field of nitrogen compounds, Miss Fulton[5] and Mr. E. C. Cornell[6] have found that a number of fatty acids of the ammonia system, $\mathrm{R{-}C}\begin{smallmatrix}\mathrm{=NH}\\ \mathrm{-NH_2}\end{smallmatrix}$, yielded hydrocarbons when heated with potassium amide, the reactions proceeding qualitatively in accordance with the equation

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[1] Presented at the Berkeley Meeting of the A. A. A. S., Pacific Division, June, 1929; from the Ph.D. thesis of R. A. Fulton.

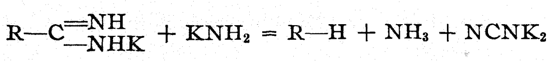
[2] (a) Dumas, *Ann.*, 33, 181 (1840); (b) Berthelot, *Ann. chim.*, [3] **53,** 79 (1858); (c) Schorlemmer, *Chem. News*, 29, 7 (1874); (d) Kolbe, "Ausf. Lehrbuch Org. Chem.," Vol. I, p. 275; (e) Moser, "Die Reindarstellung von Gasen," p. 130, Ferdinand Enke. Stuttgart; (f) Frankland and Thorne, *J. Chem. Soc.*, 33 91 (1878); (g) Hill and Hunt, THIS JOURNAL, 17, 988 (1895); (h) Freyer and Meyer, *Z. physik.* Chem., 11, 29 (1893).

[3] Dr. H. S. Fry has obtained methane and sodium carbonate by passing the vapors of acetic acid through fused sodium hydroxide. At present Dr. Fry and his students are examining the reaction of some of the other fatty acids with the fused alkalies. Personal communication.

[4] Mai, Ber., 22, 2133 (1897).

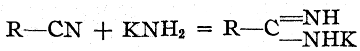
[5] Dissertation, Stanford University, 1925.

[6] Cornell, THIS JOURNAL, 50,3317 (1928).



$$R{-}C\begin{matrix}=NH\\ -NHK\end{matrix} + KNH_2 = R{-}H + NH_3 + NCNK_2 \qquad (B)$$

The acid amidines, $R{-}C\begin{matrix}=NH\\ -NH_2\end{matrix}$, themselves not being readily available were prepared for the most part by the action of potassium amide on the corresponding acid anammonide (acid nitrile) as represented by the equation



$$R{-}CN + KNH_2 = R{-}C\begin{matrix}=NH\\ -NHK\end{matrix} \qquad (C)$$

The similarity between equations (A) and (B) is to be especially noted. In each case there results a hydrocarbon that contains one less carbon atom than the fatty acid entering the reaction. In the first case, potassium aquo carbonate, K_2CO_3, is formed; in the second case, a potassium ammono carbonate, dipotassium cyanamide, $NCNK_2$.

The quantitative formation of the hydrocarbon to be expected from equation (B) is scarcely to be anticipated if these reactions are strictly analogous to the decomposition of the salts of the aquo fatty acids by heated soda lime or sodium hydroxide. Therefore it becomes desirable to repeat the work of Miss Fulton and Mr. Cornell on a larger scale and under more carefully regulated conditions. To this end a number of the nitriles of the lower fatty acids were passed through molten potassium amide, in the cell described in the next section, to convert them to the potassium salts of the corresponding *ammono* fatty acid, in accordance with equation (C). These salts—in the presence of the heated potassium amide in the cell—were at once decomposed into di-potassium cyanamide and a mixture of hydrocarbon gases, which were collected and analyzed.

Apparatus and Manipulation

The apparatus used in the present work is shown in Fig. 1. It was fabricated entirely of nickel, since this metal appears to be unattacked by the fused amides even at temperatures well in excess of 400°.[7] The two small needle valves were made of monel metal.

The fusion chamber F is made of a 20-cm. length of seamless nickel tube, 3.75 cm. in internal diameter and 3 mm. in thickness. A thick plug of nickel, Q, is silver soldered into the bottom of the tube in such a manner that about two-thirds of the plug projects outside. Two parallel flats are milled on this portion to permit the plug to be clamped in a vise while the hexagonal head G is being screwed into place or removed.

The nitrile is dropped from a small buret, S, into the tube P from which it is carried by a current of dry ammonia through the needle valve, A, and thence through the fused potassium amide in the bottom of the cell. The enlargement near the bottom of H is designed to prevent the fused amide from backing up into the smaller tube and solidifying. The tube T-N-H is broken at L with a compression joint, the threads on which have the same pitch as the threads on the top of F. This allows the hexagonal cap, *G*, to be removed at the end of a run, leaving H embedded in the solidified potassium amide. The lock-nut N allows the tip of the tube H to be adjusted at any suitable height from the bottom of the fusion chamber. Since the two valves A and D are

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[7] Fernelius and Bergstrom, J. Phys. *Chem.*, 35, 742 (1931).

rather close together, it would be very difficult to screw both into place if it were not for the union at T.

The gases liberated in the reaction are vented through D and passed through a mercury bubbler, U, into a gas collector, V, containing dilute sulfuric acid,[8] where the ammonia is absorbed. The unabsorbed gases are then passed through a drying tube, W, into a modified Shepherd–Porter apparatus where they are analyzed.[9] The use of the apparatus may best be illustrated by the description of a typical run.

The thoroughly cleaned cell, assembled as in Fig. **1,** is placed in a large electric crucible furnace, K, and heated to a temperature of **300**" while a current of dry ammonia[10] is passed through it for about half an hour. The cell is now thoroughly dry. The plug B is unscrewed and valve D closed, allowing a stream of ammonia to escape from B. Through this hole was inserted a short length of capillary sealed to the bottom of a 25-mm. test-tube. Approximately **3** g. of metallic potassium was placed in this test-tube and the top closed by a stopper through which passed a tube leading to a supply of ammonia under pressure (ammonia tank).[7] The potassium was melted by carefully applying a flame to the outside of the test-tube. The molten potassium was then forced into the cell by judicious application of ammonia pressure, the oxide remaining behind. The weight of the tube plus the potassium less the weight of the tube containing only the residual oxide equaled the weight of the potassium introduced into the cell. This generally varied between **3** and **3.5** g.

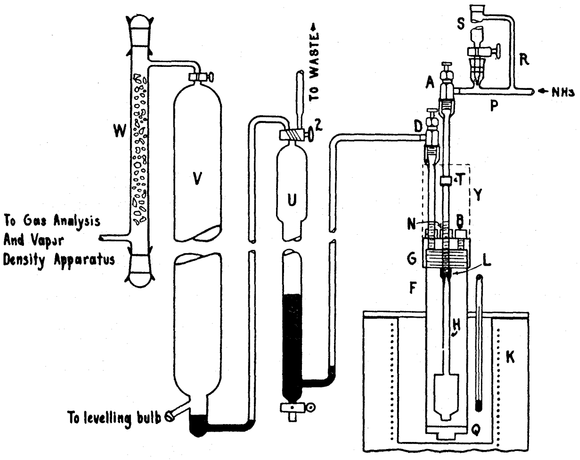

Fig. 1.

After the introduction of the potassium, B was replaced and the water jacket Y screwed into position (shown in dotted lines in Fig. 1). The jacket was kept about two-thirds full of water for the purpose of keeping the valves cool, thus facilitating their manipulation. The lock nut *N* was loosened and the ammonia inlet tube H adjusted so that its tip was, by calculation, about 2 mm. below the surface of the molten

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[8] *Cf.* Kraus and White, THIS JOURNAL, **45, 768 (1923);** White, ***ibid.,*** **45,779 (1923);** Wooster, ***ibid.,*** **51,1859 (1929);** Fernelius and Bergstrom, **J.** Phys. ***Chem.,*** **35,742 (1931).**

[9] Burrell, "The Recovery of Gasoline from Natural Gas," **A.** C. S. Monograph, p. **101.** Shepherd and Porter, ***Ind. Eng. Chem.,*** **15,1143 (1923).**

[10] Dried over sodium according to the method of Franklin and Kraus, ***Am. Chem.*** **J.,23,285 (1900).**

potassium. Then *N* was tightened. The temperature of the cell was raised to about 400° and a rapid current of ammonia passed through to convert the potassium to potassium amide (stopcock *2* was opened to the waste). This generally required about half an hour to an hour. The complete conversion was recognized by the cessation of the evolution of hydrogen. (Stopcock **2** turned to direct ammonia into the absorption tower.)

The nitrile was now introduced into the cell by means of the buret in the manner already described. Duplicate runs are comparable, since the amount of potassium used in each experiment was very closely the same and since the opening at the lower end of I was kept at approximately the same distance underneath the surface of the molten amide. All nitriles were passed through the cell at a rate of about 0.1 cc. per minute, that is, at such a rate that all of the nitrile reacted with the potassium amide. The weight of nitrile entering the reaction varied between one-half gram and two grams (see Table I). A more rapid rate of addition of nitrile caused the production of tar.

The gases formed in the reaction and collected in the gasholder, V, were passed through a barium perchlorate tube, W, and thence to a slightly simplified Shepherd–Porter gas analysis apparatus. The modification consisted in the use of a single tube, with indentations like a Vigreux column, for the condensation of the hydrocarbons gases by liquid air. Since the volume of gas formed in the reactions seldom exceeded one liter, a fairly complete separation of the constituents of the mixture was effected by removing the nitrogen–hydrogen, methane, ethane, propane and butane fractions with a Topler pump, the condensation tube being held at the temperatures recommended by Shepherd and Porter. Thus, none of the hydrocarbons were re-fractionated, as in the original method to which reference was made. The efficiency of separation of the hydrocarbon gases was verified by burning them in the slow combustion pipet of the Shepherd–Porter apparatus, and by determining their vapor density. To this end the individual hydrocarbon fractions, which were collected in the graduated delivery tube of the Topler pump, were passed through a phosphorus pentoxide drying tube and thence into an evacuated vapor density bulb. The gas so collected was weighed under a known pressure, indicated by a manometer attached to the system. The higher hydrocarbons, liquid at ordinary temperatures, were separated by repeated distillations from a small flask with a fractionating column.

The cell containing the non-volatile reaction products, together with the excess of potassium amide, was cooled in ice water and half filled with benzene. Water was then slowly introduced until the contents of the cell were completely hydrolyzed. The resulting strongly alkaline aqueous solution was separated from the benzene, diluted and almost neutralized with dilute nitric acid (cooling). Then an excess of ammonia water was added and this was followed by an aqueous solution of silver nitrate to precipitate the yellow di-silver cyanamide (silver ammono carbonate), which was filtered off, dried in *vacuo* at 60° and weighed.

It is evident that this procedure will give only an approximately accurate measure of the amount of cyanamide formed, since this is known to be slowly converted to urea in strongly alkaline solution. Buchanan and Barsky[11] have found that normal solutions of sodium hydroxide slowly and quantitatively convert cyanamide to urea. The rate of hydrolysis of the cyanamide is almost independent of the hydrogen-ion concentration in the more strongly alkaline solutions, the velocity constant for a first-order reaction being (0.74–0.96) 10^{-2}. The amount of cyanamide converted to

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[11] Buchanan and Barsky, THIS JOURNAL, 52,202 (1930).

Table I

Results of Experiments

Nitrile	A RCN added, g.	B[a] Gas formed, cc.	C Mol. wt. of hydrocarbons				D Calcd. mol. wt.				E Di-silver cyanamide g.	F Moles of di-silver cyanamide, per mole of RCN	G Temp., °C.
CH_3CN[b]	2.21	1197.3	15.92				16.0				13.683	1.0 ±	300
CH_3CN	1.82	973.2	16.11				16.0				11.162	1.0 ±	360
CH_3CN	1.24	618.3	15.89				16.0				7.458	1.0 ±	400
CH_3CH_2CN	1.68	897.4	15.95	27.72			16.0	30.0			9.876	1.24	300
CH_3CH_2CN	1.13	753.2	15.92	29.87			16.0	30.0			7.217	1.35	360
CH_3CH_2CN	1.28	826.9	15.97	29.92			16.0	30.0			9.089	1.49	400
$CH_3CH_2CH_2CN$	1.35	613.4	15.8	29.3	43.9		16.0	30.0	44.1		6.132	1.207	300
$CH_3CH_2CH_2CN$	1.52	763.8	15.9	29.8	43.7		16.0	30.0	44.1		8.197	1.43	360
$CH_3CH_2CH_2CN$	1.19	686.2	15.9	29.9	43.8		16.0	30.0	44.1		7.973	1.78	400
$CH_3CH_2CH_2CH_2CN$	0.92	403.2	15.8	29.9	43.9	57.7	16.0	30.0	44.1	58.1	4.587	1.61	300
$CH_3CH_2CH_2CH_2CN$	0.74	337.2	15.9	30.1	43.9	57.8	16.0	30.0	44.1	58.1	3.968	1.69	360
$CH_3CH_2CH_2CH_2CN$	0.87	447.4	15.8	30.0	44.2	58.9	16.0	30.0	44.1	58.1	5.149	1.88	400
$(CH_3)_2CHCH_2CH_2CN$	0.81	282.2	16.1	30.2	58.1	71.9	16.0	30.0	58.1	72.1	1.985	0.94	300
$(CH_3)_2CHCH_2CH_2CN$	0.55	233.7	16.2	30.1	58.2	71.8	16.0	30.0	58.1	72.1	1.523	1.05	360
$(CH_3)_2CHCH_2CH_2CN$	0.68	321.0	16.1	30.2	58.3	71.9	16.0	30.0	58.1	72.1	2.140	1.19	400

[a] Under standard conditions. [b] All nitriles were dried over phosphorus pentoxide, separated from the latter and redistilled.

urea during the hydrolysis of the potassium amide fusions here discussed should not exceed a very few per cent. The analytical results for cyanamide are thus only approximately correct, especially since the di-silver cyanamide precipitates are often impure.

Results of the Experiments

The experiments described in this paper were all performed in duplicate, the conditions of the two sets of runs being as nearly identical as possible. The analyses of the gases formed in the two runs checked to within a few tenths of one per cent. in nearly all cases. Undoubtedly alteration in the speed of addition of the nitrile and in the height of fused potassium amide through which the nitrile was passed would alter the relative proportions of the hydrocarbons that were formed. The average values are given.

Table I shows the weight of the nitrile entering the reaction at the three temperatures of the experiments (300, 360 and 400") (column **A**); the total volume of gas formed (column B); the molecular weight of the hydrocarbon fractions as determined by the vapor density method (column C); the calculated molecular weights of these hydrocarbons (column D); the weight of di-silver cyanamide obtained from the hydrolyzed solid reaction product (column E), and the number of moles of di-silver cyanamide obtained per mole of the reacting nitrile (column F).

Tables II, III and IV summarize the results of the analyses of the gases whose volumes are given in column B of Table I.

TABLE II

THE DECOMPOSITION OF NITRILES BY POTASSIUM AMIDE

(Temp., 300°)[12]

	Hydrogen	Methane	Ethane	Propane	Butane	Iso-butane	Iso-pentane
CH_3CN	1.8	98.2					
CH_3CH_2CN	18.6	16.4	65.1				
$CH_3CH_2CH_2CN$	16.1	14.5	11.6	57.8			
$CH_3CH_2CH_2CH_2CN$	52.3	1.9	2.8	10.6	32.4		
$(CH_3)_2CHCH_2CH_2CN$	59.3	Trace	2.5			9.5	28.7

Discussion

It is evident that potassium amide and acetonitrile react at all three temperatures to form methane and dipotassium cyanamide in almost theoretical yields, in accordance with the type equation B. Propionitrile and solid potassium amide react at 300° to form a gas which is 65% ethane,

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[12] The nitrogen–hydrogen–methane fraction, pumped from the solidified hydrocarbon gases at liquid air temperatures, was analyzed by combustion in a slow combustion pipet, the amount of methane being determined from the carbon dioxide formed in the reaction. The remainder of the combustible gas, as calculated from the contraction in volume on burning with air was hydrogen. However, since nitrogen was not obtained in significant amounts in the preliminary runs, the hydrogen in the above tables was determined by difference, the volume of methane being known.

TABLE III

THE DECOMPOSITION OF NITRILES BY POTASSIUM AMIDE

(Temp., 360°)

	Hydrogen	Methane	Ethane	Propane	Butane	Iso-butane	Iso-pentane
CH_3CN	2.2	97.8					
CH_3CH_2CN	26.7	22.8	50.6				
$CH_3CH_2CH_2CN$	22.8	21.1	12.3	43.8			
$CH_3CH_2CH_2CH_2CN$	57.2	2.2	3.5	11.4	25.6		
$(CH_3)_2CH_2CH_2CH_2CN$	63.8	0.03	3.2			10.7	21.3

TABLE IV

THE DECOMPOSITION OF NITRILES BY POTASSIUM AMIDE

(Temp., 400°)

	Hydrogen	Methane	Ethane	Propane	Butane	Iso-butane	Iso-pentane
CH_3CN	2.5	97.5					
CH_3CH_2CN	39.7	32.4	27.9				
$CH_3CH_2CH_2CN$	42.5	31.6	10.5	15.4			
$CH_3CH_2CH_2CH_2CN$	63 9	2.2	3.5	11.4	25.6		
$(CH_3)_2CH_2CH_2CH_2CN$	71.5	4.2	5.6			13.8	4.9

16.4% methane and 18.6% hydrogen. All of the higher nitriles behave similarly, that is, the expected hydrocarbon is formed, together with varying amounts of all of the hydrocarbons down to and including methane. Hydrogen is always formed at the same time.

The yields of the lower hydrocarbons and of hydrogen increase with increasing temperature of fusion (Tables III and IV), while the yield of the expected hydrocarbon (equation A) decreases. This points most obviously to a catalytic decomposition or cracking of the expected hydrocarbon which increases with increasing temperature. The nickel of the cell at the temperatures of the reactions was found to have little effect on vapors of the hydrocarbons below pentane, when these were passed through the empty cell. The potassium amide itself must therefore have caused the decomposition or cracking of the anticipated hydrocarbons. This was indeed found to be the case, since the hydrocarbons from n-heptane down to ethane were partially cracked when passed through molten potassium amide under the conditions of the present experiments. This work will be discussed in detail in a forthcoming paper.

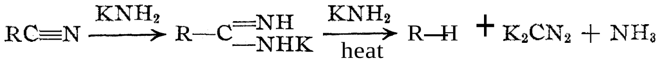
In an entirely analogous manner it was found that n-pentane was cracked readily by soda lime at a temperature of 400°, yielding hydrogen and a mixture of the lower hydrocarbons with a large preponderance of methane. This will perhaps account for the impracticability of preparing ethane and its higher homologs in accordance with the generalized reaction of equation A.

The decomposition of some of the higher nitriles by fused potassium amide (Table I) has given more than one mole of cyanamide per mole of reacting nitrile. It is known that carbon may be converted by the fused amides to cyanamide.[13]

Summary

1. A nickel apparatus has been devised for carrying out reactions in pure fused sodium or potassium amides.

2. The ammono fatty acid anammonides—that is, the nitriles of the fatty acids—react with fused potassium amide in accordance with the type equation



$$RC\equiv N \xrightarrow{KNH_2} R-C{=NH \atop -NHK} \xrightarrow[\text{heat}]{KNH_2} R-H + K_2CN_2 + NH_3$$

In other words, the salts of the fatty acids of the ammonia system are decomposed by heating with a base of the same system into a hydrocarbon and a sodium ammono carbonate (di-sodium cyanamide). The hydrocarbon R—H is cracked by the molten amide to simpler hydrocarbons and hydrogen, the degree of decomposition increasing with increase in the temperature of the fusion.

3. The failure to obtain the expected hydrocarbon in the reaction $R-COONa + NaOH$ (heated) $= Na_2CO_3 + R-H$ appears to be due in part at least to the cracking of the expected product R—H to lower hydrocarbons and hydrogen under the catalytic influence of soda lime or sodium hydroxide.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE CONSTITUTION OF MELEZPTOSE AND TURANOSE

BY EUGENE PACSU

RECEIVED MAY 25, 1931 PUBLISHED AUGUST 5, 1931

Investigations[1] have shown that when the natural non-reducing trisaccharide melezitose is gently hydrolyzed by weak acid solutions, there results as one of the products the reducing disaccharide, turanose. This sugar is the first known true isomer of sucrose and was first obtained in a pure crystalline condition by C. S. Hudson and the present author.[2] The failure in the past to secure a crystalline turanose has compelled investigators to use melezitose as the starting material in their efforts to solve the problem of the constitution of these two sugars.

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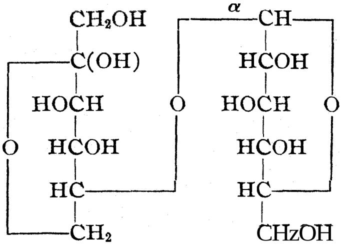
[13] English Patents 12,219; 21,732 (1894). German Patents 117,623; 124,977; 126,241 (1900); 148,045 (1901). Cf. *Chem. Zentr.*, [I] 75,411 (1904).

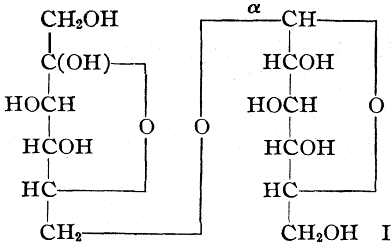
[1] Alekhine, *Ann.* phys. *chim.*, 18, 532 (1889); G. Tanret, *Bull. soc. chim.*, [3] **35**, 816 (1906); R. Kuhn and G. E. von Grundherr, *Ber.*, 59,1655 (1926).

[2] C. S. Hudson and E. Pacsu, *Science*, **69**, 278 (1929); THIS JOURNAL, 52, 2519 (1930).

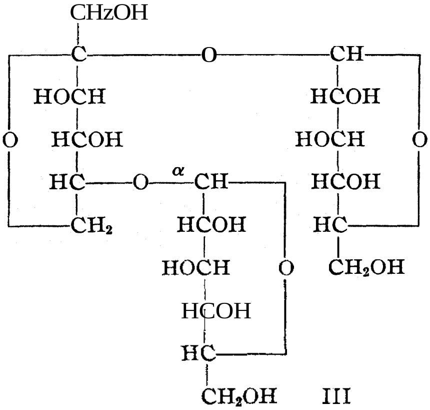
At the present time two different formulas are assigned for both turanose (I and II) and melezitose (III and IV):



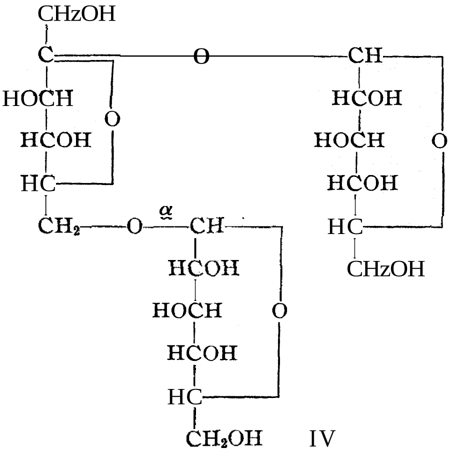
I



II



III



IV

It is my purpose to show that now we can ascribe a definite constitution for these two sugars based on methylation studies of former investigators and on new evidence recently obtained in this Laboratory using crystalline turanose as a starting material.

It is now quite beyond question that the general composition of melezitose is a-glucopyranose<fructose<>glucopyranose, where the reducing disaccharide, a-glucopyranose<fructose< is turanose. The α-glycosidic linkage in turanose has been proved by Bridel and Aagaard,[3] but the identity of the other potential disaccharide fructose<>glucopyranose is not as certain. Unlike turanose it cannot be isolated in a free state. It may be sucrose or a ring isomer of sucrose. Neither will methylation experiments answer this question. A completely methylated melezitose would yield on hydrolysis 2,3,4,6-tetramethylglucopyranose and a trimethylfructose. The structure of this fructose derivative would be the key to the true constitution of melezitose and turanose. Unfortunately, however, none of the theoretically possible isomeric trimethylfructoses has

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[3] M. Bridel and T. Aagaard, *Bull. soc. chim. biol.*, 9,884 (1927); T. Aagaard, *Tids. Kemi Bergwesen*, *8*, *5*, *16*, 35 (1928).

so far been prepared, and therefore this direct method of comparison is not available.

If we assume with Zemplén and Braun[4] that the fructose fragment of melezitose contains the same 2,6-oxide linkage as it was believed exists in the fructose part of sucrose, their conclusion that their partially methylated fructose has the structure of 1,3,4-trimethylfructose<2,6> leads to (I) for the structure of turanose and (III) for melezitose. However, Haworth and Hirst[5] have shown that the fructose constituent of sucrose does not belong to the normal fructopyranose type and they have suggested the presence of a fructofuranose in sucrose. If such a sucrose be the constituent of melezitose then we must agree, as Zemplén[6] points out, that the structure of the trimethylfructose is 1,3,4-trimethylfructose<2,5> and therefore turanose and melezitose should be represented by (II) and (IV), respectively. The trimethylfructose in question has been methylated by Leitch[7] and 1,3,4,6-tetramethylfructose<2,5> was obtained. This same fructose derivative is claimed by Haworth to be found when octamethylsucrose is hydrolyzed. According to Leitch this result is evidence that Zemplén's assumption that sucrose is the non-reducing potential disaccharide of melezitose is correct and that therefore the structure of turanose and melezitose must be (II) and (III). However, reflection will show that this conclusion is not justified. If we consider the possibility that 1,3,4-trimethylfructose may easily acquire two different rings,[8] it is possible that the non-reducing disaccharide in melezitose is not the common sucrose but rather a ring isomer containing a 2,6-oxygen bridge in the fructose component. The completely methylated derivative of such a melezitose (III) still may yield on hydrolysis 1,3,4-trimethylfructose<2,5> because the expected 1,3,4-trimethylfructose<2,6> may easily shift its pyranoid ring into a furanoid ring.

Further evidence which leads us to doubt that ordinary sucrose is a constituent of the melezitose molecule is found in certain investigations of Bridel and Aagaard[3] on the hydrolysis of melezitose by various enzymes.

It therefore appears that the "proved structures of melezitose and turanose are still questionable. Indeed experiments which I am now reporting indicate that the structures originally assigned to these sugars by Zemplén and Braun are the more probable.

It has been shown by Helferich[9] in his studies on triphenylmethyl deriva-

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[4] G. Zemplén and G. Braun, *Ber.*, 59, 2230 (1926).

[5] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, 1858 (1926).

[6] G. Zemplén, *Ber.*, 59, 2539 (1926).

[7] Grace Leitch, *J. Chem. Soc.*, 588 (1927).

[8] This is a logical assumption since the potential ketone group as well as the fifth and sixth OH groups are free.

[9] B. Helferich and J. Becker, *Ann.*, 440, 1 (1924); B. Helferich, L. Moog and A. Jünger, *Ber.*, 58, 872 (1925).

tives of the sugars and glucosides that triphenylchloromethane reacts only with the primary alcoholic groups in these compounds. It is evident, therefore, that triphenylchloromethane may be used to advantage in investigating the structure of turanose. The quantity of this reagent taken up by the sugar will give us an indication of the number of primary alcoholic groups present in the molecule. This method has been used by Josephson[10] in his studies on maltose, sucrose and raffinose. He has shown that hydrogen bromide dissolved in glacial acetic acid easily removes the triphenylmethyl residue as triphenylbromomethane and, if this be determined quantitatively, the number of primary alcoholic groups can be readily ascertained.

If we apply this method of analysis to turanose, certain possibilities suggest themselves. If formula (II) be correct, a di-(triphenylmethyl)-turanose will be obtained. However, if the correct structure of turanose be that represented by formula (I), a tri-(triphenylmethyl)-turanose may result inasmuch as the sixth OH group of the fructose residue though involved in ring formation may become free due to a shift of the ring. That such a ring shift may be expected is justified by the observation of Josephson.[10] This investigator has shown that both arabinose and xylose in their normal forms react slowly with triphenylchloromethane in pyridine solution.

Experiments carried out with crystalline turanose show that this sugar readily combines with triphenylchloromethane to give a tri-(triphenylmethyl)-turanose which on acetylation yields a pentaacetyl derivative. These facts point clearly to the conclusion that the glucose residue in the turanose molecule cannot be attached to the sixth carbon atom of the fructose constituent. This obviously rules out formula (II) for the constitution of the turanose component in melezitose and also indicates that the true constitution of melezitose is as represented by formula (III). Such a formula for melezitose confirms the above statement that the potential nonreducing disaccharide in the molecule is not sucrose but rather a ring isomer of it. As regards the structure of the free turanose we can state with some degree of certainty that it is a 5-α-glucosido$<1,5>$fructose containing a 2,4-ring in its fructose part or a 2,6-ring which in solution shifts into the 2,4-position. That such a ring shift takes place is supported by evidence which will be published later. If turanose be acetylated in acetic anhydride solution at room temperature in the presence of the catalyst zinc chloride, three well-defined crystalline octaacetates are produced instead of the two foreseen by theory if a ring shift is excluded.

Finally it may be added that the fact that all the known disaccharides are linked either to the fourth or sixth carbon atom and never to the fifth position should not concern us seriously if it be observed that the fifth

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[10] K. Josephson, *Ann.*, **472,230** (1929).

carbon atom of fructose where the glycosidic linkage in the turanose molecule occurs is in reality the fourth carbon atom counted from the potential reducing group of the fructose component.

Experimental Part

Preparation of **Tri-(triphenylmethyl)-turanose.**—Three and a half grams of crystalline turanose was dissolved in 60 cc. of hot pyridine and to the cooled solution 14 g. of triphenylchloromethane was added. On standing for a short time at room temperature a white crystalline material was deposited from the solution which in all probability is triphenylmethyl pyridine chloride. After four to five days the solution was cooled in an ice-bath and water was added to it drop by drop. When the double compound went into solution, more water was carefully added until cloudiness developed. The liquid was kept below 0° for several hours and the triphenylcarbinol which separated during this time removed by filtration. The clear filtrate was poured under vigorous stirring into one and one-half liters of ice water. The gummy precipitate so obtained was allowed to stand for several days in water which was occasionally renewed. At the end of this time the gummy precipitate had changed into a white, solid mass. This was collected at the pump, dissolved in alcohol, the solution decolorized with charcoal and stirred into a large amount of ice water. After standing for two days in the ice box the treatment was repeated. Finally it was filtered and dried for several days at room temperature over phosphorus pentoxide in a vacuum desiccator to constant weight; yield, 2–3 g. of colorless, white powder. The specific rotation was found to be $[\alpha]^{20}_{D}$ 30.87° (0.7046 g. in 25 cc. of chloroform solution rotated 1.74° to the right in a 2-dm. tube). No mutarotation of the solution could be observed. This material melted at 105–115°, a phenomenon which is due to the presence of the α- and β-forms. It is insoluble in water and petroleum ether but is readily soluble in the common organic solvents.

Anal. Calcd. for di-(triphenylmethyl)-turanose, $C_{50}H_{50}O_{11}$: C, 72.60, H, 6.10; for tri-(triphenylmethyl)-turanose, $C_{69}H_{64}O_{11}$: C, 77.50, H, 6.04. Found: C, 77.06; H, 6.21.

Preparation of **Tri-(triphenylmethyl)-turanose Pentaacetate.**—Two grams of tri-(triphenylmethyl)-turanose was dissolved in 10 cc. of pyridinc and to the ice-cold solution 6 cc. of acetic anhydride was added. On standing for two days at room temperature a few drops of water were carefully added to the cooled solution and after half an hour it was stirred into 500 cc. of ice water. The sirup which was precipitated very soon turned into a solid. This was allowed to stand for several days in water which was occasionally changed. The filtered substance was then dissolved in alcohol, the solution decolorized with charcoal and stirred into ice water. After repeating this treatment the filtered substance was dried in a vacuum desiccator over phosphorus pentoxide and solid sodium hydroxide to constant weight: yield, 2.2 g. of colorless fine powder having a specific rotation in chloroform of $[\alpha]^{20}_{D}$ 75.85" (0.6889 g. in 25 cc. of chloroform solution rotated 4.18° to the right in a 2-dm. tube). The substance does not possess a sharp melting point as it begins to sinter at about 85° and melts at 95–105°. It is insoluble in water but is soluble in the common organic solvents except petroleum ether.

Anal. Calcd. for di-(triphenylmethyl)-turanose hexaacetate, $C_{62}H_{62}O_{17}$: C, 68.98; H, 5.79; for tri-(triphenylmethyl)-turanose pentaacetate, $C_{79}H_{74}O_{16}$: C, 74.14; H, 5.83. Found: C, 73.92; H, 5.93.

In an acetyl estimation made by the method of Kunz,[11] 0.4060 g. of substance was dissolved in 80 cc. of pure acetone to which 24.6 cc. of 0.1 N sodium hydroxide was sub-

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[11] A. Kunz and C. S. Hudson, THIS JOURNAL, 48,1982 (1926).

sequently added. The acetylated triphenylmethyl derivative of turanose neutralized 16.8 cc. of decinormal alkali, whereas the value calculated for tri-(triphenylmethyl)-turanose pentaacetate is 15.9.

The triphenylmethyl estimation was carried out by the method of Josephson,[10] 0.1525 g. of substance was dissolved in 0.5 cc. of cold glacial acetic acid and mixed with 0.4 cc. of glacial acetic acid saturated at 0° with hydrogen bromide. After a transitory halochromic coloration due to the formation of a double compound between triphenyl carbinol and hydrogen bromide, triphenylbromomethane separated from the cold liquid. The crystals were collected on a Jena glass filter and washed by means of a pipet with 0.4 cc. of glacial acetic acid. After being dried over solid potassium hydroxide in a vacuum desiccator to constant weight, the triphenylbromomethane formed weighed 0.1088 g., which is 94.13% of the theoretical amount required for tri-(triphenylmethyl)-turanose pentaacetate.

Summary

Two different formulas for both turanose and melezitose are recorded in the literature. Evidence is submitted to show that turanose has three primary alcoholic groups in its molecule in that a tri-(triphenylmethyl)-turanose and its pentaacetate could be prepared. This fact together with certain methylation experiments of former investigators leads to the conclusion that the formulas of turanose (I) and melezitose (III) originally suggested by G. Zemplén and G. Braun should be chosen for these rare compound sugars.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MUNICH AND THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. THE RESOLUTION OF 8,8'-DICARBOXY-1,1'-DINAPHTHYL

BY W. M. STANLEY[1]

RECEIVED MAY 28, 1931 PUBLISHED AUGUST 5, 1931

The resolution of 2,2'-dicarboxy-1,1'-dinaphthyl[2] (I) demonstrated that the 2,2'-carboxyl groups and the 8,8'-hydrogen atoms are sufficiently large to interfere with each other and thus allow resolution into optical isomers. This indicates that a carboxyl group and a hydrogen atom are large enough to interfere across the space AB (III) which may be calculated as 2.51 Å. by assuming the usual angles in the benzene ring. The fact that this compound was found to be quite stable toward racemization indicates that this interference is fairly large. The compound in which the carboxyl groups and the hydrogen atoms are interchanged, 8,8'-dicarboxy-1,1'-dinaphthyl (II), should also be resolvable, since the 8,8'-carboxyl groups and the 2,2'-hydrogen atoms should interfere across the space AB as in the previous compound, assuming that no additional fac-

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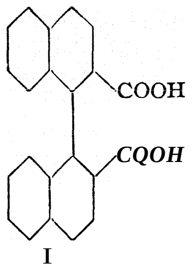
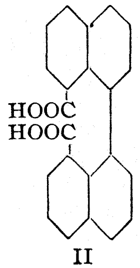
[1] National Research Fellow in Chemistry.

[2] Kuhn and Albrecht, Ann., 464, 282 (1928).

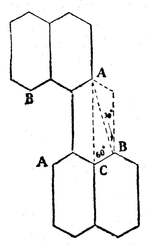
tors enter the case. This compound (II) is of unusual interest since it may be readily seen that it is an example of an α,α'-disubstituted diphenyl derivative. Although the resolution of α,α'-disubstituted diphenyl derivatives has been predicted,[3] attempts at resolution, up to the present time, have been unsuccessful.



I



II



III

In the present investigation 8,8′-dicarboxy-1,1′-dinaphthyl was resolved into its optical isomers by fractionation of the monoquinine salt from benzene. Pyridine solutions of the d- and I-acids gave $[\alpha]_D^{20}$ + 198.1° and $[\alpha]_D^{20}$ − 185.8°, respectively. Practically complete racemization occurred in pyridine solution on standing for five weeks at 19°, and complete racemization occurred in 2 N ammonium hydroxide solution on standing at 19° for fifteen hours. The optically active acids were also completely racemized by heating in pyridine solution at 100° for thirty minutes or by heating in 0.1 *N* sodium hydroxide at 90° for thirty minutes.

The correct explanation as to why 8,8′-dicarboxy-1,1′-dinaphthyl is readily racemized while 2,2′-dicarboxy-1,1′-dinaphthyl is quite stable toward racemization is not yet clear. The difference in stability may be due to the fact that the peri-substituted carboxyl groups in 8,8′-dicarboxy-1,1′-dinaphthyl render the molecule more labile and more capable of distortion than when the carboxyl groups are in the 2,2′ positions.

The set of interference values which has been suggested3 was designed primarily to enable estimation of the interferences between 2,6 and 2′,6′ groups in diphenyl derivatives. In such compounds the interfering groups were assumed to be at an angle of 60" from the line of nearest approach (AC). However, in the case of 8,8′-dicarboxy-1,1′-dinaphthyl the 2,2′- and the 8,8′-groups cause the interference and these groups may be assumed to be at an angle of 30" from the line of nearest approach (AB). The effective diameter of the groups would probably be a little larger since they are directed more toward each other (by 30°); consequently in compounds of this type the interference values would probably need to be slightly increased.

The author wishes to express his sincere thanks to Professor Ludwig Kalb for the 8,8′-dicarboethoxy-1,1′-dinaphthyl used in this investigation.

[3] Stanley *and Adams,* THIS *JOURNAL, 52,* 1200 (1930); 53,2364 (1931).

Experimental Part

8,8′-Dicarboxy-1,1′-dinaphthyl.—A mixture of 0.65 g. of 8,8′-dicarboethoxy-1,1′-dinaphthyl[4] and 2 g. of potassium hydroxide in 50 cc. of amyl alcohol was refluxed for seven hours. About 45 cc. of alcohol was then removed by distillation under vacuum and 100 cc. of water added to the residue. The acid was then precipitated by the addition of concentrated hydrochloric acid, removed by filtration and dissolved in 50 cc. of dilute aqueous ammonia. This solution was treated with animal charcoal to give a colorless solution, from which the acid was precipitated by the addition of hydrochloric acid. The yield was 0.5 g. (91%) of a product melting at 298–300° to a red liquid. Upon recrystallization from ethyl alcohol the melting point was raised to 306–307°. The 8,8′-dicarboxy-1,1′-dinaphthyl is insoluble in xylol, acetone, ether and chloroform, slightly soluble in ethyl alcohol, ethyl acetate and acetic acid, and soluble in pyridine and hot acetic anhydride. The ester was only partially saponified by the use of methyl or ethyl alcoholic potassium hydroxide.

Anal. Subs., 5.025 mg.: CO_2, 14.20 mg.; H_2O, 1.89 mg. Calcd. for $C_{22}H_{14}O_4$: C, 77.17; H, 4.12. Found: C, 77.07; H, 4.21.

Resolution of 8,8′-Dicarboxy-1,1′-dinaphthyl.—To a cloudy solution of 0.4367 g. of 8,8′-dicarboxy-1,1′-dinaphthyl in 150 cc. of absolute ethyl alcohol was added 0.4138 g. (1 equivalent) of quinine. The solution, which became perfectly clear upon the addition of the quinine, was evaporated to dryness. The mono-quinine salt is very soluble in methyl alcohol, ethyl alcohol, acetone and chloroform, slightly soluble in benzene and insoluble in ether and water. The mono-quinine salt was taken up in 20 cc. of benzene and a few drops of ethyl alcohol was added to make the solution clear. The solution was then boiled for five minutes and allowed to stand. After standing for two days at room temperature, the clear solution was decanted from a thin glassy film (0.24 g.) which had formed on the sides and bottom of the Bask.

Rotation. 0.0566 g. made up to 3 cc. with chloroform at 20° gave α_D −0.45"; $l = 1$; $[\alpha]^{20}_D$ −23.9".

After standing two more days a mass of fine crystals (0.25 g.) and two large clusters of fine needles (0.1 g.) had separated from the decanted solution. These were removed and dried. The melting point of the 0.1-g. portion was 195° with sintering at 175".

Rotation of the 0.1 g. portion: 0.0548 g. made up to 3 cc. with chloroform at 20° gave α_D −3.1°; $l = 1$; $[\alpha]^{20}_D$ −169.7'.

The 0.1-g. portion was recrystallized from benzene. The melting point was unchanged.

Rotation. 0.0292 g. made up to 2 cc. with chloroform at 20" gave α_D −2.42'; $l = 1$; $[\alpha]^{20}_D$ −165.8'.

Rotation of the 0.25-g. portion: 0.0604 g. made up to 3 cc. with chloroform at 20° gave α_D −2.75'; 1 = 1; $[\alpha]^{20}_D$ −136.6".

Anal. Calcd. for $C_{42}H_{38}O_6N_2$: C, 75.64; H, 5.75. Found: C, 75.47; H. 5.71.

The remaining salt solution was evaporated to dryness and gave 0.25 g. of salt which sintered at 173° and melted at 190°.

Rotation. 0.0570 g. made up to 3 cc. with chloroform at 20° gave α_D = +3.65°; $l = 1$; $[\alpha]^{20}_D$ +192.1°.

The first portion (0.24 g.) of salt which was obtained in the fractionation consisted mainly of the *d,l*-salt. Upon refractionation from benzene the partially pure d- and *l*-salts were obtained.

***d*-8,8′-Dicarboxy-1,1′-dinaphthyl.**—To 0.24 g. of salt having a rotation of +192.1° in chloroform was added 10 cc. of 0.5 *N* hydrochloric acid. After stirring for ten

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[4] Kalb, Ber., 47, 1724 (1914).

minutes the mixture was filtered. This treatment was repeated twice and the precipitated acid was dissolved in 15 cc. of 0.1 N sodium hydroxide and extracted twice with 5 cc. of chloroform. The active acid was then precipitated from the alkaline solution with dilute hydrochloric acid. After drying, the product melted to a red liquid at 305–306°.

Rotation. (a) 0 0210 **g.** made up to 2 cc. with pyridine at 20° gave α_D +2.08°; 1 = 1; $[\alpha]_D^{20}$ +198.1°. **(b)** 0.0336 g. made up to 15 cc. with 0.1 *N* sodium hydroxide gave a, —0.28'; 1 = 0.5; $[\alpha]_D^{20}$ —250.0°. (c) 0.0190 g. made up to 5 cc. with **2** *N* aqueous ammonia gave a, —0.35°; *l* = 0.5; $[\alpha]_D^{20}$ —184.2".

A portion of the d-salt having a rotation of +44.5° in chloroform was hydrolyzed in a similar manner to give partially pure d-acid.

Rotation. (a) 0 02.50 g. made up to 9 cc. with 0.5 N aqueous ammonia gave a, —0.12"; *l* = 1; $[\alpha]_D^{20}$ —43.2'. (b) 0.0240 g. made up to 2 **cc.** with pyridine at 20° gave α_D +0.88°; 1 = 1; $[\alpha]_D^{20}$ +73.1°.

It was necessary to use dilute alkaline solutions of the d-acid since concentrated alkaline solutions of the d-acid were always cloudy. Repeated solution in alkali, extraction with chloroform and precipitation with hydrochloric acid did not change this property.

***l*-8,8'-Dicarboxy-1,1'-dinaphthyl.**—A portion of I-salt having a rotation of **—169.7°** in chloroform was hydrolyzed by treatment with three 5-cc. portions of 0.5 *N* hydrochloric acid and extraction of the alkaline solution with chloroform. The Z-acid so obtained melted to a red liquid at 304.5–305.5°.

Rotation. 0.0240 g. made up to 2 cc. with pyridine at 20° gave α_D **—2.25°; *l* = 1;** $[\alpha]_D^{20}$ —185.8'.

Anal. Subs.. 4.447 mg.: CO_2, 12.57 mg.: H_2O, 1.68 **mg. Calcd.** for $C_{22}H_{14}O_4$: C, 77.17; H, 4.12. Found: C, 77.02; H, 4.23.

A portion of 1-salt having a rotation of —136.6° in chloroform was hydrolyzed ***by*** treatment with three 10-cc. portions of 0.5 *N* hydrochloric acid, solution in 0.5 *N* aqueous ammonia and immediate precipitation with dilute hydrochloric acid.

Rotation. 0.0225 **g.** made up to 2 cc. with pyridine at 20° gave α_D —2.02"; *l* = **1;** $[\alpha]_D^{20}$ —179.6'.

The I-acid was precipitated from the pyridine solution by the addition of concentrated hydrochloric acid at 0°. The rotation was again taken.

Rotation. 0.0187 g. made up to **2** cc. with 2 *N* ammonium hydroxide at 20° gave α_D +0.31°; *l* = 1; $[\alpha]_D^{20}$ +33.1°.

Racemization Experiments

1. **A** solution of 0.0210 g. of d-acid in 2 cc. of pyridine at 20° gave a, +2.08°; *l* = 1; $[\alpha]_D^{20}$ +191.1°. Heating the solution at 100° for thirty minutes caused complete racemization of the acid.

2. **A** solution of 0.0240 g. of I-acid in 2 cc. of pyridine at 20° gave a, —2.25"; 1 = 1; $[\alpha]_D^{25}$ —185.8". Standing for five weeks at room temperature caused almost complete racemization since the rotation was —5°: a, —0.06°; 1 = 1; $[\alpha]_D^{20}$ —5.0°.

3. A solution of 0.0187 g. of *l*-acid in 2 cc. of 2 *N* aqueous ammonia at 20° gave α_D +0.31°; 1 = 1; $[\alpha]_D^{20}$ +33.1°. After standing at 19° for fifteen hours the rotation was zero.

4. A solution of Eacid in 2 *N* aqueous ammonia having a, +0.24° was allowed to stand at 19°; after two hours a, +0.18°; after four hours a, +0.13°; after six hours α_D +0.08; after ten hours a, 0°.

5. A solution of 0.0336 g. of d-acid in 15 cc. of 0.1 N sodium hydroxide gave α_D —0.28"; *l* = 0.5; $[\alpha]_D^{20}$ —250.0". After heating the solution at 90° for thirty minutes the rotation was zero.

6. A portion of 0.0314 g. of acid having a rotation of −179° in pyridine was added to 3 cc. of acetic anhydride. The mixture was heated to boiling during one minute to effect solution and then immediately cooled to 20°. The rotation of the acetic anhydride solution was zero. The acetic anhydride was removed below 20° by means of a stream of air under vacuum and the residue dissolved in 2 cc. of pyridine. The rotation of the pyridine solution was zero.

The material recovered from the pyridine solution was recrystallized from benzene and had a melting point of 179–180°. It was insoluble in cold alkali and but slowly soluble in hot alkali, from which solution the original acid of m. p. 306–307° was obtained upon acidification. An analysis proved it to be the mixed acid anhydride of one molecule of 8,8′-dicarboxy-1,1′-dinaphthyl and two molecules of acetic acid.

Anal. Subs., 5.063 mg.: CO_2, 13.66 mg.; H_2O, 1.89 mg. Calcd. for $C_{26}H_{18}O_6$: C, 73.21; H, 4.25. Found: C, 73.68; H, 4.18.

When this mixed acid anhydride was heated above its melting point (180°) bubbles were evolved from the light yellow liquid and at 198–202° the liquid was converted to a red colored solid. After washing with hot dilute sodium hydroxide and recrystallization from chloroform this material melted at about 340°. This compound proved to be the anthanthron which was previously prepared by Kalb[4] by the action of concentrated sulfuric acid on 8,8′-dicarboethoxy-1,1′-dinaphthyl. Solution in concentrated sulfuric acid caused a bright green coloration.

Anal. Subs.: 2.619 mg.: CO_2, 8.26 mg.; H_2O, 0.77 mg. Calcd. for $C_{22}H_{10}O_2$: C, 86.25; H, 3.29. Found: C, 86.01; H, 3.29.

Summary

1. 8,8′-Dicarboxy-1,1′-dinaphthyl has been resolved into optical isomers by fractionation of the monoquinine salt from benzene.

2. This compound is the first α,α'-disubstituted diphenyl derivative which has been resolved.

3. The optically active acids were readily racemized.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 74]

SIGNIFICANT TEMPERATURES IN THE PYROLYSIS OF CERTAIN PENTANES AND PENTENES[1]

BY JAMES F. NORRIS AND GEORGE THOMSON

RECEIVED MAY 29, 1931 PUBLISHED AUGUST 5, 1931

Previous determinations in this Laboratory of the temperatures at which certain ethers[2] and a number of alkyl derivatives of malonic acid[3] begin to decompose when heated under definite conditions showed that these temperatures could be determined in independent experiments that gave results which agreed within ±2 degrees. The values obtained made it possible to correlate the temperatures at which certain bonds were broken

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[1] From the thesis presented by George Thomson in partial fulfilment of the requirement for the degrer of Doctor of Philosophy, 1930.

[2] Norris and Young, THIS JOURNAL, 52, 753 (1930).

[3] Norris and Young, *ibid.*, 52, 5066 (1930).

by pyrolysis with the rates at which these bonds were broken in a chemical reaction. The results showed, also, the effect of the structure of the alkyl radicals present on the temperature of pyrolysis.

The satisfactory results obtained in the earlier experiments led to the study in a similar way of the temperatures at which certain pentanes and pentenes begin to decompose when heated. With this information it would be possible to effect the pyrolysis of the hydrocarbons at or near their cracking temperatures and thus obtain the products first formed in their decomposition. It was expected that the results would lead to a better understanding of the mechanism of pyrolysis and to added knowledge of the effect of structure on the lability under the influence of heat of the carbon-carbon and carbon–hydrogen bonds in hydrocarbons.

This 'method of investigating the cracking of hydrocarbons seemed worthy of study, because previous work in this field has been carried out at such temperatures that profound decomposition resulted, and the number of products formed was so large that it was impossible to draw any definite conclusions as to the mechanism of the many reactions involved. For example, the pyrolysis of pentane and isopentane have been studied by Calingaert[4] at 600° and by Hague and Wheeler[5] at temperatures between 600 and 850°. Calingaert determined quantitatively eight products of the pyrolysis.

It is shown in this paper that normal pentane begins to pyrolyze at 391° and isopentane at 383°. Experiments now in progress indicate that at ten degrees above these temperatures a simple decomposition takes place as the result of the breaking of a single carbon–carbon linkage in each case. These experiments will be reported later. This paper is confined to the consideration of the temperatures at which the hydrocarbons begin to pyrolyze and the rates at which the reactions proceed at different temperatures.

In the determination of the temperature at which pyrolysis begins, the hydrocarbon was heated for about one hour, at a definite temperature, in a glass apparatus in which the expansion that occurred under approximately atmospheric pressure could be measured. At temperatures below that of decomposition no expansion was evident after thermal equilibrium had been established. As the temperature at which the vapor was held was raised, step by step, a temperature was reached at which expansion due to pyrolysis continued throughout the hour. From the increase in the volume of the vapor in a measured time, the rate of expansion at this temperature was calculated. The values of these rates at different temperatures were plotted against the temperatures. Figure 1 shows the results of an experiment when n-pentane was used.

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[4] Calingaert, THIS JOURNAL, *45*, **130** (1923).

[5] Hague and Wheeler, *J. Chem. Soc.*, **378** (1929).

It is seen that intersecting straight lines can be drawn through the points. In the case of this hydrocarbon at temperatures up to 389° there was no expansion when the hydrocarbon was held at these temperatures for an hour. Above 389° expansion continued throughout the hour at the rates indicated.

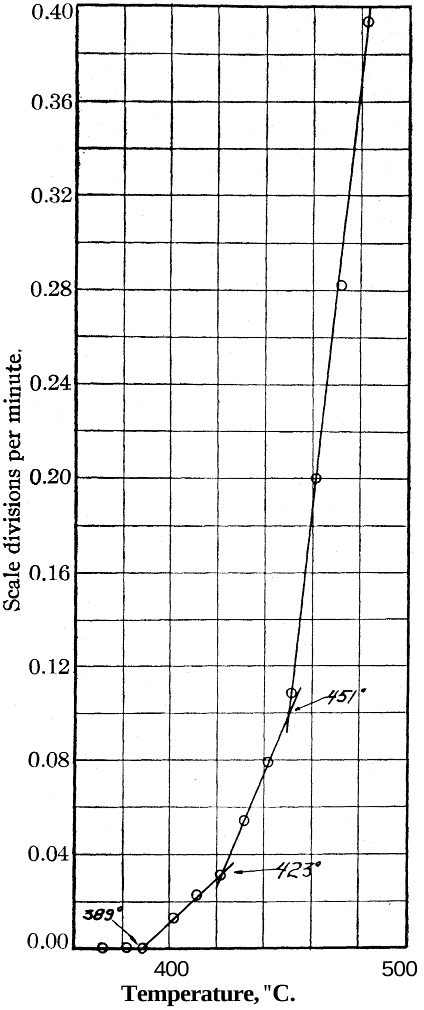

Fig. 1.—n-Pentane cracking rate curve: 1 Scale div. = 0.09 cc. at 40°.

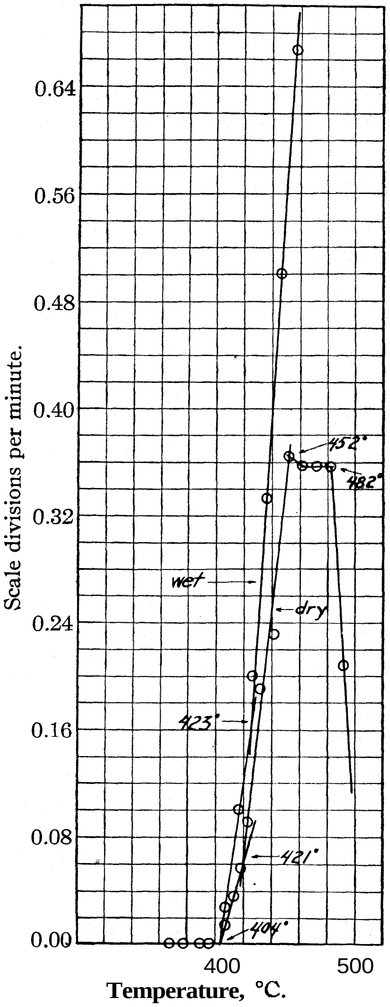

Fig. 2.—Pentene-2 cracking rate curve: 1 Scale div. = 0.09 cc. at 40°.

It appeared probable that between 389 and 423° one type of decomposition was taking place and that between **423** and 451° another type had set in. Above 451° the increased rate indicated more profound decomposition.

To determine whether or not the breaks in the lines represent real changes in the way in which the hydrocarbon undergoes pyrolysis, Mr. George Standley is now investigating the products formed at temperatures within the ranges indicated. It can be said at this time that the results are in accord with the view put forward above.

In the case of the unsaturated hydrocarbons the results were similar to those obtained with the paraffins, except that an additional significant temperature was observed. Above a certain temperature the rates of expansion either remained constant, or decreased as the temperature was increased. It is evident that at these higher temperatures two types of reactions are taking place simultaneously, namely, pyrolysis, which causes expansion, and another change which leads to contraction.

The examination of the cooled vessel in which the hydrocarbon had been pyrolyzed above the temperature at which the rate of expansion began to decrease (reversal temperature) showed that there had been formed a yellowish-brown oil less volatile than the hydrocarbon used. Below the reversal temperature there was little or no high-boiling oil formed. These observations indicate that the decrease in the rate of expansion is associated with the formation of polymers.

The behavior of pentene-2 is shown in Fig. 2 by the lines marked "dry," which record the rates of decomposition when the hydrocarbon was free from moisture. By plotting the rates it is possible to discover a temperature at which no expansion occurs (reversal temperature), since at this temperature the rates of the two types of reactions are the same.

The reversal temperatures of the three pentenes studied were from 53 to 65° above the temperatures at which the hydrocarbons began to decompose.

The influence of a trace of water in the pyrolysis of pentene-2 was investigated. The results are shown in Fig. 2. There appeared to be no influence on the pyrolysis temperature, but the rate of decomposition was doubled. Reversal in the rate, indicating polymerization, did not occur with the wet hydrocarbon at about ten degrees above the reversal temperature of the dry hydrocarbon.

The results obtained with the hydrocarbons studied are given in Table I.

The tabulated results show that n-pentane begins to decompose at a temperature higher than that at which its isomer with a branched chain begins to decompose; that pentane-2 and pentene-1 crack at about the same temperature; that pentene-2 is more stable to heat than pentene-1, and that the increase in the number of radicals joined to doubly linked carbon atoms in trimethylethylene leads to increased thermal stability.

In Table II are given for each hydrocarbon the percentage expansion per hour at ten degrees above the significant temperatures recorded in Table I and the increase in these values per ten degrees within the stated temperature intervals.

TABLE I

SIGNIFICANT TEMPERATURES IN THE PYROLYSIS OF THE HYDROCARBONS LISTED

	Initial cracking temp., °C.	Second break, °C.	Third break, °C.	Reversal temperature, °C.
Isopentane	383	419	449	
	383	426	450	
	383 Average	423 ± 3.3	45010.5	
Pentene-1	387	418		457
	388	420		455
	391	421		45611.0
	389 ± 1.4	420 ± 0.8		
n-Pentane	389	423	451	
	391	423	446	
	393	431	452	
	391 ± 1.1	426 ± 3.0	450 ± 2.0	
Pentene-2	404	419		
	404	421		
	398	425		452
	398	421		452
	396	420		454
	400 ± 2.4	421 ± 1.0		453 ± 0.8
Trimethylethylene	432	452	472	486
	432	446	477	495
	434	447		497
	433		475 ± 2.4	
		448 ± 2.0		493 ± 3.6
	433 ± 0.6			

TABLE II

THE FIGURES REFER TO THE ACTUAL EXPANSION OF THE HYDROCARBON VAPOR AT THE TEMPERATURE INDICATED

Hydrocarbon	Expansion 10° above initial break, %/hr.	Expansion Increase per 10°, %/hr.	Expansion 10° above sec. break, %/hr.	Expansion increase per 10°, %/hr.	Expansion 10 above third break, %/hr.	Expansion Increase per 10°, %/hr.	Maximum expansion, %/hr.
Isopentane	0 22	0 22 (383–423°)	1.6	0 7 (423–450°)	4.6	1 7 (450–485°)	
Pentene-1	.67	0 67 (389–420°)	4.4	2.1 (420–456°)			10.4 (456°)
n-Pentane	.22	0.22 (391–426°)	1.6	0.7 (426–450°)	5.1	2 5 (450–482°)	
Pentene-2	.68 (Dry)	0 68 (Dry) (400–421°)	3.7 (Dry)	2.4 (421–453°)			
	1.36 (Wet)	1.36 (Wet)	6.3 (Wet)	3.6 (421–459°)			8.8 (453°)
Trimethylethylene	1.2	1.2 (433–448°)	4.1	2.2 (448–475°)			9.9 (493°)

The results show that pentene-1 and pentene-2 decompose three times as rapidly as n-pentane and isopentane when the hydrocarbons are heated ten degrees above their respective cracking temperatures. Trimethylethylene decomposes about twice as fast as the straight-chain olefins and six times as fast as the paraffins at ten degrees above their respective cracking temperatures. Within the same temperature range (433–448°), it decomposes about twice as fast as the pentanes. Other significant facts which can be drawn from the table will be considered in a subsequent paper in which the study of the products of pyrolysis will be reported.

The work is being extended to other hydrocarbons. It is planned to investigate the influence of increased surface per volume of vapor, and of the presence of catalytic agents on the temperatures of pyrolysis. The theoretical aspect of the subject will be considered later.

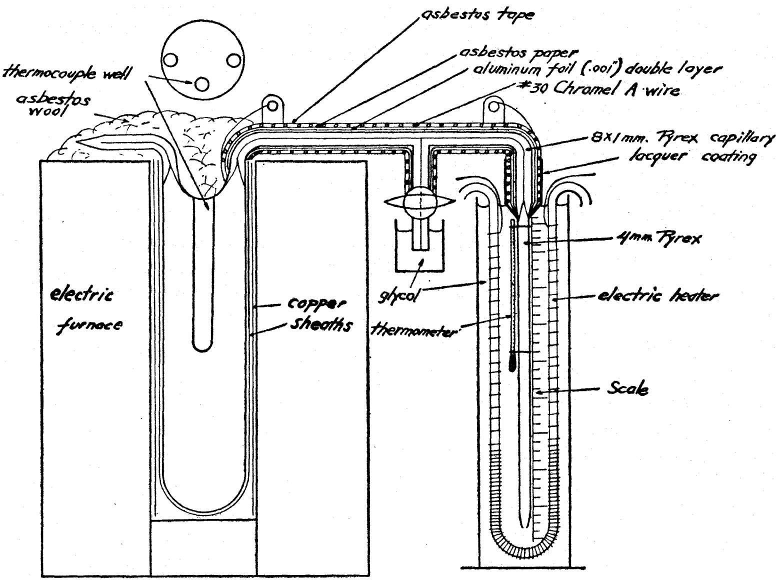

Fig. 3.

Experimental Part

Apparatus.—The apparatus consisted of an electric furnace in which was inserted a Pyrex bulb of about 52 cc. capacity connected by capillary tubing to a manometer arrangement as shown in Fig. 3. The bulb contained a thermocouple well and had another capillary opening to facilitate cleaning. Two copper sheaths surrounding the bulb in the furnace produced uniform temperature distribution. A double layer of aluminum foil underneath the electric heater on the capillary tube leading to the manometer served the same purpose.

The manometer tube was made of 4-mm. Pyrex tubing and was immersed in a hydrometer jar filled with ethylene glycol kept at a constant temperature of 40° by an electric heater. An experiment had shown that the vapors of the hydrocarbons were insoluble in glycol. The hydrometer jar was provided with a scale for reading the liquid level in the manometer tube. To prevent the glycol from soaking up into the electric heater on the capillary tube, the end of the heater was covered with several coats of lacquer.

In order to bring the manometer level to the zero mark, the stopcock on the capillary tube could be opened and gas allowed to escape.

A calibrated chromel–alumel thermocouple connected to a Leeds and Northrup portable potentiometer was used to measure the temperature of the hydrocarbon gas.

Since the olefins absorb oxygen to form peroxides on standing in bottles containing air, and the saturated hydrocarbons absorb some moisture, each hydrocarbon was distilled over sodium, just before each determination, directly into an 8 mm. × 14 cm. tube until from 1 to 1.5 cc. of hydrocarbon had collected. Chips of freshly cut sodium were then dropped in until there was enough to reach the surface of the liquid. The tube was then slipped over the end of the manometer tube on the apparatus and made tight with a short piece of pressure tubing. After surrounding the hydrocarbon with carbon dioxide snow and acetone, the apparatus was evacuated to less than 1 mm. pressure while at the same time the electric heater on the side arm was turned on and the bulb baked out with a Bunsen burner for several minutes. The heater was then turned off and the bulb allowed to cool. It was then immersed in ice and water and the carbon dioxide snow and acetone substituted by glycol at about the same temperature as the boiling point of the hydrocarbon. This caused the hydrocarbon to distil slowly over and condense in the bulb, which was then inserted in the electric furnace and the tube containing the sodium residue immersed in the hydrometer jar filled with warm glycol so that the rubber connection was just covered. As soon as the temperature of the bulb reached the boiling point of the hydrocarbon, this tube with its rubber connection was pushed off with a pair of tongs and the hydrometer jar raised to the position shown in the sketch. The sweeping action of the excess hydrocarbon boiling out was an added assurance of the absence of air.

When pentene-2 was run wet, the hydrocarbon was distilled over sodium into the 8 mm. tube as before but instead of adding chips of sodium a drop of water was added. The rest of the procedure was the same as when *dry*.

If, after holding the bulb at constant temperature for one hour, no expansion occurred, the temperature was raised 10° and again held constant for one hour. Eventually a temperature was reached at which expansion was appreciable. Scale readings were then taken over a period of sixty to eighty minutes. As the rate became greater this period was shortened until at 80 to 100° above the initial temperature readings were taken over a period of twenty minutes. These readings (4 at the higher temperatures, 8–9 at the lower temperatures) when plotted against time fell on straight lines the slopes of which were plotted against the corresponding temperatures. The intersection of this curve with the zero rate line fixed the initial temperature more accurately.

Materials

Pentene-1 was prepared in this Laboratory by Dr. R. L. Wakeman from ethylmagnesium bromide and allyl bromide. Final distillation over sodium gave a boiling point of 30.0–30.1" (corr.),[6] d_4^{20} 0.641.

Pentene-2 was made by dehydrating secondary amyl alcohol with sulfuric acid according to the method of Norris ["Organic Syntheses," Vol. VII, p. 76]. After drying and distilling over sodium it boiled at 36.3–36.4° (corr.).

2 Methylbutene-2 was obtained from tertiary amyl alcohol by dehydrating with oxalic acid. The mixture of 2-methylbutene-2 and 2 methylbutene-1 after many distillations through a Davis' column gave about a 12% yield of 2-methylbutene-2, b. p. 38.3–38.4° (corr.).

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[6] Kirrmann, [Bull. *soc. chim.*, 39, 988 (1926)] gives the b. p. as 30.5–31.0° but Hyman and Wagner, [THIS JOURNAL, 52, 4346 (1930)] found the b. p. to be 30.0" (corr.).

[7] H. S. Davis, *Ind. Eng. Chem., Analytical Edition*, 1, 61 (1929).

***n*-Pentane.**—By hydrogenating the above pentene-2, using nickel catalyst and purifying the product with sulfuric acid, very pure pentane was obtained, boiling at 36.1–36.2° (corr,).

Isopentane was obtained in a manner similar to that used for n-pentane but using the amylene mixture from the dehydration of *tert.*-amyl alcohol. The final product boiled at 27.9–28.0° (corr.).

Summary

1. The temperatures have been determined at which n-pentane, isopentane, pentene-1, pentene-2 and trimethylethylene begin to decompose when heated in a Pyrex glass vessel for one hour.

2. The determination of the rates at which these hydrocarbons decompose showed that for each hydrocarbon the increase in rate per ten degrees was constant within certain temperature limits and that this increase in rate was greater within the higher temperature limits. It appears probable that the limiting temperatures of the several ranges are the temperatures at which certain bonds undergo pyrolysis.

3. It was found that a trace of moisture had no effect on the cracking temperature of pentene-2, but that it doubled the rate at which the hydrocarbon decomposed.

4. When the olefins were heated at increasing temperatures, a temperature was found at which no expansion took place. The results indicate that at this point the expansion which results from pyrolysis is equal to the contraction resulting from polymerization.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE STRUCTURE AND SOME DERIVATIVES OF PARA-DIMETHYLAMINO-PARA-CHLOROBENZOIN

BY SANFORD S. JENKINS[1]

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The object of this report is to present the experimental evidence in support of a structure which is assigned to *p*-dimethylamino-*p*-chlorobenzoin[2] and to describe the preparation and some properties of a number of related compounds.

The starting material was prepared by condensing *p*-dimethylaminobenzaldehyde and *p*-chlorobenzaldehyde by means of potassium cyanide. The substance thus prepared melts at 128° and is readily oxidized with Fehling's solution to the corresponding benzil, which fuses at 144.5°.

Several methods have been employed for determining the structures

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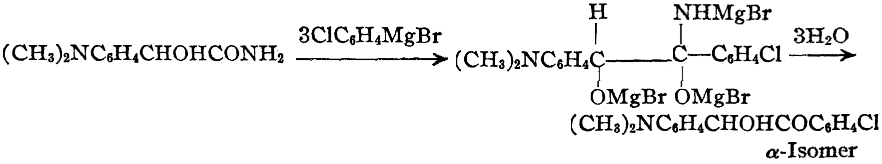
[1] Grafflin Scholar, 1930–1931.

[2] Staudinger, Ber., 46,3538 (1913).

of unsymmetrical benzoins. For example, Meisenheimer and Jochelson[3] obtained benzanisoin by the action of alkali on a-bromobenzyl *p*-methoxyphenyl ketone. Tiffeneau and Levy[4] have determined the structures of a number of these substances by fission with potassium hydroxide and more recently the method of Werner and Detscheff,[5] which makes use of the Beckmann rearrangement of the benzoin oximes has been extended by Buck and Ide.[6] The foregoing, however, cannot be classed as direct methods since other standards are required for comparison. Other methods,[7] in which the Grignard reaction is used, are directly applicable to studies of this nature, since they lead to the synthesis of isomers of known structure and hence direct comparison with the original material is possible.

Thus, with the aid of the Grignard reaction[7'] both of the isomeric *p*-dimethylamino-*p'*-chlorobenzoins were prepared and studied. *p*-Dimethylaminomandelamide was condensed with *p*-chlorophenylmagnesium bromide and after hydrolysis of the resulting complex *p*-dimethylamino-α-hydroxybenzyl *p'*-chlorophenyl ketone was obtained and for convenience will be called α-*p*-dimethylamino-*p'*-chlorobenzoin. This melted at 104.5° and on oxidation with Fehling's solution it produced the same benzil as did the "starting material" with like treatment; however, a mixed melting point determination with the latter substance showed a large depression. It is thus evident that α-*p*-dimethylamino-*p'*-chlorobenzoin is different from but isomeric with the starting material. In order to obtain the other or β-isomer, *p*-chloromandelamide[8] was reacted with *p*-dimethylaminophenylmagnesium bromide and p-chloro-a-hydroxybenzyl *p'*-dimethylaminophenyl ketone was obtained. This substance melted at 128,° produced the above benzil on oxidation and when mixed with the starting material showed no depression of the melting point. Thus it is seen that *p*-dimethylamino-*p'*-chlorobenzoin as produced by condensing the respective aldehydes is the β-isomer and has the structure $(CH_3)_2NC_6H_4COCHOHC_6H_4Cl$. The reactions are



$$(CH_3)_2NC_6H_4CHOHCONH_2 \xrightarrow{3ClC_6H_4MgBr} (CH_3)_2NC_6H_4\underset{\underset{OMgBr}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{OMgBr}{|}}{\overset{\overset{NHMgBr}{|}}{C}}-C_6H_4Cl \xrightarrow{3H_2O}$$

$$(CH_3)_2NC_6H_4CHOHCOC_6H_4Cl$$

α-Isomer

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[3] Meisenheimer and Jochelson, Ann., 355, 292 (1907).

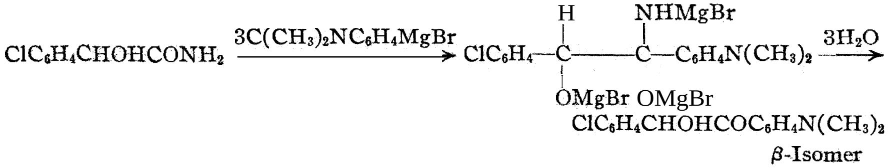
[4] Tiffeneau and Levy, *Compt. rend.*, 192,287 (1931).

[5] Werner and Detscheff, *Ber.*, 38, 69 (1905).

[6] Buck and Ide, THIS JOURNAL, 53,1912 (1931).

[7] *(a)* Asahina and Terasaka, *J. Pharm. Soc. Japan*, 494, 219 (1923); *(b)* McKenzie, Louis, Tiffeneau and Weill, *Bull. soc. chim.*, [4] 45, 414 (1929); *(c)* Jenkins, Bigelow and Buck, THIS JOURNAL, 52,5198 (1930).

[8] Jenkins, ibid., 53, 2341 (1931).



$$ClC_6H_4CHOHCONH_2 \xrightarrow{3C(CH_3)_2NC_6H_4MgBr} ClC_6H_4-\overset{H}{\underset{OMgBr}{C}}-\overset{NHMgBr}{\underset{OMgBr}{C}}-C_6H_4N(CH_3)_2 \xrightarrow{3H_2O} ClC_6H_4CHOHCOC_6H_4N(CH_3)_2$$

β-Isomer

A very interesting observation was made during the study of the above isomers. It was found that the a-derivative readily produced the β-compound when heated for a short time with alcoholic potassium cyanide. An investigation of this reaction is being made, the results of which will be published in the near future.

As was stated above *p*-dimethylamino-*p*′-chlorobenzil was obtained when either a- or β-*p*-dimethylamino-*p*′-chlorobenzoin was oxidized with Fehling's solution. On reduction with tin and hydrochloric acid the α-benzoin produced a compound melting at 140° which was found to be *p*-dimethylaminobenzyl *p*′-chlorophenyl ketone, and for convenience will be designated α-*p*-dimethylamino-*p*′-chlorodesoxybenzoin. When the @-benzoin was reduced in a similar manner, not only the a-desoxy derivative was isolated but another substance melting at 170° was obtained. The latter proved to be p-chlorobenzyl *p*′-dimethylaminophenyl ketone, which will be called β-*p*-dimethylamino-*p*′-chlorodesoxybenzoin. These compounds were readily separated since the a-isomer was much more soluble in acid solution than the @-derivative. Furthermore, on reduction with sodium amalgam β-*p*-dimethylamino-*p*′-chlorobenzoin formed the corresponding hydrobenzoin, melting at 180,° which, when heated with a mixture of acetic and hydrochloric acids, readily lost water and formed α-*p*-dimethylamino-*p*′-chlorodesoxybenzoin in good yield. No attempt was made to reduce the a-benzoin under similar conditions since only a small quantity of this material was available.

The oximes were obtained by heating the desoxybenzoins in pyridine solution with an excess of hydroxylamine hydrochloride. a-@-Dimethylamino-*p*′-chlorodesoxybenzoin oxime melted at 150.5° while β-*p*-dimethylamino-*p*′-chlorodesoxybenzoin oxime was found to melt at 152°. An interesting observation was made in preparing the a-oxime—in the reaction mixture a substance was always found, in small percentage, which melted at 229° and proved to be *p*-dimethylamino-*p*′-chlorostilbene (described below). This unusual side reaction is being studied further.

The structure of β-*p*-dimethylamino-*p*′-chlorodesoxybenzoin was deduced in the following manner. *p*-Dimethylaminobenzaldehyde was condensed with *p*-chlorobenzylmagnesium bromide and p-chlorobenzyl-*p*′-dimethylaminophenylcarbinol was obtained, which melted at 112°. When the β-desoxy derivative was reduced with sodium amalgam, this carbinol was also produced. The following reactions will make this clear.

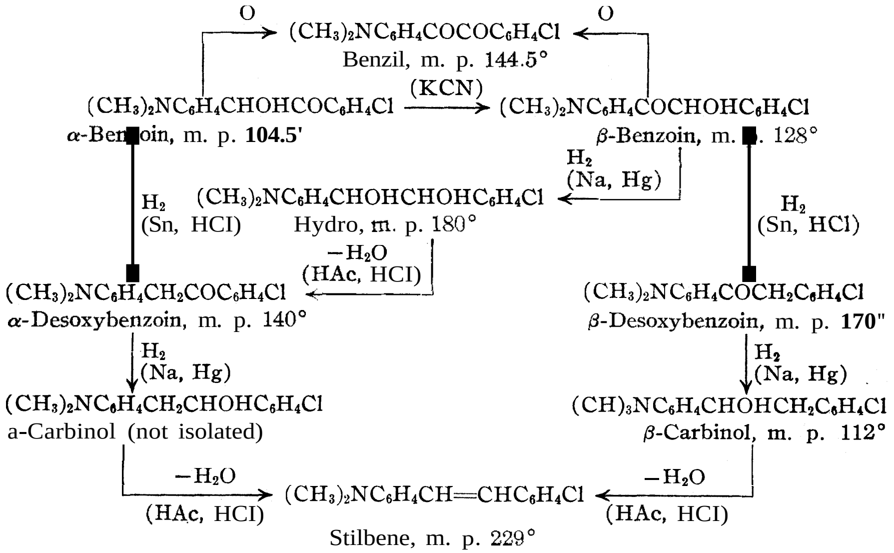
$$(CH_3)_2NC_6H_4CHO \xrightarrow{ClC_6H_4CH_2MgBr} (CH_3)_2NC_6H_4CH(OMgBr)CH_2C_6H_4Cl \xrightarrow{H_2O} (CH_3)_2NC_6H_4CHOHCH_2C_6H_4Cl \quad (I)$$

$$(CH_3)_2NC_6H_4COCH_2C_6H_4Cl \xrightarrow[(Na,\ Hg)]{H_2} (CH_3)_2NC_6H_4CHOHCH_2C_6H_4Cl \quad (II)$$

When dehydrated by the acetic–hydrochloric acid mixture the above carbinol, produced by either method (I or II), lost water and formed *p*-dimethylamino-*p'*-chlorostilbene, melting at 229°. When α-*p*-dimethylamino-*p'*-chlorodesoxybenzoin was likewise reduced with sodium amalgam, an isomeric carbinol was produced which also readily lost water in an analogous manner with the formation of this stilbene. Thus it is seen that the a- and β-desoxy derivatives are isomeric and have the structures

$(CH_3)_2NC_6H_4CH_2COC_6H_4Cl$ and $(CH_3)_2NC_6H_4COCH_2C_6H_4Cl$
α-*p*-Dimethylamino-*p'*-chlorodesoxybenzoin β-*p*-Dimethylamino-*p'*-chlorodesoxybenzoin

The reactions which have been described above are represented in the following diagram



The writer wishes to thank Dr. E. Emmet Reid for his interest and help in this work.

Experimental

α-*p*-Dimethylamino-*p*-chlorobenzoin.—A mixture of **15** g. of *p*-chlorobromobenzene, **2** g. of magnesium turnings and **50** cc. of anhydrous ether was refluxed for three hours. Then **3 g.** of *p*-dimethylaminomandelamide,[7c] finely powdered, was added in small portions, over a period of thirty minutes. After heating over a twenty-five watt light for eight hours, the solution was poured into **200** g. of water and crushed ice containing **20** g. of concentrated sulfuric acid. The ether was removed and the aqueous layer extracted with two 100-cc. portions of ether. The extracts were discarded. The acid solution was then neutralized with ammonia and the yellow precipitate which formed was separated, dissolved in 50 cc. of alcohol and filtered hot. On cooling a mass of yellow needles separated which weighed 2.0 g. and melted at 96–98". After two crystallizations from ligroin (Skellysolve "C") the product melted at 104.5° (corr.).

β-*p*-Dimethylamino-*p*′-chlorobenzoin

First Method.—To a solution of 28.7 g. of *p*-dimethylaminobenzaldehyde and 28.1 g. of *p*-chlorobenzaldehyde dissolved in 140 cc. of 95% alcohol was added 5 g. of potassium cyanide dissolved in 60 cc. of water. The mixture was refluxed for one hour and allowed to cool. The crystalline material was separated, washed twice with water and once with a small portion of alcohol; yield, 21 g. To the filtrate was added 3 g. more of potassium cyanide. The solution was then heated for an hour, allowed to cool and the solid filtered. After washing with water and alcohol it weighed 6 g. The two crops of crystals were then combined and recrystallized twice from alcohol. The almost white needles melted at 128" (corr.).

Second Method.—A mixture of 20 g. of *p*-bromodimethylaniline, 3 g. of magnesium and 100 cc. of anhydrous ether was refluxed for forty-eight hours. After the heating, 1.3 g. of finely powdered *p*-chloromandelamide[8] was added in small portions over a period of thiiy minutes. The solption was then refluxed for an additional eight hours and poured into 200 g. of crushed ice and water containing 20 g. of concentrated sulfuric acid. The mixture was stirred until all of the solid matter had dissolved. The clear solution was then extracted with six 50-cc. portions of ether. In this case the water layer was discarded. The ether solution was washed first with a 2% solution of sodium carbonate and then with water. The ether was distilled. The solid was then dissolved in a small amount of alcohol, filtered hot and allowed to crystallize; weight, 0.50 g. After two further crystallizations from alcohol, it melted at 128° (corr.).

Third Method.—Five-tenths of a gram of the a-benzoin and 0.10 g. of potassium cyanide dissolved in 20 cc. of 70% alcohol were heated for thirty minutes and allowed to cool. The crystalline material was filtered off, washed with water and recrystallized from a small portion of alcohol. It weighed 0.40 g. and melted at 128" (corr.). When this material was mixed with that obtained by the other methods, there was no depression of the melting point; when a mixed melting point determination was made with the a-benzoin, however, there was a depression of 10–15°.

***p*-Dimethylamino-*p*′-chlorobenzil.**—This material was obtained from α- or β-*p*-dimethylamino-*p*′-chlorobenzoin in 90% yield when an alcoholic solution of either of these substances was heated for half an hour with an excess of concentrated Fehling's solution on the water-bath. The benzil crystallized from alcohol in thin orange-colored needles which melt at 144.5° (corr.).

***p*-Dimethylamino-*p*′-chlorohydrobenzoin.**—To 15 g. of *p*-dimethylamino-*p*′-chlorobenzoin was added 200 cc. of alcohol. The benzoin was dissolved by heating to 50–60° on the water-bath. To the solution was added 20 cc. of water and 150 g. of 4% sodium amalgam in portions, over a period of one hour. The mixture was kept at 50–60° for four hours while a steady stream of carbon dioxide was passed into it. Small portions of acetic acid were added at intervals but at no time was the mixture allowed to become acid. The mixture was occasionally shaken. After standing overnight at room temperature, 200 cc. of water was added and the suspended matter was decanted from the mercury onto a filter. After washing several times, the solid was recrystallized from alcohol; yield, 7.5 g.; m. p. 180° (corr.). There was another substance present which was quite soluble in the dilute alcohol, perhaps the isohydrobenzoin, but no attempt was made to purify it.

α-*p*-Dimethylamino-*p*'-chlorodesoxybenzoin

First Method.—To 1 g. of the hydrobenzoin (prepared in the above manner) were added 15 cc. of glacial acetic acid and 5 cc. of concentrated hydrochloric acid. The mixture was boiled for ten minutes, after which 50 cc. of water was added. The solution was then neutralized with 10% sodium carbonate solution allowed to stand for a few minutes and filtered. The solid was washed several times with water and crystallized from alcohol. The product was obtained in a yield of 0.80 g. and melted at 140° (corr.).

Second Method.—A mixture of 0.50 g. of α-*p*-dimethylamino-*p*'-chlorobenzoin, 0.50 g. of mossy tin, 3 cc. of concentrated hydrochloric acid, a small crystal of copper sulfate and 10 cc. of alcohol was heated for five hours. The solution was filtered hot, 50 cc. of water added and neutralized with sodium carbonate. The mixture was allowed to stand for a while, after which the precipitate was filtered, washed several times with water, sucked dry and extracted twice with hot alcohol (25-cc. portions). The extract was evaporated to a volume of about 15 cc. and cooled; yield, 0.30 g. After two crystallizations from alcohol the substance melted at 140° (corr.).

Third Method of Preparing **α-*p*-Dimethylamino-*p*'-chlorodesoxybenzoin.**—The filtrate from which the β-desoxy compound (described below) had been obtained was made slightly alkaline with sodium carbonate. After standing for a while the solid was separated, washed several times with water and extracted three times with 100-cc. portions of alcohol. The solution was then evaporated to a volume of about 50 cc. and allowed to cool. The solution deposited 3.50 g. of substance which after two crystallizations from alcohol formed almost white plates and melted at 140° (corr.). Mixed melting point determinations with the substance made by methods ***one*** and ***two*** showed no depression.

β-*p*-Dimethylamino-*p*'-chlorodesoxybenzoin.—A mixture of 11 g. of β-*p*-dimethylamino-p'-chlorobenzoin, 10 g. of mossy tin, 0.50 g. of copper sulfate, 20 cc. of concentrated hydrochloric acid and 40 cc. of alcohol was refluxed for five hours. The hot solution was filtered and 10 cc. of water added. On cooling the solution deposited 5 g. of fine white prisms. To the filtrate 40 cc. of water was added and 0.50 g. more of the same material was obtained. After two recrystallizations from alcohol the substance melted at 170° (corr.).

p-Chlorobenzyl-*p*'-dimethylaminophenylcarbinol

First Method. (β-*p*-**Dimethylamino-*p*'-chlorostilbene** Hydrate.)—A mixture of 20 g. of p-chlorobenzyl bromide, 2.50 g. of magnesium turnings and 100 cc. of ether was refluxed for three hours. A solution of 14 g. of p-dimethylaminobenzaldehyde in 100 cc. of ether was then added slowly over a period of forty-five minutes from a dropping funnel. The solution was heated for two hours and poured into 200 cc. of crushed ice and water containing 20 g. of concentrated sulfuric acid. The ether layer was separated and discarded. The water layer was made slightly alkaline with ammonium hydroxide and extracted twice with 100-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate and the ether distilled off. A yield of 20 g. of crude material was obtained. After two crystallizations from 80% alcohol the substance was obtained as white needles melting at 112° (corr.).

Second Method.—A mixture of 1.0 g. of β-*p*-dimethylamino-*p*'-chlorodesoxybenzoin, 50 cc. of alcohol (90%) and 25 g. of sodium amalgam was warmed to 50–60° while a slow stream of carbon dioxide was admitted. The reaction was allowed to proceed for four hours at this temperature. During this time the mixture was frequently shaken. The solution was then decanted from the mercury and diluted with 100 cc. of water. The solid was filtered off and washed with water, after which it was recrystallized from a small amount of 80% alcohol. A yield of 0.40 g. of product melting at 109–111° was obtained. When this was mixed with the carbinol obtained by the first method, there was no depression of the melting point.

***p*-Dimethylamino-*p*'-chlorostilbene.**—The carbinol above as made by either method readily lost water when heated with a mixture consisting of 80% glacial acetic acid and 20% concentrated hydrochloric acid and produced *p*-dimethylamino-*p*'-chlorostilbene. A mixture of 10 g. of the carbinol, 40 cc. of glacial acetic acid and 10 cc. of concentrated hydrochloric acid was heated for ten minutes on the hot-plate The solution was diluted with 200 cc. of water and neutralized with sodium carbonate. The solid matter was separated, washed with water and dried; weight 8.0 g. After two crystallizations from benzene it formed almost white scales and melted at 229° (corr.)

The above stilhene was also obtained by reducing α-*p*-dimethylamino-*p*'-chlorodesoxybenzoin with sodium amalgam and dehydrating the resulting product with the acetic–hydrochloric acid mixture. A mixture of 1.0 g. of the a-desoxy compound, 25 cc. of alcohol and 25 g. of sodium amalgam was warmed to 50–60° and occasionally shaken. At intervals small portions of 50% acetic acid were added, but not enough to make the solution acid. After four hours 100 cc. of water was added, the solid filtered, washed with water and recrystallized from dilute alcohol; yield, 0.50 g. This material was heated with 10 cc. of the acetic–hydrochloric acid mixture for a few minutes, the solution then diluted with 50 cc. of water and neutralized with sodium carbonate. The solid was filtered, washed with water and recrystallized twice from alcohol. It weighed 0.20 g. and melted at 229". When mixed with p-dimethylamino-*p*'-chlorostilbene, the melting point was not depressed.

α-*p*-Dimethylamino-*p*'-chlorodesoxybenzoin Oxime.—A mixture of 1.0 g. of the or-desoxy compound, 1.0 g. of hydroxylarnine hydrochloride and 10 cc. of pyridine was heated on the water-bath for four hours. The solution was then diluted with 10 cc. of water, cooled in ice water for a while and the solid which formed separated. On recrystallization from alcohol it melted at 227–229° and proved to be p-dimethylamino-p'-chlorostilbene. It weighed 0.20 g.

The filtrate was diluted with 30 cc. of water and the precipitate which formed on standing was separated, washed with water and dried. It weighed 0.7 g. and after two crystallizations from ligroin (Skellysolve "C") it formed white prisms melting at 150.5° (corr.).

β-*p*-Dimethylamino-*p*'-chlorodesoxybenzoin Oxime.—This oxime was obtained in a manner similar to the or-compound. In this instance, however, not a trace of the

TABLE I

COMPOUNDS, CONSTANTS AND ANALYTICAL DATA

			Analytical data			
			Nitrogen, %		Chlorine, %	
Formula	Appearance	M. p.,° (corr.)	Calcd.	Found, (Kjeldahl)	Calcd.	Found, (Parr bomb)
$(CH_3)_2NC_6H_4COCOC_6H_4Cl$	Orange needles	144.5	4.87	4.78	12.32	12.35
α-$(CH_3)_2NC_6H_4CHOHCOC_6H_4Cl$	Cream needles	104.5	4.83	4.75	12.24	12.10
β-$(CH_3)_2NC_6H_4COCHOHC_6H_4Cl$	Cream needles	128	4.83	4.90	12.24	12.20
$(CH_3)_2NC_6H_4CHOHCHOHC_6H_4Cl$	White prisms	180	4.80	4.65	12.15	12.32
α-$(CH_3)_2NC_6H_4CH_2COC_6H_4Cl$	White scales	140	5.12	4.95	12.95	13.11
β-$(CH_3)_2NC_6H_4COCH_2C_6H_4Cl$	White leaflets	170	5.12	5.09	12.95	13.17
$(CH_3)_2NC_6H_4CHOHCH_2C_6H_4Cl$	Colorless needles	112	5.08	5.20	12.86	12.70
$(CH_3)_2NC_6H_4CH{=}CHC_6H_4Cl$	White scales	229	5.44	5.35	13.76	13.75
α-$(CH_3)_2NC_6H_4CH_2C{=}NOHC_6H_4Cl$	White prisms	150.5	9.70	9.63	12.28	12.40
β-$(CH_3)_2NC_6H_4C{=}NOHCH_2C_6H_4Cl$	Colorless needles	152	9.70	9.85	12.28	12.35

stilbene was obtained. This oxime could be crystallized from alcohol but ligroin proved to be a better solvent. A yield of 0.80 g. was obtained which crystallized in long colorless needles and melted at 152° (corr.). A mixed melting point determination showed that the oximes were unlike.

Summary

1. By means of the Grignard reaction both isomeric (a and β) *p*-dimethylamino-*p'*-chlorobenzoins have been synthesized. The benzoin as prepared by condensing *p*-dimethylaminobenzaldehyde and *p*-chlorobenzaldehyde was found to be *p*-chloro-α-hydroxybenzyl *p'*-dimethylaminophenyl ketone (β isomer) and has the structure $(CH_3)_2NC_6H_4$-$COCHOHC_6H_4Cl$.

2. Under the influence of potassium cyanide, α-*p*-dimethylamino-*p'*-chlorobenzoin was found to rearrange and produce the 6-isomer.

3. Upon reduction under suitable conditions, the a-benzoin produced *p*-dimethylaminobenzyl *p'*-chlorophenyl ketone. Under similar treatment, however, the β-benzoin produced the above ketone and also its isomer, *p*-chlorobenzyl *p'*-dimethylaminophenyl ketone. Nine new substances were prepared and characterized in the course of this work.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

THE AUTOXIDATION OF ALPHA NORMAL-AMYLCINNAMIC ALDEHYDE. CIS- AND TRANS-ALPHA-NORMAL-AMYLCINNAMIC ACIDS

BY MARSTON T. BOGERT AND DAVID DAVIDSON[1]

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Introduction

In the course of our study of the rates of autoxidation of commercial aldehydes,[2] we were led to examine the products resulting from the action of air on α-*n*-amylcinnamic aldehyde, $C_6H_5CH{=}C(Am)CHO$. Since, in general, the action of air or oxygen on an aldehyde leads to the formation of the corresponding acid through the intermediate per-acid, thus[3]

$$RCHO + O_2 \longrightarrow RCOOOH \qquad (+RCHO) \longrightarrow 2\,RCOOH$$

and, since unsaturated aldehydes such as crotonaldehyde and cinnamic aldehyde behave in accordance with this formulation, we expected that this aldehyde would yield a-amylcinnamic acid. Investigation revealed, however, that, when blown with air, a-amylcinnamic aldehyde undergoes

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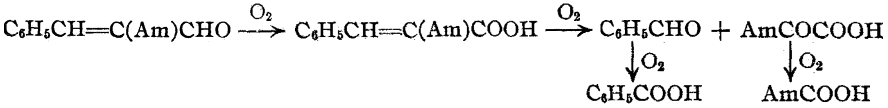
[1] Senior Research Assistant of the American Manufacturers of Toilet Articles.

[2] Bogert and Davidson, ***Am. Perfumer Ess. Oil Rev.*, *24*,** 587, 667 (1929–1930).

[3] Baeyer and Villiger, ***Ber.*,** 33, 1582 ***(1900)***; Jorissen and van der Beek, ***Rec. trav. chim.*,** 45, 245 (1926); 47, 286 (1928); H. L. J. Backstrom, ***Medd. Vetenskapsakad. Nobelinst.*, 6,** No. *15* (1927).

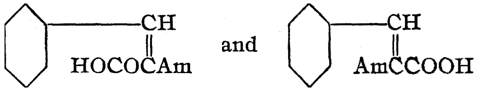
a complex autoxidation reaction leading to the formation of caproic acid, benzoic acid and a form of a-amylcinnamic acid melting at 40°, as well as benzaldehyde and other, as yet unidentified, neutral substances. The production of the three acids mentioned indicates that both the aldehyde and the ethylene functions are attacked by oxygen, perhaps as follows



$$\mathrm{C_6H_5CH{=}C(Am)CHO} \xrightarrow{O_2} \mathrm{C_6H_5CH{=}C(Am)COOH} \xrightarrow{O_2} \underset{\substack{\downarrow O_2\\ \mathrm{C_6H_5COOH}}}{\mathrm{C_6H_5CHO}} + \underset{\substack{\downarrow O_2\\ \mathrm{AmCOOH}}}{\mathrm{AmCOCOOH}}$$

Two Alpha-Amylcinnamic Acids.—Since a-amylcinnamic acid had not previously been described in the literature, it was desirable to prepare it in order to compare it with the product obtained in the autoxidation of the aldehyde. Four methods of synthesis were employed: (1) the condensation of benzaldehyde with sodium heptoate (Perkin–Stuart),[4] (2) the condensation of benzaldehyde with methyl heptoate by means of sodium (Claisen),[5] *(3)* the condensation of benzal chloride with sodium heptoate[6] and (4) the condensation of benzaldehyde with methyl hexyl ketone by means of hydrogen chloride, followed by oxidation with sodium hypochlorite. In each case an α-amylcinnamic acid was obtained which melted at 80° and was entirely distinct from that obtained by the autoxidation of the aldehyde.

The Configuration of the Alpha-Amylcinnamic Acids.—$\mathrm{C_6H_5CH{=}C(Am)COOH}$ may be represented by the two space formulas



"trans"

In harmony with the configurations of the two cinnamic acids we shall designate as "cis" that form of a-amylcinnamic acid in which the phenyl and carboxyl groups are cis.

The 40° acid differs from the 80° acid in that it forms an insoluble aniline salt in petroleum ether. By analogy with the behavior of the cis- and trans-a-methylcinnamic acids,' this marks the 40° acid as the cis form. Striking confirmation of this configuration is obtained in the behavior of the two acids toward concentrated sulfuric acid. While the 80° acid dissolves readily to form a colorless solution from which it is precipitated unchanged by water, the 40° acid forms a deep blue solution from which ice precipitates a yellow, sweet-smelling oil, freezing at 4° (a-amylindone).

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[4] Stuart, *J. Chem. Soc., 43,406* (1883).

[5] Claisen, *Ber., 23,977* (1890).

[6] Badische Anilin und Sodafabrik. German Patent 17,467, 18,232 (1880); *Friedlander, 1, 26, 28* (1888).

[7] Stoermer and Voht, *Ann.*, **409,** 36 (1915).

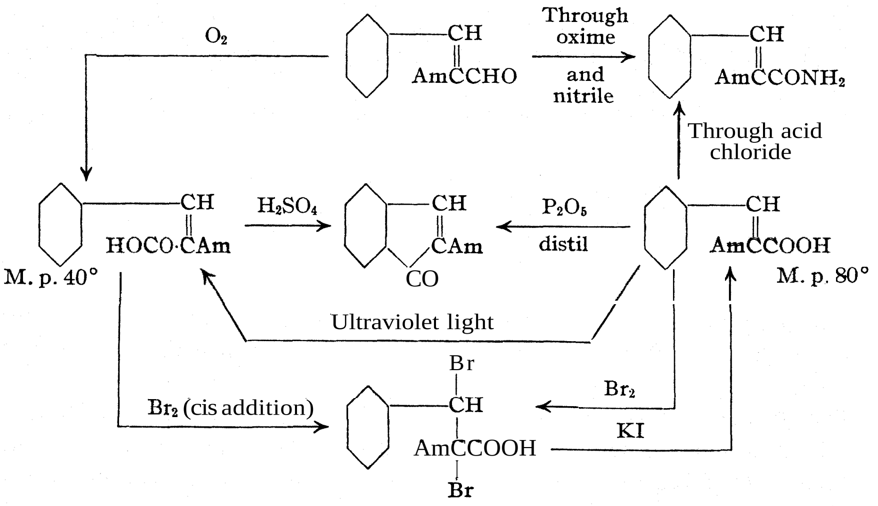
Although the 80° acid is unattacked by cold concentrated sulfuric acid, it yields this same amylindone when distilled with phosphorus pentoxide. That the two acids yield the same indone but with different ease at once establishes their isomerism and their respective configurations. The 40° acid, because of the readiness with which ring formation occurs between the ortho position in the benzene ring and the carboxyl group, is, therefore, the *cis*, while the 80° acid is the *trans* form.

Further confirmation of the isomerism of the two acids is obtained in their yielding the same dibromide, melting at 143–144.° Since the latter can be reduced to the *trans* acid melting at 80° by means of potassium iodide, a means was had of converting the *cis* acid melting *at* 40° to its geometric isomer, thus

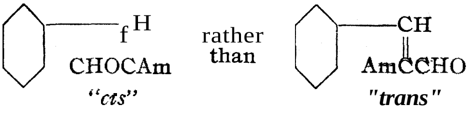
$$\textbf{\textit{Cis} form (m. p. 40°)} \xrightarrow{Br_2} \text{Dibromide} \xrightarrow{KI} \textbf{\textit{Trans}} \text{ form (m. } p. \text{ 80°)}$$

The reverse transformation of the *trans* to the *cis* form was accomplished by means of ultraviolet light. The reactions just discussed are summarized in Chart I.

Chart I



The Configuration of Alpha-Amylcinnamic Aldehyde.—Having established the configuration of the α-amylcinnamic acids beyond a reasonable doubt, and recalling that the *cis* form of the acid had been obtained by autoxidation of the aldehyde, it appeared that the commercial aldehyde possessed the *cis* configuration



Further investigation, however, showed that commercial a-amylcinnamic aldehyde is really closely related to the trans-a-amylcinnamic acid, m. p. 80°, and that, therefore, it has the trans configuration.

Thus, direct oxidation of the aldehyde to the acid by means of silver oxide yielded trans-a-amylcinnamic acid, identical with that obtained by other syntheses. Furthermore, the series of reactions, $RCHO \longrightarrow RCH{=}NOH \longrightarrow RCN \longrightarrow RCONH_2$, yielded an a-amylcinnamamide, melting at 117°, which was also obtained from trans-a-amylcinnamic acid through the acid chloride.

We are forced to the conclusion that although ordinary a-amylcinnamic aldehyde is the trans form, it reacts with oxygen to give (among other products) the cis form of a-amylcinnamic acid.[8] This inversion accompanying autoxidation may be explained by means of the following considerations. Stoermer and his co-workers have demonstrated that the trans forms of cinnamic acids are converted into the less stable cis forms by ultraviolet light.[9] On the other hand, several investigators have found that the autoxidation of aldehydes is a chemiluminescent reaction.[10] We may assume, therefore, that the radiation (or energy) emitted by the autoxidation of a-amylcinnamic aldehyde is absorbed by the product, namely, trans-a-amylcinnamic acid, which is thereby converted into its geometric isomer.

It is true that the experimental results do not enable us to decide whether this rearrangement of *trans* to cis configuration occurs wholly or partly in the initial aldehyde, the per-acid, or the trans acid stage but, in the absence of such evidence, we have assumed what seems to us the simplest interpretation of our observations.

Acknowledgments.—The authors are indebted to Mr. John Adriani for his assistance in the syntheses of a-amylcinnamic acid while he was a Senior student at Columbia College, to Dr. Eric C. Kunz, Vice President of the Givaudan–Delawanna Co. for a generous supply of a-amylcinnamic aldehyde, and to the Research Department of the American Manufacturers of Toilet Articles for financial aid.

Experimental

Autoxidation of α-*n*-**Amylcinnamic** Aldehyde.—In a darkened chamber 136.1 g. (0.675 mole) of freshly distilled a-amylcinnamic aldehyde, boiling at 161–163° at

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[8] It should be mentioned that Erlenmeyer, ***Ber.***, 38, 2562 (1905), claims to have obtained cis-cinnamic acid (allocinnamic acid) from the partial autoxidation of cinnamic aldehyde, but no details are given.

[9] Stoermer and Heymann, ***Ber.***, 46, 1256 (1913); 45, 3099 (1912); Stoermer and Voht, ***Ann.***, **409**, 36 (1915); Stoermer, Grimm and Laage, ***Ber.***, 50,959 (1917); Stoermer and Foerster, *ibid.*, 52, 1263 (1919).

[10] Radziszewski, ***Ann.***, 203, 307 (1880); Perkin, *J.* ***Chem.*** *Soc.*, ***41***, 365 (1882); Schorigen and Trautz, *Z.* wiss. *Phot.*, 3, 121 (1905)

16 mm., contained in a gas wash bottle, was blown with air, the issuing gas being passed through a second wash bottle containing dilute sodium carbonate. The increase in acidity was determined occasionally by titrating 0.3 cc. of the oil dissolved in 25 cc. of alcohol with standard sodium hydroxide solution using phenolphthalein as an indicator. The progress of the reaction is indicated in Fig. 1. After forty-two days the residual oil weighed 131.5 g. (not allowing for 2.4 cc. which had been removed for titration) and contained approximately 0.47 mole of monobasic acids. The oil was agitated with a solution of 52 g. of sodium carbonate in 500 cc. of water and then treated with ether to aid in the separation of the neutral oil from the aqueous extract. A small amount of sodium bicarbonate separated and was filtered off. The aqueous layer was extracted a second time with ether and the ether layers combined (E).

The aqueous layer was distilled to remove ether and volatile non-acidic constituents, about 300 cc. of water being collected. A mixture of 100 cc. of hydrochloric acid and 100 cc. of water was then added to the residue, and the distillation resumed, water being added from time to time. About 800 cc. of distillate (D) was collected, which contained a volatile oily acid (caproic). The residue (R) crystallized partially on standing overnight. D was made alkaline, concentrated by evaporation, acidified and distilled. The residue yielded crystals of a solid acid (benzoic). The distillate was treated as before, the oily acid finally being separated, dried over phosphorus pentoxide, and distilled (b. p. 201–208°; yield, 18.5 g.). When esterified with methyl alcohol and hydrogenchloride gas it yielded a fruity ester, boiling at 148–151°, which, when allowed to stand for two weeks with an equal volume of concentrated ammonia, yielded an amide, m. p. 99–100°. The acid was, therefore, n-caproic.

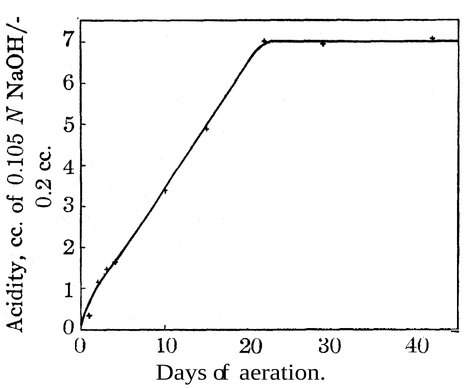

Fig. 1.

The residue (R) was filtered and the solid acid combined with the solid obtained in the purification of the caproic acid. When recrystallized from water, it yielded 7.5 g. of glistening platelets, melting at 121–122°. It was identified as benzoic acid by means of a mixed melting point, and examination of the methyl ester and amide.

The filtrate from residue (R) contained a dark oil which was distilled under diminished pressure giving the following fractions: (1) 6.7 g. partly solid, b. p. 130–190° at 18 mm., (2) 17.1 g. of a viscous yellow liquid, b. p. 190" at 18 mm., 215° at 14 mm., and a residue of 6.8 g. Fraction (1) was dissolved in dilute sodium hydroxide and the solution distilled to remove any non-acidic products formed in the distillation. The residue was then acidified with hydrochloric acid. The resulting oil yielded 2.9 g. of crude benzoic acid when extracted with hot water. Fraction (2), when chilled, deposited 2.8 g. of crystals melting at 38–39°. The filtrate was distilled, boiling mainly at 194° at 15 mm. The distillate yielded 3.6 g. of acid, m. p. 38–39", while a further quantity was obtained from the oily filtrate and other residues by dissolving in petroleum ether and precipitating with aniline. The acid was purified by precipitating the aniline salt, m. p. 65°, decomposing the latter with dilute hydrochloric acid, separating the acid, dissolving in dilute sodium hydroxide, clarifying with norite, and finally liberating the acid. This separated as an oil which slowly crystallized (m. p. 40°). Further precipitation of the aniline salt did not affect the melting point. The acid is exceedingly soluble in all common organic solvents.

Titration. 154 mg. required 8.56 cc. of standard alcoholic sodium hydroxide (0.0828 *N*). 155 mg. required 8.57 cc. Equivalent weight: calcd., 218. Found: 218, 219.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 76.9; H, 8.3.

These results indicate the substance to be an a-amylcinnamic acid.

The ether layer (E) which contained the oil from which the acids had been extracted with sodium carbonate was shaken twice with half-saturated sodium bisulfite solution. The bisulfite layers were combined and treated with hydrochloric acid, the sulfur dioxide removed by warming, and the resulting oil separated. It boiled at 174–177° and had the odor of ***benzaldehyde;*** yield, 1.3 g.[11] Its identity was confirmed by treating it with alcohol and concentrated ammonia, when colorless crystals, melting at 103°, were obtained (hydrobenzamide).

The ether layer from which the benzaldehyde had been separated was washed with sodium carbonate, dried with calcium chloride, and the ether evaporated. The residual oil weighed 61.7 g. It distilled with some decomposition at 17 mm., 49.0 g. yielding 25.6 *g.* of material boiling below 180° and 23.2 g. of a dark viscous residue. Redistillation yielded 12.2 g., boiling at 110–150° at 15.5 mm. (mainly at 143–150°) and 6.0 g. boiling at 150–170° at 15.5 mm. Both fractions yielded a small amount of a solid semicarbazone which has not been obtained sufficiently pure to be identified.

Syntheses of **α-Amylcinnamic** Acid, m. p. 80°. **(1)** Perkin–Stuart Method.—A mixture of 25 g. of benzaldehyde, 35 g. of sodium heptoate and 67 g. of heptoic acid was refluxed for thirty hours. The mixture was then distilled at 20 mm. from a bath at 180°. The residue was dissolved in boiling water and acidified with hydrochloric acid, the oil separated, the water layer extracted with ether, and the extract combined with the oil. The ether solution was extracted with sodium carbonate, the water layer extracted several times with ether to remove resinous material, warmed with norite on the hot-plate, and filtered. The almost colorless solution of sodium salts was then acidified, the oil extracted, the extract dried with sodium sulfate, the ether evaporated, and the oil distilled at 2 mm. Much heptoic acid was recovered and finally 1.6 g (3.2%) of a-amylcinnamic acid boiling at 161° at 2 mm. and melting at 69° was obtained. When purified through the sodium salt the melting point rose to 74°, and from 75% acetic acid to 80°.

(2) Claisen Method.—The directions given in "Organic Syntheses" for the preparation of ethyl cinnamate[12] were adapted for the production of methyl α-amylcinnamate by substituting methyl heptoate for ethyl acetate. The excess of methyl heptoate was removed at 20 mm. and the residue distilled at **2 mm.** The fraction boiling at 130–180° at 2 mm. and weighing 20 g. was saponified with methyl alcoholic potassium hydroxide and the acid separated. After steam distilling to remove heptoic acid, several recrystallizations from dilute alcohol yielded 6.5 g. (8%) of a-amylcinnamic acid melting at 76°. Further recrystallization from 75% acetic acid gave a product melting at 80".

(3) Badische Method.—Seven grams of sodium **was** dissolved in 65 g. of heptoic acid, 16.1 g. of benzal chloride added and the mixture refluxed for thirty hours. The product was isolated as in (1); yield, 6.0 g. (28%), m. p. 80".

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[11] Much of the benzaldehyde produced must have been lost during the aeration, since a pronounced odor of benzaldehyde was noted in the issuing air after seventeen days.

[12] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1929,** Vol. IX, p. **38.**

(4) The most satisfactory method of preparation of a-amylcinnamic acid involves the condensation of benzaldehyde with methyl hexyl ketone, followed by oxidation of the intermediate methyl a-amyl styryl ketone with hypochlorite. The details of this method will appear in a subsequent paper; yield, about 70%, m. p. 80°.

Titration. 151 mg. required 8.34 cc. of standard alcoholic sodium hydroxide (0.0828 N). 149 mg. required 8.24 cc. Equivalent weight. Calcd., 218. Found: 219. 218.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 77.0; H, 8.2.

Oxidation of a-Amylcinnamic Aldehyde **with Silver** Oxide.—To a boiling mixture of 5 g. of silver nitrate in 3 cc. of water, 2 g. of a-amylcinnamic aldehyde and 30 cc. of alcohol was added a hot solution of 2.5 g. of potassium hydroxide in 30 cc. of alcohol. The boiling was continued, water being added to replace the volatilized alcohol. After thirty minutes the alcohol was entirely removed. The clear straw-colored supernatant layer was decanted from the silver and the latter leached several times with boiling water. The combined liquors were acidified with acetic acid, whereupon slightly discolored trans-a-amylcinnamic acid, m. p. 78°, separated; yield, 1.7 g. (77%). Recrystallization from 75% acetic acid gave needles melting at 80°.

α-Amylcinnamaldoxime.[13]—50.5 g. of a-amylcinnamic aldehyde, 100 cc. of alcohol, 17.5 g. of hydroxylamine hydrochloride, and 34 g. of sodium acetate trihydrate were refluxed for an hour. On cooling and diluting with water, 44.2 g. of oxime, m. p. 74°, was obtained. It was recrystallized by dissolving in alcohol and diluting with water.

α-Amylcinnamonitrile.—27.5 g. of the oxime was boiled for three hours with one and one-half moles of acetic anhydride and one gram of anhydrous sodium acetate. The mixture was cooled and cautiously treated with dilute sulfuric acid to decompose the excess of acetic anhydride. It was then largely diluted with water, the nitrile extracted with benzene, the extract washed with sodium carbonate solution and dried over sodium sulfate. The benzene was removed and the residue distilled. The product was practically pure a-amylcinnamonitrile, b. p. 173° at 18 mm., 165° at 13 mm. and 135° at 3 mm.; yield, 21 g. (83%).

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.4; H, 8.5. Found: C, 84.4; H, 8.5.

α-Amylcinnamamide.—1.7 g. of the nitrile was refluxed for eight hours with a solution of 2 cc. of 50% sodium hydroxide and 15 cc. of n-propyl alcohol. Dilution of the alcoholic solution gave a solid, which was recrystallized from dilute alcohol and finally from ethyl acetate–petroleum ether, giving silky needles, m. p. 117°, identical with the product obtained below.

Anal. Calcd. for $C_{14}H_{19}ON$: C, 77.4; H, 8.8. Found: C, 77.4; H, 9.0.

α-Amylcinnamamide from **α-Amylcinnamic** Acid.—One gram of a-amylcinnamic acid, m. p. 80°, was heated under reflux at 80–90° for one hour with 5 cc. of thionyl chloride. The excess of thionyl chloride was then distilled off and the residue treated with concentrated ammonia. The solid obtained was recrystallized from dilute alcohol and finally from ethyl acetate–petroleum ether, giving silky needles, m. p. 117°, identical with the product obtained above.

Action of Sulfuric Acid on 40 and 80° a-Amylcinnamic Acids.—1.09 g. of cis-a-amylcinnamic acid, m. p. 40°, was added to 11 cc. of chilled concentrated sulfuric acid. The acid readily dissolved, giving a deep blue solution. The mixture was stirred for a few minutes to complete solution and then poured on ice. The yellow oil was extracted with ether, the extract washed with water and then with 10% sodium carbonate. Evaporation of the ether gave 0.9 g. of a brown oil. Distillation at 20 mm.

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[13] Rutovski and Korlev, *J. prakt. Chem.*, 119, 272 (1928).

gave 0.65 g. of a golden brown oil, which solidified to a yellow solid, m. p. 4°, when placed in a freezing mixture. The oil had an odor resembling amyl salicylate. For identification and analysis, the substance was converted into its oxime; 0.65 g. of the indone gave 0.53 g. of golden yellow leaflets, which, when recrystallized from 80% methanol, melted at 75° and were identical with the product obtained below.

Anal. Calcd. for $C_{14}H_{17}ON$: C, 78.1; H, 7.9. Found: C, 78.4; H, 8.2.

A parallel experiment with 1.09 g. of trans-a-amylcinnamic acid, m. p. 80°, and 11 cc. of concentrated sulfuric acid gave a colorless solution, which when thrown on ice precipitated a colorless solid. Recrystallized from 75% acetic acid, this yielded 0.94 g. of needles, m. p. 80". A mixture with trans-a-amylcinnamic acid also melted at 80".

Formation of a-Amyl Indone from *Trans*-α-amylcinnamic Acid.—5.45 g. of *trans*-a-amylcinnamic acid, m. p. 80°, and 8 g. of phosphorus pentoxide were placed in a Claisen flask and well mixed by shaking. Distillation with a free flame at 17 mm. gave a golden brown distillate, b. p. 157–158° at 17 mm., which froze at 1–2° to a yellow solid. When added to concentrated sulfuric acid it formed a deep blue solution. Its odor was reminiscent of amyl salicylate; yield, 4.0 g. (80%). It was identified as a-amyl indone by conversion to the oxime according to the method of Schmidt and Söll.[14] One gram of the indone was refluxed for one and one-half hours with 0.35 g. of hydroxylamine hydrochloride and 0.5 g. of barium carbonate powder in 15 cc. of methanol. The mixture was then cooled, filtered and diluted with water; 0.77 g. of yellow leaflets, m. p. 74°, were obtained and 0.28 g. of further material upon further dilution of the mother liquor. Recrystallization from twenty parts of methanol and five parts of water gave golden yellow leaflets, m. p. 75°, identical with the product obtained above.

Action of Bromine on *Trans*-α-amylcinnamic Acid.—2.18 g. of *trans*-α-amylcinnamic acid, m. p. 80°, was dissolved in 25 cc. of carbon tetrachloride, and 0.6 cc. of bromine added to the solution in diffused daylight. Decolorization soon occurred, whereupon the carbon tetrachloride was removed by means of a current of air and the residue treated with petroleum ether and chilled; 2.3 g. of a dibromide m. p. 137–139° was obtained. Recrystallization from carbon tetrachloride–petroleum ether raised the melting point to 143–144°.

Anal. Calcd. for $C_{14}H_{18}O_2Br_2$: C, 44.5; H, 4.8. Found: C, 43.7; H, 4.6.

Transformation of *Cis*-α-amylcinnamic Acid, m. p. 40°, to *Trans*-α-amylcinnamic Acid, m. p. 80°.—1.09 g. of cis-a-amylcinnamic acid, m. p. 40°, was dissolved in a few cc. of petroleum ether and excess of bromine added to the solution in diffused daylight. As the bromine was absorbed, heat was evolved, a little hydrogen bromide appeared and a crystalline deposit formed on the walls of the flask. After four hours the flask was chilled, the mother liquor poured off and the crystalline deposit washed with petroleum ether; 1.13 g. of a flesh-colored cake was obtained which melted at 139–140". Recrystallization from carbon tetrachloride-petroleum ether gave a colorless product, m. p. 143–144°. A mixture with the product obtained above also melted at 143–144°; 0.95 g. of this product, 1.7 g. of potassium iodide and 10 cc. of alcohol were refluxed for twenty minutes. The mixture was then diluted with dilute sodium bisulfite solution, whereupon a precipitate of 0.57 g. of crude trans-a-amylcinnamic acid was obtained, which, when recrystallized from 75% acetic acid, gave 0.39 g. of needles, m. p. 80° (mixed melting point). The acid obtained gave a colorless solution in concentrated sulfuric acid.

Transformation of *Trans*-α-amylcinnamic Acid, m. p. 80°, to *Cis*-α-amylcinnamic

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[14] Schmidt and Söll, Ber., 40, 2455 (1907).

Acid, m. p. **40°.**—2.18 g. of *trans*-α-**amylcinnamic** acid, m. p. 80°, spread out on a plate and placed at a distance of about fifteen inches from a Hanovia quartz mercury arc was irradiated for about 120 hours. The acid then melted at about 70° and gave a deep blue color with concentrated sulfuric acid. It was triturated with petroleum ether and filtered. The residue weighed 1.1 g., melted at 80° and gave a practically colorless solution in sulfuric acid. The petroleum ether extract was treated with several drops of aniline and seeded with the aniline salt of cis-a-amylcinnamic acid. A crop of long felted needles, m. p. 66° and weighing 0.41 g., was obtained. On decomposing the latter with dilute hydrochloric acid, 0.28 g. of cis-a-amylcinnamic acid, m. p. 38–39' (mixed melting point), was obtained. The product gave *a* deep blue color with sulfuric acid.

Summary

1. The a-amylcinnamic aldehyde of commerce is the trans isomer, since it is converted into trans-a-amylcinnamic acid by means of silver oxide, and into trans-a-amylcinnamamide through the oxime and the nitrile.

2. Autoxidation of a-amylcinnamic aldehyde proceeds readily at room temperature in the dark. Profound attack of the aldehyde ensues, leading to the production of caproic acid, benzoic acid and *cis*-α-amylcinnamic acid, m. p. 40°. The inversion of the trans to the cis form is accounted for by the chemiluminescence of the primary autoxidation.

3. Four methods of synthesis of a-amylcinnamic acid led to the same trans form, m. p. 80°.

4. The cis configuration of the 40° form of α-amylcinnamic acid is established by its ready formation of an indone. The trans form undergoes the same reaction, but only under much more vigorous conditions.

5. Cis-a-amylcinnamic acid is converted into the trans form through the dibromide.

6. Trans-a-amylcinnamic acid is converted to the cis form by means of ultraviolet light.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORY FOR PURE RESEARCH OF MERCK AND CO., INC.]

DIASTEREOMERS OF α,α',β,β'-TETRABROMOETHYL ETHER

BY WILLIAM L. RUIGH AND RANDOLPH T. MAJOR

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One of the products obtained by the bromination of paraldehyde is the so-called "Tetrabromobutyraldehyde" that was first obtained by Freundler.[1] Hibbert, Perry and Taylor[2] reported that this compound was identical with the product which they obtained by the bromination of divinyl ether. They offered further evidence to show that this compound was α,α',β,β'-tetrabromoethyl ether, $CH_2BrCHBrOCHBrCH_2Br$, and that it was not tetrabromobutyraldehyde, $CH_2BrCHBrCHBr_2CHO$.

The divinyl ether obtained by Ruigh and Major[3] was an apparently much purer product than that investigated by Hibbert, Perry and Taylor. From the description of the preparation of divinyl ether which was published by the latter authors the presence of acetaldehyde in their product was quite possible. It seemed desirable, therefore, to repeat and amplify the work of these authors and for the bromination of divinyl ether to use a product of known purity.

We have found that when pure divinyl ether was brominated in chloroform or carbon tetrachloride solutions two distinct crystalline products were obtained together with a small amount of a highly lachrymatory oil. When, however, the bromination was carried out in the presence of powdered calcium carbonate, using carbon tetrachloride as the solvent and carefully dried materials, a quantitative yield of the two solid products only was obtained. The oil obtained in the earlier brominations was probably a mixture containing bromination products of acetaldehyde, since divinyl ether is readily hydrolyzed to acetaldehyde in the presence of moisture and acids.

We were unable to effect a quantitative separation of the mixture obtained in these brominations; we were, however, able to isolate pure samples of the two products which formed this mixture. One of the products crystallized in the form of prisms, while the other formed long fine needles.

The identity of the prisms with the compound obtained by Freundler by the bromination of paraldehyde, was shown by a mixed melting point determination. This is in harmony with the view of Stepanov, Preobrashenski and Shchukina[4] that Freundler's "tetrabromobutyraldehyde" was in reality α,α',β,β'-tetrabromoethyl ether. Our analytical results

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[1] Freundler, *Compt. rend.*, 140, 1693 (1905); *Bull. soc. chim.*, [4] 1, 66 (1907).

[2] Hibbert, Perry and Taylor, THIS JOURNAL, 51, 1551 (1929).

[3] Ruigh and Major, *ibid.*, 53, 2662 (1931).

[4] Stepanov, Preobrashenski and Shchukina, *Ber.*, 59B, 2533 (1926).

confirmed the results of Hibbert, Perry and Taylor, which favored the latter structure. These authors also showed that the compound condensed with ethylene glycol to give bromoethylidene glycol, a fact which they presented as additional evidence in favor of the ether structure of the compound.

It was further found that acetaldehyde was formed when the compound was treated with sodium in xylene or zinc dust in acetic acid. By the action of *p*-nitrophenylhydrazine on the compound in acetic acid we obtained the *p*-nitrophenylosazone of glyoxal. The four carbon chain that is in tetrabromobutyraldehyde would not be expected to give a derivative of glyoxal under these conditions.[5] Dworzak and Prodinger[6] showed that $\alpha,\alpha',\beta,\beta'$-tetrabromoisobutyl ether, obtained by the bromination of isobutyraldehyde, gave a-hydroxyisobutyraldehyde when treated with a dilute solution of sodium bicarbonate. When our prisms were treated in a similar manner we found that the resulting solution contained glycolaldehyde or possibly bromoacetaldehyde.

On the basis of the evidence outlined, there seems to be no reason to doubt that this compound has the structure $\alpha,\alpha',\beta,\beta'$-tetrabromoethyl ether.

The other product of the bromination of divinyl ether which crystallized in the form of needles was obtained in pure form and free from the prisms only with great difficulty. Its melting point was only a few degrees below that of the prisms and the solubilities of the two compounds in various solvents were very much the same. The melting point of a mixture of the two compounds was considerably lower than that of either. The results obtained from analytical and molecular weight determinations of the needles corresponded with the values calculated for tetrabromoethyl ether. When treated with *p*-nitrophenylhydrazine in acetic acid, a quantitative yield of the *p*-nitrophenylosazone of glyoxal was obtained. By heating the needles above their melting point, they were converted into the isomeric prisms. This conversion also took place on long standing in solution in ether at room temperature. In petroleum ether, however, the needles were apparently perfectly stable.

The two a-carbon atoms of $\alpha,\alpha',\beta,\beta'$-tetrabromoethyl ether are asymmetric and theoretically there should exist two inactive forms, the meso and the racemic. On the basis of the evidence here presented, it appears that the two bromination products of divinyl ether are diastereomeric forms of $\alpha,\alpha',\beta,\beta'$-tetrabromoethyl ether. Although it is possible that the needles are also a product of the bromination of paraldehyde, we have not been able to isolate it from the products of this reaction.

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[5] Chattaway and Irving, J. *Chem. Soc.*, 87 (1930); Chattaway and Farinholt, *ibid.*, 94 (1930).

[6] Dworzak and Prodinger, Monatsh., 53/54, 588 (1929).

A study of the quantitative bromination of divinyl ether by the method of McIlhiney[7] was undertaken. The amount of bromine absorbed represented about 95% of that theoretically required. However, when the iodate correction was applied, the amount of bromine added to the unsaturated groups varied from 76 to 82% of the theoretical requirements. Buckwalter and Wagner[8] have recently shown that the McIlhiney method for the determination of the amount of unsaturation in organic compounds gives erratic and erroneous results. The method developed by these authors is not applicable to a determination of the amount of unsaturation in divinyl ether due to the low boiling point of the ether.

Experimental Part

Bromination of Divinyl Ether.—Five grams of pure divinyl ether in 20 g. of chloroform was chilled to −15° and 22.8 g. of bromine in 50 g. of chloroform was slowly added with stirring. All but about 0.5 cc. of the bromine solution was absorbed before a slight permanent yellow color appeared. This color was removed by the addition of a drop of divinyl ether. The solution was evaporated down to an oil (37.1 g.), which was mixed with an equal volume of petroleum ether. The solid which crystallized out was filtered off; the filtrate when chilled yielded more solid. The total yield of solid was 21.7 g. or 78% of the theoretical amount of α,α',β,β'-tetrabromoethyl ether. When 50 g. of divinyl ether was brominated in carbon tetrachloride, 222.3 g. or an 80% yield of the solid was obtained. The highly lachrymatory oil which remained after the solid products of the reaction had been removed was not investigated.

The solid from the reaction consisted of a mixture of prisms and needles. It was not possible to effect a quantitative separation but apparently about 20% of the solid consisted of the needles. When 10 g. of divinyl ether was brominated with 46 g. of bromine at −20° in the presence of an excess of calcium carbonate (precipitated chalk) in dry carbon tetrachloride solution, a quantitative yield of the mixed forms was obtained. No oil was formed in this experiment. Under these conditions, by inspection under the microscope, the needles formed about 50% of the total solid.

The prisms were fairly readily obtained when the mixture slowly crystallized from petroleum ether. The first fraction consisted of the practically pure prisms.

The needles, however, were obtained in a pure condition only with great difficulty. In order to do this the needles were allowed to grow rapidly and the ligroin solution, which was supersaturated with respect to the prisms, was decanted. Five grams of the pure needles was obtained in this manner.

In ethyl ether a slow isomerization of the needle to the prism form took place, which was complete after the mixture had stood for three weeks at room temperature. Solutions of the bromination products in acetone gradually decomposed after several days and gave a black tar. The compounds appeared to be quite stable, however, in petroleum ether.

The prisms melted at 65–66°; a mixture of these crystals with the compound obtained by Freundler by the bromination of paraldehyde also melted at 65–66°.[1]

Anal. Calcd. for $C_4H_6Br_4O$: C, 12.32; H, 1.56; Br, 82.02. Found: C, 12.47, 12.23, 12.38; H, 1.61, 1.67, 1.26; Br, 82.21, 82.47.

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[7] Hans Meyer, "Analyse und Konstitutionsermittlung organischen Verbindungen," Verlag von Julius Springer, Berlin, 1916, p. 960.

[8] Buckwalter and Wagner, THIS JOURNAL, 52, 5241 (1930).

The needles melted at 62–63°; a mixture of the needles and prisms melted at 45–57°.

Anal. Calcd. for $C_4H_6Br_4O$: C, 12.32; H, 1.56; Found: C, 12.41, 12.48; H, 1.37, 1.41.

Mol. wt. Calcd. for $C_4H_6Br_4O$, 389.7. Found: 376.3, 378.2 (Menzies–Wright ebullioscopic method).

Action of Zinc Dust and Acetic Acid on the Prisms.—About 0.5 g. of the prisms was dissolved in 15 cc. of dilute acetic acid and several grams of zinc dust was added in small portions while the reaction mixture was warmed on the water-bath. The solution was filtered, diluted with water to a volume of about 50 cc., just neutralized with sodium carbonate and distilled. The distillate reduced Tollens' reagent. A small portion of the distillate when treated with p-nitrophenylhydrazine gave the *p*-nitrophenylhydrazone of acetaldehyde; m. p. 128–129°. A mixture of this material with the *p*-nitrophenylhydrazone of acetaldehyde melted at 128–129°.[9]

Action of Sodium on the Prisms.—In a 50-cc. flask were placed 10 g. of the prisms, 4 g. of sodium and 25 cc. of dry xylene. An 8-mm. bent glass tube served as a condenser and the receiver was a flask cooled with a solid carbon dioxide–acetone mixture. The xylene was heated just to the boiling point and after about half an hour about 0 5 cc. of liquid had collected in the receiver. The distillate had a strong odor of acetaldehyde, reduced Tollens' reagent and gave the p-nitrophenylhydrazone of acetaldehyde; m. p. 128–129°. A mixture of this material with the p-nitrophenylhydrazone of acetaldehyde melted at 128–129°.[9]

Hydrolysis of Prisms.—One gram of the prisms and 100 cc. of a 2% solution of sodium bicarbonate were warmed until the prisms melted. After the mixture had been shaken for about forty-five minutes, practically all of the solid material had disappeared. The solution was then cooled and saturated with carbon dioxide. A portion of this solution reduced Fehling's solution rapidly at room temperature, a red precipitate being formed after four minutes. The solution also gave the p-nitrophenylosazone of glyoxal, m. p. 309–310°, when it was treated with p-nitrophenylhydrazine in acetic acid. When equal quantities of this solution and a 50% solution of potassium hydroxide were warmed, a yellow color developed.[10]

Action of *p*-Nitrophenylhydrazine on Prisms and Needles.—A solution of 0.5 g. of the prisms and 1 g. of p-nitrophenylhydrazine in about 50 cc. of 50% acetic acid was warmed on the water-bath for an hour. After the solution had been cooled the precipitate was removed by filtration; yield, 0.49 g. The crude product was dissolved in 40 cc. of hot pyridine from which red needles separated on cooling; m. p. 309–310°. It gave a deep blue color with a concentrated solution of potassium hydroxide to which had been added a few drops of alcohol. These facts together with the analysis identified this compound as the p-nitrophenylosazone of glyoxal.[11]

Anal. Calcd. for $C_{14}H_{12}N_6O_4$: N, 25.61. Found: N, 25.63.

A quantitative yield of 0.09 g. of the p-nitrophenylosazone of glyoxal was obtained when 0.1 g. of the needles was warmed in a 50% acetic acid solution of *p*-nitrophenylhydrazine for several hours at 50–60°.

Transformation of the Prismatic to the Needle-like Form of Tetrabromoethyl Ether.—Two-tenths of a gram of the needles was heated in a test-tube for four minutes at 100°. A slight decomposition accompanied by the evolution of hydrogen bromide took place. This was shown by the white fumes produced when a stopper wet with ammonia was held near the mouth of the test-tube used. The product obtained was

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[9] E. Hyde, *Ber.*, **32,** 1813 (1899).

[10] Fischer and Landsteiner, *ibid.*, 25,2552 (1892).

[11] Dakin and Dudley, Biochem. J.,15, 127 (1913).

recrystallized from ligroin; yield, 0 15 g. of the prisms. Evaporation of the mother liquor yielded a mixture of both needles and prisms. The crude prisms after one crystallization from ligroin melted at 64–65°. A mixture of this product with another sample of the prisms melted at 65°

Titration of Divinyl Ether by Means of Bromine.—Samples of divinyl ether were enclosed in sealed glass bulbs and broken in the presence of a standard solution of bromine in stoppered flasks chilled on ice. The flasks were kept at 0° for an hour in the dark and then allowed to stand at the temperature of the laboratory. For analyses "A" and "B" of Table I the flasks stood for twenty-four hours before the addition of the solution of potassium iodide and the titration with sodium thiosulfate, while analyses "C" and "D" stood for two hours before the titration.

The results given in Line 1 of Table I express the percentage of the theoretical amount of bromine required by divinyl ether used that was actually absorbed. Line 2 gives the results in percentage of the theoretical amount of bromine actually absorbed after the iodate correction had been made.

TABLE I

EXPERIMENTAL DATA

	A	B	C	D
1	95.5	93.0	96.6	95.0
2	76.3	78.5	67.7	82.1

We are greatly indebted to Mr. Douglass Hayman, who made most of the analyses recorded in this paper.

Summary

1. It has been shown that the bromination of pure divinyl ether gives two distinct crystalline compounds. Evidence is given to show that these compounds are diastereomers of $\alpha,\alpha',\beta,\beta'$-tetrabromoethyl ether.

2. The prismatic form of $\alpha,\alpha',\beta,\beta'$-tetrabromoethyl ether has been shown to be identical with the bromination product of paraldehyde that was first obtained by Freundler and that was called by him "tetrabromobutyraldehyde."

RAHWAY, NEW JERSEY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE ISOMERS IN "DIISOBUTYLENE." I

BY FRANK C. WHITMORE AND S. N. WRENN

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The material known as diisobutylene was first reported by Butlerow.[1] It was prepared by him from isobutylene and sulfuric acid in a sealed tube and by heating tertiary butyl alcohol with dilute sulfuric acid. Similar methods of preparation have since been used by other workers.[2] Similar materials have been prepared by heating tertiary butyl alcohol with quinoline hydrochloride for three days at 160°;[3] by the action of ferric chloride on isobutyl alcohol at 200° for 24 hours;[4] by heating tertiary butyl iodide with metallic oxides in a sealed tube;[5] by the reaction of tertiary butyl chloride and isobutylene in the presence of zinc chloride at room temperature;[6] by the action of zinc chloride on isobutyl alcohol in the presence of hydrogen chloride or traces of isobutyl chloride;[7] and by the polymerization of isobutylene at high temperature and pressure or in the presence of catalysts.[2b,8]

It was early recognized that diisobutylene probably consisted of the two isomeric octylenes, 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2. Oxidation experiments indicated the presence of these olefins in varying amounts according to the results of different investigators.[9] It was not until the work of McCubbin and Adkins that the actual presence of these olefins and their relative proportions were clearly determined.[2c] They showed that there is about four times as much 2,4,4-trimethylpentene-1 as of its pentene-2 isomer in diisobutylene as prepared by heating tertiary butyl alcohol with approximately 50% sulfuric acid.

The literature contains little information on the physical properties of diisobutylene. The boiling point is given over ranges between 101 and 113° with the most generally accepted values near 103°. The density at 20° is given from 0.715 to 0.7195. Only one reference to the refractive index is given, n_D^{20} 1.41123.[2b] The melting point is given as

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[1] Butlerow, *Ann.*, 189, 44, 46 (1877).

[2] (a) Edgar, *Ind. Eng. Chem.*, 19, 146 (1927); (b) Lebedew and Kobliansky, *Ber.*, 63, 103 (1930); (c) McCubbin and Adkins, THIS JOURNAL, 52, 2547 (1930).

[3] Van Hove, Bull. *Acad. Roy. Soc. Belg*, 540 (1908); *Chem. Zentr.*, 11, 292 (1908).

[4] Oddo, *Gazz. chim. ital.*, 31, *I*, 326 (1901).

[5] Lermontoff, *Ann.*, 196, 116 (1879).

[6] Kondakow, *J. prakt. Chem.*, (2) 54, 442 (1896).

[7] Malbot and Gentil, *Compt. rend.*, 108, 957 (1889); *Ann. chim. phys.*, (6) 19, 370 (1890).

[8] Ipatiew, J. *Russ. Phys.-Chem. Soc.*, *43*, 1420 (1911); *Ber.*, 44, 2978 (1911).

[9] Butlerow, J. *Russ. Phys.-Chem. Soc.*, 14, 201 (1882); Prileshajew, *ibid.*, 39, 769 (1907); Wagner, "Dissertation," Warschau, 1888; *Ber.*, 21, 1230 (1888).

−101°.[10] The present investigation grew out of attempts to make addition products of "diisobutylene." It was soon found that the mixtures obtained were unsatisfactory for study. Many unsuccessful attempts were made to synthesize the individual isomers said to be contained in diisobutylene. It was then decided to attempt the separation of diisobutylene into its isomers by careful fractional distillation. This method proved to be fully as difficult as the results of earlier workers would indicate but has been carried to the point where there is no longer any doubt of its possibility. The results to date are being published because this phase of the work has been interrupted by the departure of one of the authors. The separation is being continued with the use of even more efficient columns than those used in the present study.

A total amount of 19 liters of diisobutylene was subjected to 29 careful fractional distillations during 291 hours of actual distillation.

The purest samples of each isomer obtained have the following properties.

	Boiling point (corr.), Cottrell apparatus, °C.	d_4^{20}	n_D^{20}
Lower isomer	100.1–100.2 (736 mm.) 101.2–101.3 (760 mm.)	0.710	1.408
Kigher isomer	103.0–103 4 (736 mm.) 104.1–104.5 (760 mm.)	0.715	1.415

Since the lower isomer is found in much larger amounts than the higher one and in view of the results of McCubbin and Adkins,[2b] there can be little doubt that the lower isomer is 2,4,4-trimethylpentene-1 and that the higher isomer is 2,4,4-trimethylpentene-2.

Special experiments showed that diisobutylene does not polymerize or depolymerize on standing in glass bottles exposed to light for over a year or on refluxing at atmospheric pressure for six hours.

In order to make sure that the different properties of the "higher isomer" were not due to impurities of triisobutylene,[7] a 1:1 mixture of the lower isomer and triisobutylene was fractionated by means of column "H" (see below). No difficulty was experienced in separating the two substances in a single distillation. Since the column used was distinctly inferior to the two columns used in the fractionations of the two isomeric diisobutylenes, the properties of the higher isomer cannot be ascribed to impurities of triisobutylene not removed during the distillations.

Experimental

Preparation **of Diisobutylene.**[11]—Individual runs were made in 12-liter flasks provided with reflux condensers. To a cold mixture of 3300 cc. of water and 2700 cc. of C. P. sulfuric acid was added 2500 g. of commercial tertiary butyl alcohol. The thor-

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[10] Parks and Huffman, private communication.

[11] Based on directions supplied by W. W. Hartman of the Eastman Kodak Company.

oughly shaken mixture was heated on the steam-bath for twenty to thirty hours. Shortly after the heating started an oil began to separate on the surface. The oily layer was removed, washed with water and dilute potassium carbonate solution, dried over calcium chloride for several days and finally refluxed over metallic sodium for five hours. At the end of this treatment fresh sodium retained its metallic luster even after heating in the mixture for an hour. The usual yield was 2100 cc. This, on fractionation through column "J" (see below), gave 1500 cc. of the diisobutylenes boiling at 100–105" (738 mm.) and 500 cc. of residue of triisobutylene and higher polymers. Usually several runs were worked up together.

During the course of the work some diisobutylene was kindly supplied by Dr. Graham Edgar of the Ethyl Gasoline Corporation. This boiled at 98–108° (760 mm.). It had been prepared from material obtained by absorbing cracked refinery gases in sulfuric acid. This diisobutylene was refluxed over metallic sodium and given a preliminary distillation through column "J." Neither in this nor in subsequent distillation was any difference noted between the diisobutylene made in this Laboratory from tertiary butyl alcohol and that made by the Ethyl Gasoline Corporation from cracked gases containing isobutylene.

Description of Columns.[12]—Three columns were used. All were well insulated and were operated with total condensers and variable take-offs. Usually the take-off was adjusted at about 5 cc. per minute and the heat supplied was adjusted to give maximum reflux without flooding the columns.

	Height, cm.	Diameter, cm.	Material	Insulation (magnesia pipe cover)	Packing
Column "H"	120	2	Pyrex glass	3.8 cm. with electrical heating	6 × 6 mm. glass rings
Column "J"	180	3.6	Cast iron	8.9 cm.	Same
Column "W"	260	1.8	Brass	5.1 cm.	6 X 6 mm. brass rings

With columns H and J, Pyrex glass flasks were used as stills. These were heated in oil-baths. Column W was fitted with a 1500-cc. brass pot electrically heated. The boiling points were taken on a short Anschütz thermometer with the mercury thread entirely in equilibrium with the condensing vapor.

Distillations.—At first careful fractionations were carried out in the usual way according to the boiling points of the fractions. It was soon found that the refractive indices changed much more rapidly than the boiling points. Thus fractions from different distillations but having similar refractive indices were combined and refractionated. In all the distillations fractions of 50–60 cc. were taken even when the boiling point did not vary. During the early distillations such successive fractions showed changing refractive indices. In later distillations fractions were obtained which on redistillation gave successive fractions with the same boiling points and the same refractive indices.

Since the various fractionations gave over five hundred fractions, it is obviously impossible to give all the details. The fractionations are summarized in the following table. Distillations 1–17 were carried out in column J and distillations 18–29 in column W.

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[12] The design of these columns was according to suggestions by M. R. Fenske, who is in charge of the investigations on Pennsylvania petroleum in this Laboratory.

TABLE I

DISTILLATION DATA

	Charge			Distillate							
							Important Fractions				
No.	Vol., cc.	Source	n_D^{20}	Bar., mm.	Time, hrs.	Fractions taken	Vol., cc.	B. p., °C.	Ref. ind.	Ref. ind., range of all fractions	% Recovered over original ref. ind. range
1	5000	Crude		739–736	19	18	1670	100.6–100.8			
2	5100	Ethyl Gas. Corp.		721–724	20	18	2475	99–100			
3	5000	Same		724–726	18	24	2442	99.6–100.2			
4	3700	Crude		725–726	10	15	1470	98.8–100.3			
5	6690	Dist. 1–4 main fractions, b. p. 99.6 (721) to 100.8° (739)		743–739	27	21	4890	100.4–100.7			
6	815	Dist. 5, Fract. 6, 7, b. p. 100.5° (744)		722–717	5	12	510	99.2 (718)			
7	910	Dist. 5, Fract. 13,14, b. p. 100.6° (738)		731	5	5	465	100.0–100.1			
8	2300	Dist. 1–4, low boiling		730	9	6	880	99.8–99.9			
9	610	Dist. 8, Fract. 2, b. p. 99.8–99.9°		727–728	5	10	412	99.6–99.8	1.4088–90	1.4088–98	
10	510	Dist. 6, Fract. 2		743–742	4	8	304	100.4–100.5	1.4088–90	1.4088–91	
11	465	Dist. 7, Fract. 2		741	3	7	320	100.4–100.5	1.4089–90	1.4088–93	
12	5480	Dist. 1–11	1.4098–1.4138	740–737	22	51	1714	100.8–101.0	1.4100–2	1.4080–1.4142	75
13	1915	Dist. 1–11	1.4091–9	726–730	10	35	1246	99.8–100.1	1.4088–90	1.4084–1.4125	13
							180	100.5–100.8	1.4100–1.4105		
14	2010	Dist. 12, Fract. 28–47, 100.0–102.4° (738)	1.4101–31	734	9	21	724	100.7–100.8	1.4100–2	1.4097–1.4150	55
							518	101.6–104.6	1.4120–50		
15	2850	Dist. 5, Fract. 5, 8–12, Dist. 8, Fract. 3	1.4089–90	734–732	11	27	861	100.0	1.4080–4	1.4080–1.4118	18
							1140	100.0–100.1	1.4085–8		
							434	100.1–100.3	1.4089–91		

TABLE I (*Concluded*)

	Charge					Distillate					
							Important Fractions				
No.	Vol., cc.	Source	n_D^{20}	Bar., mm.	Time, hrs.	Fractions taken	Vol., cc.	B. p., °C.	Ref. ind.	Ref. ind., range of all fractions	% Recovered over original ref. ind. range
16	965	Dist. 5, Fract. 6, 7, 13, 14, Dist. 8, Fract. 2	1.4089–90	731–732	4	10	785	99.9–100.1	1.4088–90	1.4088–96	15
17	1980	Dist. 12, Fract. 15–27 Dist. 13, Fract. 29–32 Dist. 14, Fract. 2–5	1.4098–1.4102	737	10	31	919	100.4–100.7	1.4090–4	1.4090–1.4140	20
18	840	Dist. 12, Fract. 48–9 Dist. 14, Fract. 14–19	1.4112–38	728	6	17	220 210 286	102.0–104.0 100.8–101.0 102.1–103.2	1.4120–40 1.4110– 1.4130–50	1.4107–52	33
19	590	Dist. 5, 6, 12, 13, 15, low fractions	1.4080–5	733	11	15	349	100.0–100.1	1.4084–1.4089	1.4064–1.4108	23
20	1170	Dist. 15, Fract. 2–13	1.4080–5	726–729	12	21	788	99.7–100.1	1.4086–8	1.4084–90	17
21	880	Dist. 15, Fract. 14–22	1.4085–9	737–740	10	17	694	100.1–100.2	1.4087–90	1.4085–94	79
22	950	Dist. 6, Fract. 1 Dist. 9, Fract. 1 Dist. 12, Fract. 2, 3 Dist. 13, Fract. 2–14 Dist. 15, Fract. 23	1.4088–9	732–730	12	19	590	99.9–100.0	1.4082–4	1.4080–1.4128	20
23	628	Dist. 14, Fract. 10–13 Dist. 17, Fract. 26, 27	1.4105–10	735	6	13	241 133	100.4–100.7 102.0–102.7	1.4090–2 1.4117–33	1.4090–1.4133	8
24	980	Dist. 12, Fract. 6, 7 Dist. 14, Fract. 1, 8, 9 Dist. 15, Fract. 25 Dist. 17, Fract. 18–25	1.4093–1.4102	731–732	8	16	480 296	100.2–100.5 100.6–102.0	1.4090–1 1.4096–1.4120	1.4087–1.4135	19
25	510	Dist. 13, Fract. 15–24	1.4090	734–731	5	11	418	100.0–100.2	1.4085–90	1.4082–1.4120	20
26	580	Dist. 13, Fract. 25, 26 Dist. 15, Fract. 24 Dist. 17, Fract. 1–7	1.4090–3	733–732	7	12	436	100.0–100.2	1.4087–90	1.4087–1.4133	18
27	690	Dist. 13, Fract. 27, 28 Dist. 17, Fract. 8–17	1.4093–4	729–728	8	15	457	99.8–100.2	1.4087–92	1.4085–1.4130	13
28	1020	Dist. 1–17, residues	1.4093–1.4150	728–726	9	16	445	101.4–103.2	1.4120–1.4152	1.4098–1.4152	81
29	515	Dist. 22, Fract. 1–10	1.4080–4	737	6	10	357	100–100.2	1.4083–6	1.4181–97	50

Possible Changes of Diisobutylene on Standing and during Distillation.—Several samples of diisobutylene of various refractive indices were allowed to stand for over a year and then examined again. No change was observed in their refractive indices. This showed that no appreciable polymerization or oxidation had taken place under the conditions used, namely, storage in glass bottles with cork stoppers and exposure to ordinary daylight. The oxidation and polymerization products of diisobutylene all have higher indices of refraction[2]"

In order to determine the possibility of the dissociation of diisobutylene during distillation, a sample of known refractive index was refluxed through column "W" (the tallest of the columns) for six hours with total reflux. Arrangements were made to catch any escaping isobutylene in a solution of bromine in carbon tetrachloride. When the bromine was removed by sodium thiosulfate and the carbon tetrachloride was distilled, no high boiling material was obtained. A blank using known isobutylene showed there was no difficulty in detecting even a small amount of the dibromide, b. p. 146–148° (738 mm.). The material in the pot showed no change in refractive'index, thus showing that it contained no dissolved isobutylene formed during the refluxing and that it had not suffered any appreciable change during its contact with the brass column and packing. **A** small amount of dissolved isobutylene lowers the refractive index of diisobutylene notably.

Separation of Diisobutylene and **Triisobutylene.**—The possibility of separating these materials by the type of columns used was definitely settled by the following experiment. A large amount of the residues from the fractionation of crude diisobutylene was distilled from an ordinary distilling flask and the 1500 cc. boiling at 160–200° was redistilled through column "H" with the column heated to 150–160°. A fraction amounting to 850 cc. boiled at 173–174° (726 mm.). This was distilled again through column "H" as before. Twenty fractions were taken with boiling points at 738 mm. from 175.5 to 178.8' and refractive indices from 1.4300 to 1.4338. Fractions 2–14 were used for the distillation experiment with diisobutylene. These fractions ranged in boiling point from 175.7 to 176.4° (738 mm.) (corr.) and in refractive index from 1.4300 to 1.4305. A sample of the mixture on distillation through column H gave the following results, 170.6–175°, 8.5 cc.; 175.0–176.2°, 419 cc., n_D^{20} 1.4300; 176.2–176.6° (flask dry), 95 cc., n_D^{20} 1.4308.

Diisobutylene, fractions 14 to 18 of Distillation 20, b. p. 100.0–100.1° (727–729 mm.), n_D^{20} 1.4087–1.4088, was distilled through column "H." Practically all (97%) distilled at 99.8–100.0° (734 mm.) and had a refractive index of 1.4085.

The above diisobutylene (156 cc.) and triisobutylene (156 cc.) were distilled through column "H" with the results given in the following table.

Bar., mm.	Time, min.	B. p., °C.	Fraction	Vol., cc.	Ref. index	% Distilled (total)
733	0	99.6				
	18	99.8	1	4.5	1.4085	1.3
732.5	85	99.8	2	99	1.4086	34.7
	130	99.8	3	17	1.4087	40.4
	190	99.8	4	20	1.4087	47.1
	200	100.0	5a	2		47.7
	235	101.0	5b	6	1.4090	49.8
Heat on column	245	110.0	6a	4		
	254	127.0	6b	1		
	257	132.0	6c	0.5	1.4099	51.6
	292	171.0	7	7	1.4210	54.0
	314	175.0	8	8	1.4288	56.6
732	328	175.4	9	13	1.4300	61.0
	388	175.8	10	94	1.4300	92.4
	400	175.8	11	22	1.4303	100.0

The flask was dry at the end of the distillation. The hold-up and loss amounted to 14 cc.

Physical Properties.—The boiling points were determined at various pressures near **735** mm. in a Cottrell boiling point apparatus with a standardized Anschiitz thermometer having the mercury thread entirely exposed to the vapor. The value of $\Delta p/\Delta$ b. p. for each isomer was found to be about 21.8 mm. per degree C. The boiling points at 760 mm. were calculated from this relation.

The refractive indices were determined to four places with an Abbé refractometer with prism kept at a constant temperature by water from a bath held at 20.0°. Observations taken at different times on the same samples checked within one or two in the fourth decimal place.

When larger amounts of the pure isomers are available they are to be submitted to various physical chemists and physicists to be measured accurately as was done in connection with the classical researches of Edgar, Calingaert and Marker on the isomeric heptanes.

Summary

1. By repeated fractionation through improved laboratory columns of the adiabatic, total condensation, variable take-off type, "diisobutylene" can be separated into 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2, the former being present in much the larger amount.

2. The boiling points, densities and refractive indices of the isomers have been determined.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

NITRATION OF ACYLANILINES

BY L. CHAS, RAIFORD AND JACOB NELSON WICKERT

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Nitration of phenol and the cresols, except the para compound, gives isomeric mononitro derivatives. Zincke and collaborators[1] found that when an acetic acid solution of a brominated cresol is treated with sodium nitrite, the halogen atom, if it occupies a favorable position, may be replaced by the nitro group. In this way they obtained from the meta series a product in which the halogen atom para to hydroxyl was replaced, while in the ortho and para series the atom ortho to hydroxyl was substituted. In no case did they record the formation of isomeric nitro compounds in a single nitration.

Work in this Laboratory and elsewhere by Raiford and students[2] has proved that when halogenated phenols containing bromine or iodine as substituents are nitrated by this method they may exchange halogen in the ortho and para positions for the nitro group and thus give rise to isomeric mononitro derivatives.[3] On this account it was desired to study halogen substitution products of benzene in which position 1 is occupied by some radical other than hydroxyl. Aniline derivatives suggested themselves.

When an acyl or alkyl aniline is subjected to bromination or nitration,[4] the new substitueat usually enters the anilide rather than the other radical, if either of the *o,o,p*-positions is available. Replacement of halogen by the nitro group in such products is extremely rare. Hiibner[5] obtained a monobromodinitro derivative by nitration of benzoyl-2,4-dibromoaniline with fuming nitric acid, but the structure of the product was not determined. Treatment of *p*-bromodimethylaniline with nitrous acid[6] gave *p*-bromophenylmethylnitrosamine, and *p*-nitrodimethylaniline. When the starting material contained chlorine instead of bromine, no replacement of halogen was observed, but the products were *p*-chlorophenylmethylnitrosamine and 3-nitro-4-chlorodimethylaniline.

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[1] Zincke, *J. prakt. Chem.*, [2] 61, 561 (1900).

[2] Raiford and collaborators, THIS JOURNAL, 44, 158 (1922). This paper contains important references to other work.

[3] All attempts to replace chlorine in this way have been unsuccessful. Thus, when Raiford and Heyl [*Am. Chem. J.*, *43*, 397 (1910)] and Raiford [*ibid.*, 46, 425 (1911)] subjected *sym.*-trichlorophenol and 2,4,6-trichloro-*m*-cresol, respectively, to the action of nitrous acid under the conditions indicated, only starting material could be recovered. More vigorous treatment of the cresol derivative with fuming nitric acid removed chlorine from the para position and gave a quinone instead of a nitro compound.

[4] Remmers, *Ber.*, 7, 346 (1874); Huhner, *Ann.*, 208, 292 (1881).

[5] Hubner, *Ber.*, 10, 1710 (1877).

[6] Wurster and Scheibe, ibid., 12, 1816 (1879); Koch, *ibid*, **20**, 2460 (1887)

Borrelli[7] treated benzoyl-2,4,6-tribromoaniline with fuming nitric acid, and obtained two products that melted at 227 and 272–273°, respectively, and which were recorded on the basis of analyses[8] for nitrogen and bromine as isomeric dinitrotribromobenzanilides. Since the structures of these compounds were not proved either by synthesis[9] from the required amines and acid chlorides, or by the study of their possible hydrolysis products, it was of interest to consider them further.

In the present study Borrelli's work has been repeated by following his brief directions as closely as possible. The results obtained did not agree entirely with what he reported. The nitration product was a mixture of substances with different solubilities in benzene, as the previous author found. The two least soluble ones that melted at 242 and 266°, respectively, were isolated.[10] Analyses indicated that they were mononitro derivatives, and hydrolysis gave, in each case, *sym.*-tribromoaniline, which showed that in the anilide the nitro group was attached to the benzoyl radical. The lower melting anilide was identified (see experimental part) as the *m*-nitrobenzoyl derivative, and the higher one as the ortho isomeride. Theory requires the existence of four mononitro and ten dinitro derivatives of benzoyl-2,4,6-tribromoaniline. To learn whether Borrelli's products might be included in that list all possible isomers were synthesized and examined. The identity of each was further established by study of its hydrolysis products. None of them corresponds in terms of physical constants with either of the compounds recorded by Borrelli.

When an acetanilide instead of a benzanilide substitution product was nitrated isomers were again obtained. Treatment of acetyl-2,4-dibromoaniline[11] with fuming nitric acid alone gave an 86% yield of the corresponding 2,4-dibromo-6-nitro compound.[12] When the starting material was first dissolved in concentrated sulfuric acid and fuming nitric acid was added to this solution, the reaction was much more rapid than before and required cooling to control it. Fractional crystallization of the product gave the 6-nitro compound mentioned above and the isomeric acetyl-2,4-dibromo-5-nitroaniline.[13] This behavior is, in part, in accordance with the observation of others.[14]

[7] Borrelli, *Gazz. chim. ital.*, 17, 527 (1887).

[8] The percentages reported do not indicate that the compounds were pure. The methods of analysis, the weights of materials used, the quantities of reagents, and the weights of final products are omitted. The results cannot, therefore, be checked by calculation.

[9] *Cf.* Daccomo, *Ber.*, 18, 1168 (1885).

[10] Evaporation of the mother liquor left a brown residue that was not obtained in crystalline form.

[11] Chattaway and Clemo, *J. Chem. Soc.*, **109**, 90 (1916).

[12] Remmers, *Ber.*, 7, 348 (1874).

[13] Korner and Contardi, [*Atti Accad. Lincei*, [5] *17*, *I*, 465 (1908)] obtained this derivative in another way and proved its structure.

[14] Hollemann, Hartogs and van der Linden, [*Ber.*, 44, 727 (1911)] found that nitra-

Experimental Part

3,4-Dinitrobenzoyl Chloride.—A mixture of equal weights of phosphorus pentachloride and the required dinitrobenzoic acid[15] was heated on a water-bath for thirty minutes, phosphorus oxychloride was distilled off and the residue allowed to cool and solidify. It melted at 45–47°.[16]

Anal. Subs., 0.1837: AgCl, 0.1128. Calcd. for $C_7H_3O_5N_2Cl$: Cl, 15.40. Pound: Cl, 15.19.

Preparation of **Benzoyl** Derivatives.—With the exceptions indicated in the tables, the benzoyl derivatives were prepared in the following way. An intimate mixture of the required aniline and acid chloride in a suitable flask, set in an oil-bath and attached to an air condenser, was slowly raised to 120–130° and heated there until hydrogen chloride was no longer evolved, usually three to six hours.[17] The powdered residue was then

TABLE I

MONONITROBENZOYL-2,4,6-TRIBROMOANILIDES ($C_{13}H_7O_3N_2Br_3$)[18]

Substituted benzoyl	Yield, %	M. p., °C.	Analysis Subs., g.	AgX, g.	Halogen,[c] % Calcd.	Found
2-Nitro-	81	265[a]	0.2020	0 2389	50.10	50.33
3-Nitro-[b]	91	242"	2303	2703	50.10	49.89
4-Nitro-	96	246–247[a]	2070	.2430	50.10	49 96

[a] Nearly colorless needles by repeated crystallization from alcohol. [b] Composition checked by analysis for nitrogen. *Anal.* Subs., 0.2001: 9.8 cc. of N_2 at 22° and 746.9 mm. Calcd. for $C_{13}H_7O_3N_2Br_3$: N, 5.84. Found: N, 5.49. [c] Analyses were made by the Carius method.

TABLE II

DINITROBENZOYL-2,4,6-TRIBROMOANILIDES ($C_{13}H_6O_5N_3Br_3$)

Dinitrobenzoyl radical	Yield, %	M. p., °C.	Analyses Subs., g.	AgX, g.	Halogen," % Calcd.	Found
2,3-	53[f]	282–283[b]	0.2007	0.2166	45.80	45.93
2,4-	93	307–308[c]	.2031	.2179	45.80	45.66
2,5-	66	286–287[c]	.1660	.1777	45.80	45.56
2,6-	86	334–336[d]	.1590	.1703	45.80	45.68
3,4-	94	263–264[c]	.1856	.1991	45.80	45.65
3,5-	95	288[e]	.1836	.1979	45.80	45.87

[a] Halogen was determined by the Carius method. [b] Colorless leaflets after three crystallizations from alcohol. [c] Nearly colorless needles from alcohol. [d] Felted masses of colorless needles from alcohol. [e] Repeated crystallization from alcohol gave nearly colorless irregularly shaped masses. [f] Represents the amount of material after final crystallization.

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tion of aniline in the presence of concentrated sulfuric acid gave a high percentage of meta derivative.

[15] Obtained in 86% yield as directed by Sirks [*Rec trav. chim.*, 27, 221 (1908)].

[16] The acid chlorides of 2,3- and 2,5-dinitrobenzoic acids were obtained as oils by the method given above. Since the amounts available were small it was not feasible to attempt further purification. The identity of each was fixed by examination of the anilide obtained from it.

[17] Limpricht, *Ann.*, 99,249 (1856); also Danckwortt, *Arch. Pharm.*, 228,581 (1890).

[18] The 2- and 3-nitro derivatives are the ones obtained also by nitration of Borrelli's starting material.

TABLE III

MONONITROBENZOYL-2,4,6-TRIBROMO-3-NITROANILIDES[a] ($C_{13}H_6O_5N_3Br_3$)

Substituted benzoyl	Yield, %	M. p., °C.	Analyses Subs., g.	0.1 N[d] AgNO₃, cc.	Halogen, % Calcd.	Found
2-Nitro	88	269–270[b]	0.1634	9.37	45.80	45.89
3-Nitro	93	236–237[c]	.1971	11.23	45.80	45.59
4-Nitro	92	299–300[b]	.1944	11.19	45.80	46.05

[a] The nitrotribromoaniline used here was obtained in 93% yield by Wheeler's method [*Am. Chem. J.*, 17, 701 (1895)]. [b] small colorless needles from acetic acid. [c] Colorless, silky needles from alcohol. [d] Analyses made with the Parr bomb as directed by Brown and Beal [THIS JOURNAL, 45, 1291 (1923)].

TABLE IV

BENZOYL DERIVATIVES OF OTHER SUBSTITUTED ANILINES

Substituted aniline	Formula	Yield, %	M. p., °C.	Analyses Subs., g.	AgX, g.	Halogen,"% Calcd.	Found
2,5-Dibromo-[c]	$C_{13}H_9ONBr_2$	96	152	0.1967	0.2070	45.07	44 78
2,6-Dibromo-4-nitro-	$C_{13}H_8O_3N_2Br_2$	97	190–191[b]	.1671	.1579	40.00	40 21
2-Methyl-4,6 dibromo-[c]	$C_{14}H_{11}ONBr_2$	57	181–182[d]	.2151	.2179	43.36	43.12
2,4,6-Tribromo-3-nitro-	$C_{13}H_7O_3N_2Br_3$	94	234–235[d]	2067	.2449	50.10	50.37
2,4,6-Tribromo-3,5-dinitro-"	$C_{13}H_6O_5N_3Br_3$	93	271–272[f]	.1602	.1730	45.80	46.06

[a] Halogen was determined by the Carius method. [b] Crystallized three times from alcohol. [c] Obtained by the Schotten–Baumann method. 2-Methyl-4,6-dibromoaniline was prepared in 77% yield as directed by Fries [*Ann.*, 346, 165 (1906)]. [d] Colorless needles after repeated crystallization from alcohol. " Obtained from 2,4,6-tribromo-3.5-dinitroaniline that was prepared in 52% yield by Blanksma's method [*Rec. trav. chim.*, 21, 255 (1902)]. [f] Colorless needles from alcohol.

extracted with sodium carbonate solution and finally crystallized from a suitable solvent. The composition of these products is shown by analytical data in the accompanying tables, and the structure of each was further established by hydrolysis and identification of the corresponding acid and amine.

Summary

1. Nitration of benzanilide or its halogen substitution products in the absence of sulfuric acid introduces the new substituent into one of the *o,o,p*-positions of the anilide residue if either of them is available. When the benzoyl derivative of *sym.*-tribromoaniline is used the substituent enters the acyl radical and gives a mixture of the isomeric 2-nitro- and 3-nitrobenzoyltribromoanilides.

2. When the acetyl derivative of 2,4-dibromoaniline was nitrated in the presence of concentrated sulfuric acid a mixture of the isomeric 5-nitro- and 6-nitrodibromo compounds was obtained.

3. In none of the aniline derivatives here studied was halogen replaced by the nitro group.

4. All mono- and dinitro substitution products of benzoyl-2,4,6-tri-

bromoaniline demanded by theory have been synthesized and their structures determined.

5. Further work is in progress in this Laboratory.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

BENZALPYRUVIC ACID DIBROMIDE

BY MARIE REIMER

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The action of sunlight on β-bromobenzalpyruvic acid has been the subject of study in this Laboratory for several years.[1] The fact that large quantities of this unsaturated bromo compound have been required has led to improved methods of preparation of benzalpyruvic acid and of its dibromide from which the unsaturated bromo compound is prepared and to the observation that a marked characteristic of the dibromide is the ease with which it forms addition compounds with various solvents. In view of a recent paper by Musajo[2] in this same field it seems advisable to publish results already obtained.

The melting points of different samples of benzalpyruvic acid dibromide prepared in the early work varied from 125 to 142° and this variation was ascribed to contamination of the substance with the unsaturated bromo compound formed from it by loss of hydrogen bromide. It has now been found that the dibromide readily forms a hydrate in the presence of even traces of moisture and that the purest sample of the dibromide described previously contained enough of this hydrate to lower the melting point although not enough to affect the analytical results. In the present work, in which benzalpyruvic acid and the reagents used in the bromination reaction were thoroughly dried, the crude dibromide, obtained in 92 to 97% yield, has been found to melt at 148–150°; recrystallized from dried benzene, at 150–151°. The compound described by Musajo as melting at 147–150° is probably this substance and is certainly not a racemic isomer of the acid melting at 142° as he suggests. Under the conditions used in this Laboratory for the bromination no isomer is formed.

Experimental Part

Preparation of Benzalpyruvic Acid.—For the preparation of pure samples of the acid its methyl ester, obtained readily from crude acid and easily purified, was hydrolyzed in methyl alcoholic solution with potassium hydroxide. The marked insolubility of the potassium salt of the acid in methyl alcohol suggested the following procedure for the condensation reaction which is found to give better yields of pure product and in a much shorter time than the former method adapted from that of Erlenmeyer.

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[1] Reimer, THIS JOURNAL, 48, 2454 (1926).

[2] Musajo, *Gazz. chim. ital.*, **60**, 669 (1930).

Seventeen and six-tenths grams (0.2 mole! of pyruvic acid was mixed with 21.2 g. (0.2 mole) of benzaldehyde, the mixture cooled and 55 cc. of a 25% solution of potassium hydroxide (0.24 mole) in methyl alcohol added slowly with constant shaking and cooling. The solution became dark reddish yellow but there was no evidence of condensation as long as the mixture was kept at or below 10°. As the temperature rose, crystals of the potassium salt of benzalpyruvic acid slowly separated and the solution became warm. After twelve hours at room temperature there was an almost solid mass of crystalline potassium salt. This was filtered, washed with a few cubic centimeters of methyl alcohol and with ether and air dried. From 70 to 80% yields of analytically pure salt were obtained.

Anal. Calcd. for $C_{10}H_7O_3K$: K, 18.22. Found: K, 18.42.

From the alcoholic filtrates, after spontaneous evaporation of the alcohol and acidification of the aqueous solution of the residue, a dark reddish-yellow oil was obtained This is evidently a mixture containing the oily acid described by Claisen and Claperède.[3]

From cooled, concentrated solution of the potassium salt iced hydrochloric acid precipitated benzalpyruvic acid in more than 90% yield. To prevent the separation of the acid as an oil which subsequently solidifies in impure condition, it was found advisable to seed the potassium salt solution with crystals of the acid before acidification. The product was dried over sulfuric acid and recrystallized from benzene; melting point, 61–62°.

Reaction with Bromine.—The bromination was carried out in carefully dried chloroform with bromine freshly distilled from phosphorus pentoxide. To 10 g. of the dried acid in 60 cc. of chloroform, cooled with ice, 3.03 cc. of bromine was added slowly. The solid that separated toward the end of the reaction was filtered and washed with cooled chloroform. From the filtrate the chloroform was evaporated almost completely in a current of dry air. The yield of dibromide from both sources was 92 to 97%. When the bromination was carried out with air-dried acid, a considerable portion of the substance in the chloroform filtrates was found to be the unsaturated acid, β-bromobenzalpyruvic acid. The crude dibromide is faintly yellow. It softens in the melting point tube at 147° and melts with vigorous decomposition at 149–150°. It crystallizes slowly from dried benzene in fine, stiff, almost colorless needles melting at 150–151° with effervescence.

Anal. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.71; H, 2 38. Found: C, 35.92; H, 2.47.

The hydrate was formed by dissolving 1 g. of the dibromide in 15 cc. of warm benzene to which 0.3 cc. of water had been added. From the moist benzene solution, very fine shining soft white needles separated almost immediately. The crystals soften markedly at about 90°. If the heating is rapid, the substance melts, with vigorous decomposition, at about 140°. If heated slowly, the decomposition may take place at as low a temperature as 120°.

Anak. Calcd. for $C_{10}H_8O_3Br_2 \cdot H_2O$: C, 33 89; H, 2.82. Found: C, 33 78; H, 2.99.

A sample of this substance sealed in a specimen bottle was unchanged after many months. On exposure to the air, even after four months, the substance softened at 90° and melted at 142–143°.

With methyl alcohol the dibromide also forms a solid addition product which separates from solution when almost all the solvent alcohol has evaporated. The solid softens between 70 and 80° to an opaque mass which melts at about 125° with slow evolution of gas above this temperature. This behavior is unchanged after many weeks.

Anal. Calcd. for $C_{10}H_8O_3Br_2 \cdot CH_3OH$: C, 35.86; H, 3.26. Found: C, 36 18; H, 3.15.

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[3] Claisen and Claperède, Ber., 14, 2472 (1881).

The stability of this product suggests that it is a hemi-acetal and is in marked contrast with that of the methyl alcoholic addition product of β-bromobenzalpyruvic acid. This addition compound separates from methyl alcohol solution in large transparent prisms which almost immediately became opaque through loss of methyl alcohol.

Anal. Calcd. for $C_{10}H_7O_3Br \cdot CH_3OH$: C, 45.99; H, 3.83. Found: C, 46.10; H, 4.10.

When benzalpyruvic acid dibromide is boiled with methyl alcohol for five or ten minutes, the methyl ester previously described, melting at 117°, is formed in good yield. There is no loss of hydrogen bromide as is the case when the dibromide is boiled with water[1] nor is there replacement of bromine with methoxyl as with the dibromide of 2,4-dimethoxy-5-bromocinnamic acid.'

In **ethyl** alcohol the dibromide is readily soluble in the cold and does not separate from the solution on spontaneous evaporation of the solvent. The yellow oil remaining gave analytical results indicating it to be a mixture. After standing for several days, the oil deposited a few crystals which melted at 61-62' and were proved to be the ethyl ester of benzalpyruvic acid dibromide by a mixed melting point determination with that substance. The ester was readily obtained in quantity by bromination of ethyl benzalpyruvate.6 The product crystallizes from ether in very pale yellow stocky needles melting at 61-62°.

Anal. Calcd. for $C_{12}H_{12}O_3Br_2$: C, 39.56; H, 3.29. Found: C, 39.22; H, 3.39.

The ester crystallized from ethyl alcohol in less pure condition, and, after standing in contact with alcohol for several days, the product was a yellow oil which analyses showed to be a mixture of the ester with that substance in combination with alcohol.

The ease of esterification of benzalpyruvic acid dibromide is interesting when contrasted with the behavior of the unsaturated @-bromobenzalpyruvic acid. The unsaturated acid cannot be esterified directly, crystallizing unchanged after standing for many hours in solution in alcohol saturated with hydrogen chloride.

Summary

Improved methods of preparation of benzalpyruvic acid and of benzalpyruvic acid dibromide have been described as well as addition compounds of the dibromo compound with various solvents.

NEW YORK, N. Y.

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[4] Reimer and Tobin, THIS JOURNAL, 52, 341 (1930).

[5] Reimer, *ibid.*, 46, 783 (1924).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOBART COLLEGE]

ACTION OF HYDROGEN CHLORIDE ON STANNANES OF THE TYPE $R_2SnR'_2$

BY RALPH H. BULLARD AND FRANCIS R. HOLDEN

RECEIVED JUNE 10, 1931 PUBLISHED AUGUST 5, 1931

In a previous paper[1] the action of halogens on some mixed stannanes was discussed. It was shown that the replacement series of some organic groups in decreasing order of ease of removal from tin by halogen is phenyl, benzyl, methyl, ethyl and n-propyl. F. B. Kipping,[2] on halogenating certain mixed stannanes, found that the ease with which various radicals are removed by iodine from a molecule containing two or three different groups decreases in the order: o-tolyl, *p*-tolyl, phenyl and benzyl. Hence the replacement series based on the halogenation reaction becomes: o-tolyl, *p*-tolyl, phenyl, benzyl, methyl, ethyl and n-propyl.

It was considered of interest to ascertain whether or not this order is observed when mixed stannanes are treated with dry hydrogen chloride. Kipping states that the order in which the groups are removed from his unsymmetrical stannanes by warm or hot concentrated hydrochloric acid solutions is in general the same as that with iodine. He notes one exception: tribenzylethylstannane when refluxed with hydrochloric acid yields tribenzylstannyl chloride.

To simplify the problem it was decided in this investigation to prepare symmetrical stannanes of the type $R_2SnR'_2$ and to treat these with dry hydrogen chloride under conditions such that two groups, and only two groups, would be removed. Examination of the resulting dichloride would then show which groups had been removed. For this purpose dimethyldiethylstannane, diethyldi-n-propylstannane, and diphenyldiethylstannane were prepared and treated with dry hydrogen chloride at temperatures such that two groups were removed. If the above replacement series of groups is valid in connection with this reaction, one would predict (1) that both methyl groups would be removed from dimethyldiethylstannane, (2) that both ethyl groups would be removed from diethyldi-n-propylstannane, and (3) that both phenyl groups would be removed from diphenyldiethylstannane. A study of the reaction products showed them to be (1) methylethylstannyl dichloride, (2) ethyl-n-propylstannyl dichloride and (3) diethylstannyl dichloride. In the first two instances the two groups substituted by the chlorine of the hydrogen chloride were one of each kind.

Experimental Part

Preparation of the Stannanes.—Dimethyldiethylstannane, $(CH_3)_2(C_2H_5)_2Sn$, was prepared by the Grignard reaction from methylmagnesium iodide and diethylstannyl

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[1] Bullard, THIS JOURNAL, 51, 3065 (1929).

[2] F. B. Kipping, *J. Chem. Soc.*, 131, 2365 (1928).

dichloride. It was purified by distilling under reduced pressure. It distilled at 32° under 14 mm. pressure and at 132° under atmospheric pressure; yield of the pure stannane, 75% of the theoretical.

Anal. Subs., 0.1351: SnO_2, 0.0986. Calcd. for $(CH_3)_2(C_2H_5)_2Sn$: Sn, 57.40. Found: Sn, 57.48. *Mol. wt.* Subs., 0.2248, 0.1334, 0.2418: C_6H_6, 21.42, 19.78, 21.47: *At*, 0.261, 0.167, 0.279. Calcd. for $(CH_3)_2(C_2H_5)_2Sn$: mol. wt., 206.8. Found: mol. wt., 205.9, 206.6, 206.6.

Diethyldi-n-propylstannane, $(C_2H_5)_2(n\text{-}C_3H_7)_2Sn$, was similarly prepared by the Grignard reaction using n-propyl bromide and diethylstannyl dichloride. It was purified by distilling under reduced pressure. It boiled at 84.5° under 10 to 11 mm. pressure. Under atmospheric pressure it distilled at 205 to 207° with slight decomposition; yield of the pure stannane, 88% of the theoretical.

Anal. Subs., 0.2282, 0.2534: SnO_2, 0.1307, 0.1448. Calcd. for $(C_2H_5)_2(n\text{-}C_3H_7)_2$, Sn: Sn, 45.15. Found: Sn, 45.11, 45.01. *Mol.* wt. Subs., 0.1570, 0.3976: C_6H_6, 20.15, 19.82: *At*, 0.155, 0.406. Calcd. for $(C_2H_5)_2(n\text{-}C_3H_7)_2Sn$: mol. wt., 262.9. Found: mol. wt., 257.4, 253.0.

Diphenyldiethylstannane, $(C_6H_5)_2(C_2H_5)_2Sn$, was likewise prepared by the Grignard reaction from ethylmagnesium bromide and diphenylstannyl dichloride. It was purified by distilling under reduced pressure. It boiled at 155–157° at 4 mm. pressure; yield of the pure stannane, 78.5% of the theoretical.

Anal. Subs., 0.3513, 0.3457: SnO_2, 0.1601, 0.1575. Calcd. for $(C_6H_5)_2(C_2H_5)_2Sn$: Sn, 35.88. Found: Sn, 35.90, 35.89.

Treatment of **Dimethyldiethylstannane** with Dry Hydrogen Chloride.—Dry hydrogen chloride was bubbled through 10.89 g. of the stannane contained in a round-bottomed flask. An oil-bath was placed around the flask and the temperature was gradually raised to 140–145° over a period of two hours. The temperature was then maintained at this point for two hours more. On cooling, the contents of the flask solidified. The product was recrystallized from hot petroleum ether; 10.67 g. was obtained. The crystals melted at 52°; yield, calculated as methylethylstannyl dichloride, $(CH_3)(C_2H_5)SnCl_2$, 86.7% of the theoretical.

Anal. Subs, 0 1812, 0 2100: SnO_2, 0.1167, 0.1356. Subs., 0.2015, 0.2724: AgCl, 0.2438, 0.3319. Calcd. for $(CH_3)(C_2H_5)SnCl_2$: Sn, 50.80; Cl, 30.35. Found: Sn, 50.73, 50.86; Cl, 29.93, 30.14. *Mol. wt.* Subs., 0.2323, 0.3860: C_6H_6, 20.44, 20.44: *At*, 0.248, 0.405. Calcd. for $(CH_3)(C_2H_5)SnCl_2$: mol. wt., 233.7. Found: mol. wt., 234.6, 238.7.

Some of the methylethylstannyl dichloride was converted into the oxide by dissolving it in water and treating this solution with sodium hydroxide solution. The resulting precipitate was filtered, washed with water, alcohol, ether, and then dried.

Anal. Subs., 0.3652, 0.2618: SnO_2, 0.3065, 0.2202. Calcd. for $(CH_3)(C_2H_5)SnO$: Sn, 66.40. Found: Sn, 66.10, 66.25.

Methylethylstannyl dichloride was converted into **trimethylethylstannane** by treatment with sodium and methyl iodide in liquid ammonia. On dissolving 0.5049 g. of the dichloride in liquid ammonia, a clear solution was obtained. Sodium, in weighed amounts, was added to this solution. When 0.0913 g., approximately two atoms of sodium per molecule of dichloride, had been added a yellow gummy precipitate had formed. This was presumably the methylethyltin free group. The further addition of 0.0454 g. of sodium, approximately one more atom of sodium per molecule of dichloride, caused the free group to dissolve and gave a yellow solution. The addition of a further 0.0449 g. of sodium resulted in the formation of a deep red solution of the disodium methylethylstannide, $Na_2Sn(CH_3)(C_2H_5)$. A very small amount of sodium in addition gave a deep blue solution, showing that the end-point of the reaction had been passed with this last addition. Methyl iodide was then added until a clear colorless solution was obtained. This produced a white precipitate. On evaporating the ammonia and vapor distilling with ammonia gas through a condenser cooled with liquid ammonia, a few drops of a liquid boiling at 109° (uncorr.) was obtained. Trimethylethylstannane, $(CH_3)_3(C_2H_5)Sn$, boils at 108.2° corr.[3] The reactions involved in the above transformations are therefore

$$
\begin{aligned}
(CH_3)(C_2H_5)SnCl_2 + 2Na &= (CH_3)(C_2H_5)Sn + 2NaCl \\
(CH_3)(C_2H_5)Sn + 2Na &= Na_2Sn(CH_3)(C_2H_5) \\
Na_2Sn(CH_3)(C_2H_5) + 2CH_3I &= (CH_3)_3(C_2H_5)Sn + 2NaI
\end{aligned}
$$

The identification of the trimethylethylstannane formed by these reactions gives rather conclusive proof that the product of the action of hydrogen chloride on dimethyldiethylstannane is methylethylstannyl dichloride.

Treatment of **Diethyldi-*n*-propylstannane** with Dry Hydrogen Chloride.—Dry hydrogen chloride was bubbled through 4.778 g. of the stannane for four hours at 100°. The solid product was recrystallized from hot petroleum ether; 3.25 g. was obtained; yield, calculated as ethyl-n-propylstannyl dichloride, 68.9% of the theoretical. The reaction had not been run quite to completion because the piercing odor of a monohalide was present. The purified substance melted at 53°.

Anal. Subs., 0.1653, 0.1761: SnO_2, 0.0961, 0.1021. Subs., 0.2045, 0.2465: AgCl, 0.2247, 0.2691. Calcd. for $(C_2H_5)(n\text{-}C_3H_3)SnCl_7$: Sn, 45.35; Cl, 27.10. Found: Sn, 45.79, 45.67; Cl, 27.18, 27.01.

Treatment of **Diphenyldiethylstannane** with Dry Hydrogen Chloride.—Dry hydrogen chloride was bubbled for forty minutes through 15.6 g. of the stannane heated at 150–160°. The escaping vapors were passed through a small water condenser. A liquid was obtained which was identified as benzene. The solid residue in the reaction flask was crystallized from petroleum ether; 10.46 g. was obtained; yield, calculated as diethylstannyl dichloride, 89.6% of the theoretical. The purified crystals melted at 84°. Diethylstannyl dichloride melts at 84–85°.[4]

The authors wish to acknowledge their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which assisted in defraying the expenses of this investigation.

Summary

The preparation of dimethyldiethylstannane, diethyldi-n-propylstannane and diphenyldiethylstannane has been described.

On treating dimethyldiethylstannane with dry hydrogen chloride under conditions such that two groups are substituted by chlorine, one methyl group and one ethyl group are removed with the resulting formation of methylethylstannyl dichloride.

Diethyldi-n-propylstannane on similar treatment yields ethyl-n-propyl stannyl dichloride.

Diphenyldiethylstannane, however, on similar treatment yields diethyl stannyl dichloride.

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[3] Bullard and Haussmann, *J. Phys. Chem.*, 34,746 (1930).

[4] Pfeiffer, *Z. anorg. Chem.*, 68, 102 (1910).

The replacement series of organic groups as derived from the halogenation of mixed stannanes is not generally applicable and must be restricted in use to the reaction from which it was derived.

GENEVA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

THE FRIEDEL AND CRAFTS REACTION WITH MALEIC ANHYDRIDE AND RESORCINOL DIMETHYL ETHER. THE ADDITION OF AROMATIC ETHERS TO UNSATURATED SUBSTANCES

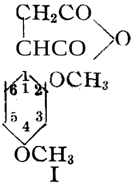
BY GRACE POTTER RICE

RECEIVED JUNE 11, 1931 PUBLISHED AUGUST 5, 1931

Several examples of the reactivity of maleic anhydride in addition reactions have been recorded in the literature in recent years. Diels and Alder[1] have studied the reactions which this anhydride and other substances, having extremely reactive double linkages, undergo when treated with a large and varied list of unsaturated substances. So specific is this type of reaction that it has been used by Windaus[2] to prove that a conjugated system of double linkages in an ergosterol derivative is destroyed by irradiation, since the irradiated product failed to react with maleic anhydride.

Kuhn and Wagner-Jauregg[3] have studied the addition of maleic anhydride to polyenes and very recently Conant and Scherp[4] have obtained evidence that a reaction takes place between maleic anhydride and free radicals.

In this Laboratory it has now been found that maleic anhydride combines with resorcinol dimethyl ether in the presence of aluminum chloride to give a saturated anhydride, dimethoxyphenylsuccinic anhydride (I). This reaction can be explained by a mechanism involving a 1,4-addition to maleic anhydride. The anhydride I was unexpectedly obtained, along with other substances, when the Friedel and Crafts reaction with maleic anhydride and resorcinol dimethyl ether was carried out for the purpose of preparing dimethoxybenzoylacrylic acid, II. The fact that this unsaturated acid has been shown to form an addition product with resorcinol dimethyl ether in the presence of aluminum chloride may account in part for the low yield.



I

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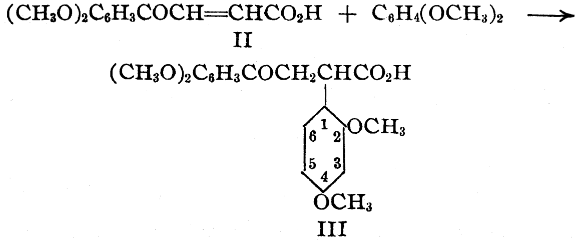
[1] Diels and Alder, *Ann.*, **460, 98 (1928);** *Ber.*, **62, 554, 2081, 2087 (1929); Ann., 486,191,202,211 (1931).**

[2] Windaus, Gaede, Koser and Stein, *ibid.*, **483,** 27 **(1930).**

[3] Kuhn and Wagner-Jauregg, Ber., **63,2662 (1930).**

[4] Conant and Scherp, THIS **JOURNAL, 53,1941 (1931).**



$(CH_3O)_2C_6H_3COCH{=}CHCO_2H + C_6H_4(OCH_3)_2 \longrightarrow$

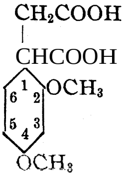
II

$(CH_3O)_2C_6H_3COCH_2CHCO_2H$

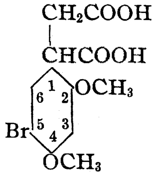
III

Certainly a diminished yield of unsaturated acid II accompanies an increased yield of the ketonic acid III in the Friedel and Crafts reaction.

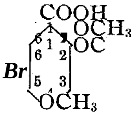
That the substituting group in III is in the a-position to the COOH group rests on the analogy with the mode of addition of various addends to benzoylacrylic ester and its substitution products.[5] That the point of union of the substituting group is that indicated at carbon atom 1 in III is based on the proof of the point of union of this same substituting group in dimethoxyphenylsuccinic acid IV, obtained from the anhydride I by hydrolysis. It is as follows



IV

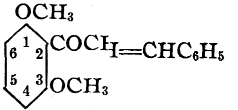


V



Dimethoxyphenylsuccinic acid IV forms one monobromo substitution product and it has not been possible to prepare a dibromo compound from this acid. If the side chain were at carbon atom 3 or at carbon atom 6, both of those substances would be expected to form dibromo substitution products since both of them have two hydrogen atoms which are alike. The bromodimethoxysuccinicacid obtained from IV gives a known product on oxidation, 5-bromo-2,4-dimethoxybenzoic acid.[6] The position of the side chain in IV must, therefore, be that indicated.

The structure of the acid IV is interesting in view of the fact that cinnamyl chloride is reported to react with resorcinol dimethyl ether to form the compound[7] (A).



A

The ketonic acid III could be formed in the Friedel and Crafts reaction from the anhydride I as well as from the unsaturated acid II; in fact it has been shown to be formed when this anhydride is treated with resorcinol dimethyl ether and aluminum chloride, but along with the

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[5] Kohler and Engelbrecht, This Journal, 41,764 (1919); Rice, ibid., 50,233 (1928).

[6] Rice, ibid., 48,3125 (1926).

[7] Simonis and Danischewski, Ber., 59,2914 (1926).

acid III there is also obtained about an equal quantity of an isomeric acid,[8] $(CH_3O)_2C_6H_3COCHCH_2(COOH)C_6H_3(CH_3O)_2$. Since not a trace of the isomeric acid has been detected in the reaction with maleic anhydride and resorcinol dimethyl ether, it seems probable that the ketonic acid III is formed from the unsaturated acid and not from the anhydride.

Numerous examples have been reported of the use of aluminum chloride and of sulfuric acid to bring about addition reactions between unsaturated substances and benzene, toluene, phenol, resorcinol, and hydroquinol.[9] The reaction between resorcinol dimethyl ether and maleic anhydride, however, is not brought about by either hydrogen chloride or sulfuric acid but only by aluminum chloride. In view of the fact that anisole does not add to the unsaturated ketone, $C_6H_5CH{=}CHCOC_6H_4OCH_3$,[10] even in the presence of aluminum chloride, it seems of interest to attempt to determine how general is the reaction between aromatic ethers and unsaturated substances with unusually reactive conjugated systems of double linkages such as maleic anhydride and substituted benzoylacrylic acids. An investigation of this subject is under way in this Laboratory.

Experimental Part

The Friedel and Crafts Reaction.—Freshly distilled maleic anhydride,[11] 53.6 g., which was recrystallized from chloroform immediately before using, was dissolved in 71.5 g. of resorcinol dimethyl ether. This solution, which had a characteristic dark, yellow-green color,[12] was treated with 150 g. of carbon disulfide slowly while being stirred rapidly with an electric stirrer in order that the maleic anhydride might separate in as small crystals as possible. The mixture was cooled with ice, 80 g. of finely powdered aluminum chloride was added gradually and the stirring continued until the dark red product turned to a solid mass. This was decomposed with ice and concd. hydrochloric acid and the granular solid which separated was filtered by suction and left to dry; 111 g. of product melting at 105–130° was obtained. This solid was powdered and extracted several times with small quantities of ether, which removed most of the resorcinol dimethyl ether and left 76 g. of a slightly yellow product melting at 135–160°. When this was dissolved in acetone, dimethoxyphenylsuccinic anhydride I (37.4 g.) crystallized in fine, colorless needles; the residue from the acetone filtrate was boiled with a small quantity of toluene, which left undissolved 3.7 g. of yellow dimethoxybenzoylacrylic acid, II. The toluene solution held a mixture of anhydride and yellow acid. Part of the residue from the toluene was separated by taking advantage of the fact that the yellow acid creeps from a benzene solution of the mixture and leaves the anhydride in solution; the rest of the residue from toluene was dissolved in 50% acetic acid. The yellow acid crystallized in almost pure condition and the filtrate deposited dimethoxyphenylsuccinic acid IV formed by hydrolysis of the anhydride; 49.2 g. of anhydride,

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[8] Compare Mayer and Stamm, *Ber.*, 56, 1424 (1923).

[9] Liebermann and Hartmann, *ibid.*, 24, 2582 (1891); 25, 957 (1892); Eijkman, *Chem. Centr.*, II, 2045 (1907); II, 1100 (1908); Kohler, *Am. Chem. J.*, 31, 642 (1904); 42, 379 (1909); Niederl and Natelson, THIS JOURNAL, 53, 272 (1931).

[10] Kohler, *Am. Chem. J.*, 44, 63 (1910).

[11] Terry and Eichelberger, THIS JOURNAL, 47, 1076 (1925).

[12] Pfeiffer and Bottler, *Ber.*, 51, 1819 (1919).

5.6 g. of unsaturated acid and 5.2 g. of dimethoxyphenylsuccinic acid were separated in pure condition. The residue left after evaporation of the ether used for washing the crude solid was distilled with steam; this removed resorcinol dimethyl ether and left a dark red oil from which no solid could be separated.

Dimethoxyphenylsuccinic Anhydride I, $(CH_3O)_2C_6H_3\overline{CH—CH_2CO—O—CO}$.—The anhydride crystallizes from acetone, benzene, toluene, chloroform and a mixture of chloroform and ether in colorless needles melting at 147°. It is readily obtained by warming dimethoxyphenylsuccinic acid with acetyl chloride and by distilling the acid in a vacuum. On boiling with water or 50% acetic acid it gives the corresponding acid.

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.08. Found: C, 61.07; H, 5.01.

Dimethoxyphenylsuccinic Acid IV, $(CH_3O)_2C_6H_3CH(COOH)CH_2COOH$.—The acid crystallizes from water, methyl alcohol, acetone and 50% acetic acid in large, transparent crystals which melt at 160°, leaving a purple coloration in the top of the melting point tube.

Anal Calcd. for $C_{12}H_{14}O_6$: C, 56.69; H, 5.51; CH_3O, 24.40. Found: C, 56.87; H, 5.79; CH_3O (Pregl), 24.86.

Dimethoxybenzoylacrylic Acid II, $(CH_3O)_2C_6H_3COCH{=}CHCO_2H$.—The acid is sparingly soluble in toluene and boiling water, readily soluble in chloroform, acetone and boiling methyl alcohol; it separates in fine yellow needles which lose their color at 180° and then darken and melt at 189° with decomposition.

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.08. Found: C, 60.63: H, 5.01.

Methyl Dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_3COCH{=}CHCO_2CH_3$.—A poor yield of the ester was obtained by refluxing a methyl alcohol solution of the acid with concd. sulfuric acid. It forms yellow needles which melt at 85° after two recrystallizations from methyl alcohol.

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.40; H, 5.60. Found: C, 62.80; H, 5.77.

The unsaturated acid gives a product containing nitrogen when treated with diazomethane; this reaction as well as a method for the preparation of the ester in good yield is still under investigation.

α-Dimethoxyphenyl-β-dimethoxybenzoylpropionic Acid III, $(CHO_3)_2C_6H_3COCH_2—CH(COOH)C_6H_3(CH_3O)_2$.—When the Friedel and Crafts reaction was repeated under as nearly the same conditions as was possible, only 0.4 g. of unsaturated acid was separated. In this case the crystalline solid, left after removal of the anhydride and unsaturated acid, was treated with cold methyl alcohol; 9.7 g. of substance melting at 125–147° was obtained. By fractional recrystallization from 50% acetic acid this mixture was separated into two acids; the more soluble one was dimethoxyphenylsuccinic acid IV and the less soluble one an acid which melted at 160° on recrystallization from methyl alcohol; it is α-dimethoxyphenyl-β-dimethoxybenzoylpropionic acid, III. From 9.7 g. of solid, 4.7 g. of IV and 3.7 g. of III were obtained in pure condition. The residue from the ether used for washing the crude product deposited 2 g. of III when it was treated with methyl alcohol.

Anal. Calcd. for $C_{20}H_{22}O_7$: C, 64.17; H, 5.88; CH_3O, 33.15. Found: C, 64.38; H, 5.92; CH_3O (Pregl), 33.67.

The Friedel and Crafts reaction has been carried out fourteen times under a variety of conditions, using carbon disulfide as solvent, petroleum ether as solvent and using no solvent and the temperature has been varied over a wide range. One reason that the best yield in these many reactions was only 60% of all products together is the lack of solubility of maleic anhydride at the temperature at which the reaction gives the smallest quantity of unmanageable oil. The solid anhydride becomes coated with the viscous aluminum chloride addition product and is not attacked. When the reaction was carried out without a solvent it was extremely vigorous and a large amount of oil was obtained from which only a few grams of the products described could be separated. From this reaction a fifth substance melting at 185–187° was isolated which may be a result of demethylation, in the presence of aluminum chloride, of one methoxyl group in each aromatic nucleus of the acid III. It has not Wen possible, however, to change it into III by methylation with dimethyl sulfate.

Anal. Calcd. for $C_{18}H_{18}O_7$: C, **62.42; H,** 5 **20.** Found: C, **61.83**; H, **5.87.**

Perkin and Robinson[13] have found that an analogous reaction takes place when resorcinol dimethyl ether and succinic anhydride are treated in the molten condition with aluminum chloride. It is probable that a large part of the untractable material is formed as a result of the demethylating action of aluminum chloride. No reaction, however, could be made to take place between maleic anhydride and resorcinol dimethyl ether by using gaseous hydrogen chloride or sulfuric acid in place of aluminum chloride.

5-Bromo-2,4-dimethoxyphenylsuccinic Acid, V, $(CH_3O)_2C_6H_2BrCH(COOH)CH_2$-COOH.—Dimethoxyphenylsuccinic acid was brominated in carbon disulfide, chloroform, glacial acetic acid and ether. The same product was always obtained and this could not be induced to react with a second molecule of bromine in boiling glacial acetic acid or in the sunlight. The crude product, after washing with ether, was a chalk-white powder melting at 219°; yield, 88%.

Anal. Calcd. for $C_{12}H_{13}O_6Br$: C, **43.24;** H, **3.90.** Found: C, **43.54;** H, **3.99.**

One gram of this acid was refluxed for fifteen hours in acetone solution with potassium permanganate. On acidifying the aqueous solution obtained by boiling the oxides of manganese with water, **0.3** g. of solid melting at **186–193"** was precipitated. After recrystallization from acetone the solid showed no depression of melting point when mixed with a specimen of 5-bromo-2,4-dimethoxybenzoic acid.

Dimethyl Dimethoxyphenylsuccinate, $(CH_3O)_2C_6H_3CH(COOCH_3)CH_2COOCH_3$.—This ester, prepared by refluxing a methyl alcohol solution of the acid IV with concd. sulfuric acid, could not be induced to crystallize before it was distilled in a vacuum (b. p. 231° at **31** mm.). The solid separates from methyl alcohol in heavy transparent plates which melt at 60°; yield of pure product, **92%.**

Anal. Calcd. for $C_{14}H_{18}O_6$: C, **59.57; H, 6.38.** Found: C, **59 66; H, 6.34.**

Methyl **5-Bromo-2,4-dimethoxyphenylsuccinate,** $(CH_3O)_2C_6H_2BrCH(COOCH_3)$-$CH_2COOCH_3$.—This ester a a s brominated in order to determine whether it is possible to obtain isomeric monobromo derivations or a dibromo derivative in spite of the fact that only one bromine compound is formed from the corresponding acid. Bromination in chloroform solution gave a quantitative yield of bromo ester which melted at 90° after two recrystallizations from methyl alcohol.

Anal. Calcd. for $C_{14}H_{17}O_6Br$: C, **46.53;** H, **4.70.** Found: **C, 46.22; H, 4.70.**

α-Dimethoxyphenylethane-α,β-dicarbonic Acid-&methyl Ester, $(CH_3O)_2C_6H_3CH$-$(COOH)CH_2COOCH_3$.—A solution of **17.2** g. of dimethoxyphenylsuccinic anhydride in **200** cc. of methyl alcohol was refluxed for three hours and the solution evaporated to 150 cc., **2** g. of anhydride separated and on further evaporation the filtrate deposited **12.4** g. of ester melting at **139–141.5'; yield, 72%.** After recrystallization from methyl alcohol the colorless needles melted at 142.5°. This ester was first obtained in the course of purifying a Friedel and Crafts product, as the acid IV is readily esterified by boiling it with methyl alcohol.

Anal. Calcd. for $C_{13}H_{16}O_6$: C, 58 20; **H, 5.97.** Found: C, **58.20;** H, **6.13.**

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[13] **Perkin** and Robinson, **J.** *Chem. Soc.,* **93,509 (1908).**

α-Dimethoxyphenylethane-α,β-dicarbonic Acid-a-methyl Ester, $(CH_3O)_2C_6H_3CH(COOCH_3)CH_2COOH$.—This ester is obtained from the dimethyl ester of IV by allowing it to stand for two hours at room temperature with a methyl alcohol solution of potassium hydroxide. The product from hydrolysis of 5.5 g. of dimethyl ester was poured onto ice, the dimethyl ester (2.1 g.) was filtered off and the filtrate extracted with ether; evaporation of the ether left a solid (2.3 g.) melting at 100–115°. By repeated recrystallizations from methyl alcohol, 0.3 g. of pure ester melting at 117" was separated. Analysis indicated that the rest was a mixture of the two isomeric mono esters. On hydrolysis with aqueous potassium hydroxide it gave a quantitative yield of the acid IV.

Anal. Calcd. for $C_{13}H_{16}O_6$: C, 58.20; H, 5.97. Found: subs. (117°), C, 58.06; H, 5.90; mixture: C, 58.03; H, 6.12.

The structures of these two isomers are inferred from analogy with the corresponding esters of phenylsuccinic acid.

The ketonic acid III is formed as the only product of reaction when resorcinol dimethyl ether is treated with dimethoxybenzoylacrylic acid and aluminum chloride.

Methyl **α-Dimethoxyphenyl-β-dimethoxybenzoylpropionate,** $(CH_3O)_2C_6H_3COCH_2CH(COOCH_3)C_6H_3(CH_3O)_2$.—This ester was prepared by saturating a methyl alcohol solution of the acid with hydrogen chloride. The solid, obtained in quantitative yield, crystallizes in clusters of silky needles melting at 140°.

Anal. Calcd. for $C_{21}H_{24}O_7$: C, 64.94; H, 6.18. Found: C, 65.07; H, 6.37.

Semicarbazone of α-Dimethoxyphenyl-β-**dimethoxybenzoylpropionic** Acid, $(CH_3O)_2C_6H_3C({=}NNHCONH_2)CH_2CH(COOH)C_6H_3(CH_3O)_2$.—The ketonic acid gives a 90% yield of semicarbazone on standing for twelve hours with semicarbazide; after washing with boiling methyl alcohol, the powder melted at 204°.

Anal. Calcd. for $C_{21}H_{25}O_7N_3$: C, 58.46; H, 5.80. Found: C, 58.52; H, 6.13.

α-5-Bromo-2,4-dimethoxyphenyl-β-bromo-β-(5-bromo-2,4-dimethoxybenzoyl)-propionic Acid, $(CH_3O)_2C_6H_2BrCOCHBrCH(COOH)C_6H_2(CH_3O)_2Br$.—The ketonic acid, suspended in carbon disulfide and cooled with ice, was treated with three molecular equivalents of bromine. On removal of the solvent the crude, colorless solid forms a cerise-colored coating which was removed by washing with cold methyl alcohol. The acid then melts (dip) with decomposition at 213° to a cherry-red melt.

Anal. Calcd. for $C_{20}H_{19}O_7Br_3$: C, 39.28; H, 3.10. Pound: C, 39.26; H, 2.97.

The methyl ester of this bromo acid was prepared by bromination of the ester of the ketonic acid (140°) in carbon disulfide solution. After washing with cold methyl alcohol, the crude product melted at 161–181° and decomposed at 191°.

Anal. Calcd. for $C_{21}H_{21}O_7Br_3$: C, 40.32; H, 3.36. Found: C, 39.91; H, 3.37.

The crude bromo ester is a mixture of two substances, one melting at 210° and the other at 165–173° and not pure. From the analysis of the crude product it may be concluded that these are probably racemic compounds as the ester has two unequal asymmetric carbon atoms.

And. Subs. (210°). Calcd. for $C_{21}H_{21}O_7Br_3$: C, 40.32; H, 3.36. Found: C, 40.34; H, 3.41.

The Friedel and Crafts Reaction with Resorcinol Dimethyl Ether and Dimethoxyphenylsuccinic Anhydride

β-Dimethoxyphenyl-β-dimethoxybenzoylpropionic Acid and Methyl **β-Dimethoxyphenyl-β-dimethoxybenzoylpropionate,** $(CH_3O)_2C_6H_3COCH(CH_2COOH)C_6H_3(CH_3O)_2$ and $(CH_3O)_2C_6H_3COCH(CH_2COOCH_3)C_6H_3(CH_3O)_2$.—A solution of 29 g. of resorcinol dimethyl ether in 70 cc. of carbon disulfide was treated with an intimate mixture of 10

g. of the anhydride I and 20 g. of aluminum chloride, both finely powdered. The mixture was warmed in a water-bath and stirred vigorously as long as there was evidence of reaction; the orange-colored viscous mass was decomposed with ice and concd. hydrochloric acid and the product filtered off and washed with cold benzene when dry; yield, 12.7 g. of substance melting at 90–135°. The crude solid can be partially separated with 50% acetic acid as a solvent. The first crop of crystals is the ketonic acid III (160°) and the second crop a new acid melting at 157° after a second recrystallization; the mixture of III and this substance melts at 140–145°.

Anal. Calcd. for $C_{20}H_{22}O_7$: C, 64.17; H, 5.88. Found: C, 64.22; H, 6.17.

The residue after these two crops had been removed persistently separated as a mixture, so it was turned into a mixture of esters which could be separated.

The aqueous solution left after filtering off the solid formed in the reaction was mixed with the residue left after removal of the benzene used to wash this solid and the mixture distilled with steam. The insoluble residue which failed to crystallize was esterified and the solid product dissolved in methyl alcohol. The ester of the acid III separated first; from the filtrate the ester of the isomeric acid was obtained as a solid melting at 104° after washing with ether.

Anal. Calcd. for $C_{21}H_{24}O_7$: C, 64.94; H, 6.18. Found: C, 65.26; H, 6.46.

The yield of pure products (65%) was as follows: 4.9 g. of acid III, 1.2 g. of the ester of acid III, 0.3 g. of isomeric acid and 3.9 g. of the ester of the isomeric acid. After this isomeric acid and its ester had become familiar substances, the residues from two Friedel and Crafts reactions with maleic anhydride were examined most carefully but the acid (157°) could not be found nor could its ester be identified when a residue was esterified. If this acid is formed in the Friedel and Crafts reaction with maleic anhydride, it has defied isolation.

Summary

In the presence of aluminum chloride resorcinol dimethyl ether combines with maleic anhydride to form dimethoxyphenylsuccinic anhydride, which may be interpreted as the result of a 1,4-addition reaction. Along with this anhydride four other substances are formed in the Friedel and Crafts reaction. These have been identified, their formation explained and derivatives of them have been prepared.

NEW YORK CITY

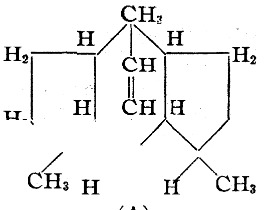
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

THE SYNTHESIS OF 5,6-DIHYDROPYRINDINE

BY WILLARD C. THOMPSON

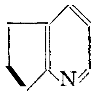
RECEIVED JUNE 12, 1931 PUBLISHED AUGUST 5, 1931

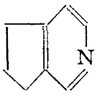
Introduction



(A)

In connection with American Petroleum Institute Project 20 there appeared recently a paper describing a hydroaromatic base of the formula $C_{16}H_{25}N$[1] to which was assigned provisionally the structure shown (A). This substance, the first hydroaromatic base to be obtained from petroleum in pure form, is now being investigated in the Texas Laboratory in order to clear up certain doubtful features in connection with the above formula.

5,6-Dihydropyrindine  was discovered in shale oil by Takashi Eguchi[2] in 1927 but, because of the failure of Chemical *Abstracts* to abstract that part of the Eguchi paper[3] dealing with the base in question, this work was overlooked until after the Thompson and Bailey paper had been submitted for publication. Therefore, the assignment of the pyrindacine structure to the $C_{16}H_{25}N$ compound was in no way influenced by the discovery of the Japanese chemist.

At the suggestion of Professor Bailey the author has synthesized 5,6-dihydropyrindine, following a method suggested by von Braun's synthesis[4] of 5,6,7,8-tetrahydroquinoline, and thus confirmed the structure originally assigned to the C_8H_9N shale oil base.[5] The fact that Eguchi obtained quinolinic acid on oxidation of his product excluded the isopyridine structure,  and leaves no doubt as to the discovery of the first base of this type to be found in nature.

In recent preliminary experiments in the Texas Laboratory in connection with the bases occurring in California crude kerosene distillates, the procedure for the isolation of a number of these in pure form has been developed. Their refractivity indicates both aromatic and hydroaromatic types, and, along with the difficulty of resolution of the .distillation

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[1] Thompson and Bailey, THIS JOURNAL, 53, 1002 (1931).

[2] Eguchi, Bull. *Chem.* Sor. *Japan,* 3,239 (1928); *Chem. Zentr.,* 100,331 (1929).

[3] Eguchi, *Chem. Abstracts,* 23,391 (1929).

[4] Von Braun and Lemke, *Ann.,* 478, 191 (1930).

[5] For other syntheses in the pyrindine series, see T. Zincke, *Ann.,* 290, 321 (1896); Curt Striegler, *J. prakt. Chem.,* [2] 86, 241 (1913).

fractions into individual components, the wide range of 180 to 335° in their boiling points suggests an exceptionally complex mixture. In line with the cyclopentane structure, so typical of many petroleum hydrocarbons and naphthenic acids, it may be expected that, even if the Eguchi base does not occur among the kerosene bases, numerous hydrides of pyrindine or methylated pyrindines, or it may be isopyrindines, will be encountered.[6]

Since the method employed in the synthesis of 5,6-dihydropyrindine is analogous to that followed by von Braun for 5,5,7,8-tetrahydroquinoline, an outline of von Braun's procedure is subjoined. (1) 2-Hydroxymethylenecyclohexanone (A) results in the Claisen condensation of cyclohexanone with amyl formate.[7] (2) Product (A) with cyanacetamide yields 2-hydroxy-3-cyano-5,6,7,8-tetrahydroquinoline (B) and 2-keto-3-cyano-8a-hydroxy-1,2,3,5,6,7,8,8a-octahydroquinoline (C).[8] (3) Products (B) and (C) yield on heating with concentrated hydrochloric acid 2-hydroxy-5,6,7,8-tetrahydroquinoline, (D).[9] (4) With phosphorus pentachloride product (D) is converted to 2-chloro-5,6,7,8-tetrahydroquinoline, (E).[4] (5) Finally product (E) is reduced to 5,6,7,8-tetrahydroquinoline, (F).[4]

Could a similar series of reactions be carried out, with cyclopentanone replacing cyclohexanone in the first step, it is obvious that in step *(5)* 5,6-dihydropyrindine would result. Here the only part of the synthesis previously effected involves the condensation of cyclopentanone with amyl formate to yield hydroxymethylenecyclopentanone.[10] Steps corresponding to (1), (2) and (4) when applied to the synthesis of 5,6-dihydropyrindine, under the conditions employed by the author, result in poor yields; the other reactions proceed smoothly. The dihydropyrindine, although not prepared in an amount sufficient for purification through fractional distillation, was analyzed in the form of picrate. In accordance with the method of Skraup the synthetic product was oxidized to quinolinic acid and this proved to be identical with quinolinic acid made from quinoline. Furthermore, its physical properties are entirely in agreement with those determined by Eguchi on the shale oil base.

The various reactions involved in the synthesis as outlined can be elucidated through the following structural formulas

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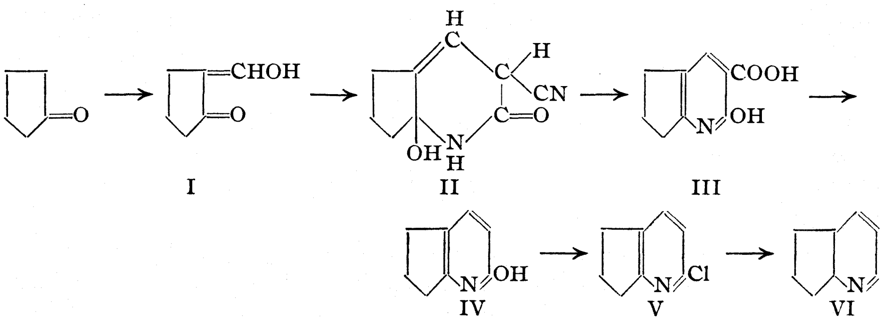
[6] The Texas Laboratory has obtained recently three barrels of kerosene bases, extracted from 9000 barrels of crude kerosene distillate, from the Union Oil Company of California, and a search will be instituted in fractions in the 200° zone for the C_8H_9N shale-oil base as soon as this large supply has been submitted to exhaustive fractional distillation.

[7] Wallach, Ann., 329, 117 (1903).

[8] Sen-Gupta, J. *Chem. Soc.*, 107, 1354 (1915).

[9] Ref. 8, p. **1367.**

[10] Adolf Steindorff, "Dissertation," Gottingen, 1903, p. *32;* Wallach, ***Ann.***, 329, 114 (1903).



Experimental Part

2-Hydroxymethylenecyclopentanone, I.—In this preparation the procedure of Steindorff[10] was followed with minor modifications. To a cooled solution of 20 g. of cyclopentanone and 17.6 g. of ethyl formate in 100 cc. of anhydrous ether was added 5.5 g. of sodium in small pieces. Most of the sodium reacted within an hour and, after standing in the ice box overnight, the mixture was treated with 100 cc. of ice water. The aqueous layer was extracted with ether, the reaction product precipitated as an oil with the required amount of acetic acid, and the oil taken up in ether. On evaporation of the ether solution, previously dried over calcium chloride, the hydroxymethylenecyclopentanone was obtained as a viscous liquid which, after sublimation at 100° in a vacuum, melted at 73°. A 15 to 20% yield was obtained. The use of isoamyl formate instead of ethyl formate did not give an increase in yield.

2-Keto-3-cyano-7a-hydroxy-1,2,3,5,6,7a-hexahydropyrindine, 11.—Enough alcohol to effect solution was added to a mixture of 8.4 g. of cyanacetamide, 11.2 g. of hydroxymethylenecyclopentanone, 2 cc. of piperidine and 35 cc. of water. After standing for several days at 40°, 4 g. of a crude crystalline condensation product separated. This was decolorized by boiling its acetic acid solution with animal charcoal and after several recrystallizations from hot glacial acetic acid it was obtained as microscopic, rhombic prisms which did not melt even at 310°. The substance is only slightly soluble in water, alcohol and ether.

Anal. Calcd. for $C_9H_{10}O_2N_2$: C, 60.68; H, 5.62; N, 15.73. Found: C, 60.23; H, 5.72; N, 15.62.

2-Hydroxy-5,6-dihydropyrindine-3-carboxylic Acid, 111.—Product II was heated with concentrated hydrochloric acid in a sealed tube at 120–130° for two hours. The solution was diluted with an equal volume of water and boiled with animal charcoal. After filtering and cooling the acid separated in a 50% yield as a white solid and was recrystallized from boiling water, from which it separated as fine slender needles, melting at 272° with decomposition. It is slightly soluble in cold but readily soluble in hot water and alcohol. Its aqueous solution gives a red coloration with ferric chloride and a yellow coloration with ferrous sulfate. A silver salt, insoluble in cold water and soluble in hot water, is formed with silver nitrate.

Anal. Calcd. for $C_9H_9O_3N$: C, 60.32; H, 5.06; N, 7.82. Found: C, 59.87; H, 5.20; N, 7.95. *Equivalent weight.* Calcd. for $C_9H_9O_3N$: 179. Found: 170.

2-Hydroxy-5,6-dihydropyrindine, IV.—Five grams of product II and 15 cc. of concentrated hydrochloric acid were heated for two hours at 120–130° and then at 150 160° for three hours. From the acid solution, diluted with an equal volume of water and boiled with animal charcoal, there separated on cooling 3.5 g. of the hydroxy base as fine slender rods. After several recrystallizations from hot water the base was obtained as a white product, melting at 187–188". It is slightly soluble in cold water and cold alcohol but dissolves readily in ether, hot water and hot alcohol. The hydroxy compound gives a red coloration with ferric chloride and yields a picrate that can be recrystallized from alcohol in the form of small, flat, right prisms, melting at 164°.

Anal. Calcd. for C_8H_9ON: C, 71.08; H, 6.71; N, 10.36. Pound: C, 70.79; H, 6.85: N. 10.46.

2-Chloro-5,6-dihydropyrindine, V.—Four grams of 2-hydroxy-5,6-dihydropyrindine, 4 g. of phosphorus oxychloride, and 15 g. of phosphorus pentachloride were heated at 120–130° under pressure for four hours. The chlorodihydropyrindine, admixed with a considerable amount of tarry material, was treated with ice water, made alkaline and steam distilled. About 0.5 g. of a white solid, insoluble in water, was obtained. After several recrystallizations from 50% alcohol the product separated in the form of colorless rhombic prisms melting at 70–71°.

Anal. Calcd. for C_8H_9NCl: N, 9.12. Found: N, 8.87.

5,6-Dihydropyrindine, VI.—Three grams of 2-chloro-5,6-dihydropyrindine was heated with 15 g. of zinc dust and 60 cc. of concentrated hydrochloric acid for six hours. The solution was then diluted with an equal volume of water, filtered, made alkaline and steam distilled. The distillate was extracted with ether, which, on evaporation, yielded 2–3 cc. of a base having a pyridine-like odor. The product was distilled under reduced pressure, a middle fraction of about 0 3 cc. heing reserved for refractive index and boiling point determinations. The freshly distilled base is colorless but soon darkens on standing. The following physical constants were determined: b. p. at 750 mm 199°; n_D^{25} 1 5407. The corresponding constants of the Fguchi base are: b. p at 761 mm. 199.8"; n_D^{25} 1.541.

The first runnings and residue in the distilling flask were dissolved in alcohol and the base precipitated as picrate. After several recrystallizations from alcohol the yellow picrate was obtained in the form of flat rhombic prisms melting at 181–182°. The picrate of the shale-oil base as described by Eguchi crystallizes in "flat needles," soluble in hot alcohol and melting at 181°.

Anal. Calcd. for $C_8H_9N{\cdot}C_6H_2OH(NO_2)_3$: C, 48.28; H, 3.45; N, 16.09. Found: C, 48.36; H, 3.63; N, 16.05.

Oxidation of **Dihydropyrindine.**—To 0.2 g. of the base, in 25 cc. of water and heated under reflux in a boiling water-bath, 1.5 g. of potassium permanganate was added in small portions over a period of eight hours. Finally the solution was heated to boiling, filtered and evaporated to dryness. The residue was dissolved in water and the quinolinic acid precipitated as silver salt, from which it was recovered in the usual way. The acid was recrystallized from alcohol and on heating in a capillary tube a vigorous evolution of gas took place at 180–190°. As the heating was continued, the product solidified at about 200° and melted at 231°. A mixture of this product with a sample of quinolinic acid, prepared according to the directions of Skraup,[11] showed the same behavior on heating. With copper sulfate solution the acid gave a blue precipitate, insoluble in boiling water and boiling acetic acid, and with ferrous sulfate an orange coloration, characteristic properties of quinolinic acid.

Conclusion

The discovery in the Texas Laboratory of a petroleum base of the formula $C_{16}H_{25}N$, which is probably a hydro-pyrindacine, has directed

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[11] Skraup, *Monatsh.*, 2, 147 (1881); Hoogewerff and Van Dorp, *Rec. trav. chim.*, **1**, 107 (1882).

attention to the possibility of cyclic nitrogen bases occurring in petroleum distillates of the pyrindine type. The structural relationship of pyrindine to pyrindacine is similar to that between quinoline and acridine.

The occurrence of 5,6-dihydropyrindine in shale oil distillates and the $C_{16}H_{25}N$ base in crude kerosene distillates contributes to the importance of the five-membered carbon ring and will direct the attention of the chemist toward a further search for natural products of these types. Furthermore, it is to be expected that further research in the Texas Laboratory on the kerosene bases will develop a relationship between petroleum bases and naphthenic acids, more especially as concerns cyclopentane structure.

A synthesis of 5,6-dihydropyrindine seemed desirable in confirmation of Eguchi's interpretation of his C_8H_9N base, although the proof of structure furnished by the Japanese chemist was apparently conclusive. It is realized that the method of preparing this substance, as described in the present paper, must be improved in several steps before 5,6-dihydropyrindine becomes available in quantity for further research.

AUSTIN, TEXAS

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

THE C_4-SACCHARINIC ACIDS. V. THE PREPARATION OF 2,3-DIHYDROXYBUTYRIC ACID LACTONE. 3-HYDROXYISOCROTONIC ACID LACTONE. AN ATTEMPT TO PREPARE 2,2'-DIHYDROXYISOBUTYRIC ACID[1]

BY J. W. E. GLATTFELD, GLADYS LEAVELL, GEORGE E SPIETH AND DONALD HUTTON

RECEIVED JUNE 15, 1931 PUBLISHED AUGUST 5, 1931

The resolution of 2,3-dihydroxybutyric acid (hereafter called "2,3-acid") has already been reported in a paper from this Laboratory.[2] The acid used for the resolution experiments was prepared in accordance with the procedures of the two previous workers, Hanriot, and Nef.[3] As neither of these authors was interested specifically in this acid, they did not make a very extended study of its preparation. No mention is made by them, for instance, of the simultaneous formation of an unsaturated acid, 3-hydroxyisocrotonic acid, although the formation of this acid is mentioned by Carré.[4] This unsaturated acid was formed to some extent in every one of our runs, in some cases even to the exclusion of the desired 2,3-acid. It was isolated in the form of its lactone in large quantities during

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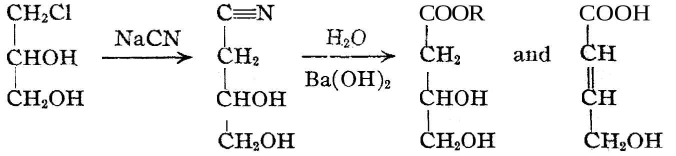
[1] This article is constructed largely from dissertations presented by Gladys Leavell, George E. Spieth and Donald Kutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

Glattfeld and Miller. THIS JOURNAL, 42, 2314 (1920).

[3] Hanriot. Ann. *chim. phys.*, [5] *17*, 104 (1879); Nef, Ann., 376, 35 (1910).

[4] Carré, Bull. *soc. chim.*, [4] 3,834 (1908); *Compf.rend.*, 146,1282 (1908).

the work of preparation reported below. It is a very valuable by-product as it serves as a source for erythronic acid, which it yields when oxidized with permanganate,[5] or with barium or silver chlorate.[6] Although many experiments were carried out in an attempt to prevent the formation of the unsaturated acid, none of them was entirely successful. During this work, however, a satisfactory procedure for the preparation of the 2,3-acid and its separation from the unsaturated acid was developed and is given below because no detailed directions are at present available in the literature. By following these directions a reasonably good yield of the 2,3-acid (28%) may be obtained. This procedure does not differ in principle from that of Nef, but it does differ in some important details. It may be outlined as follows



CH_2Cl–CHOH–CH_2OH $\xrightarrow{NaCN}$ C≡N–CH_2–CHOH–CH_2OH $\xrightarrow[Ba(OH)_2]{H_2O}$ COOR–CH_2–CHOH–CH_2OH and COOH–CH=CH–CH_2OH

Glycerol-a-chloro-hydrin

Nitrile of 2,3-dihydroxybutyric acid

2,3-Dihydroxy-butyric acid

3-Hydroxyisocrotonic acid

2,3-Dihydroxybutyric Lactone

Glycerol-α-chlorohydrin.—As indicated above, glycerol-a-chlorohydrin is the starting product in this synthesis. It was prepared by the action of 1350 cc. of hydrochloric acid of sp. gr. 1.18 on 1 kg. of glycerol in the presence of 48 cc. of glacial acetic acid. The reaction mixture was introduced into pressure bottles, heated in an oil-bath at 120° for seven hours, and then fractionated at 15 mm. The 110–160° fraction was refractionated at 3 4 mm. The average yield of the fraction of b. p. 101–105" at 3–4 mm. in five runs was 707 g., or 59% (Cl, calcd., 32.08; found, 32.24, 32.14).

Preparation of the Lactone.—A solution made by the addition of 32.6 g. of potassium cyanide (or the equivalent in sodium cyanide) in 50 cc. of water, to 55 g. of glycerol-a-chlorohydrin in 225 cc. of 95% alcohol, was kept with occasional shaking in a closed towel-wrapped pressure bottle (tested citrate of magnesia bottle) in a water-bath at room temperature for thirty-six hours. The water-bath was then heated to boiling and so maintained for two and one-half to three hours, the bottle cooled and contents subjected to filtration to remove salts. The filtrates in two such experiments were combined and the solvents removed as completely as possible with water pump (15–20 mm.) and water-bath at 60". The residue was treated with 200 cc. of 95% alcohol, the mixture warmed, subjected to filtration and the salts washed with alcohol. The filtrate was again concentrated under the conditions mentioned above. The residue was dissolved in 200 cc. of water and added to a mixture of 160 g. of hydrated barium hydroxide in 800 cc. of water. The mixture was then kept in a boiling water-bath for four hours while a stream of air, washed by passage through sodium hydroxide solution, was drawn through it (evaporated water not replaced). The hot mixture was then added to a hot solution made up of 166 cc. of 6 *N* sulfuric acid in 2 liters of water, and the mixture kept hot while

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[5] Lespieau, *Bull. soc. chim.*, [4] 1, 1113 (1907).

[6] Géza Braun, THIS JOURNAL, 51, 235, 246 (1929).

the final quantitative precipitation of the barium was effected by the use of a dilute solution of sulfuric acid. The barium sulfate was removed and the filtrate and washings from the barium sulfate, which contained a trace of barium ion, were subjected to distillation (at 15–20 mm. and water-bath finally at 90°) to remove the water completely; the residue was extracted with absolute alcohol, the alcohol solution decanted and the salts thoroughly washed by decantation. The alcohol was removed from the extract and washings by distillation at 15–20 mm. with water-bath finally at 90°. The residue was then transferred to a Claisen flask and distilled at 3–8 mm., from an oil-bath by the use of an oil pump. The material which boiled below 60° was discarded and two fractions 60–140° and 140–200° collected. The average yields of these two fractions in thirty experiments were 21 g. and 55 g., respectively. These two fractions were twice refractionated and the final fractions, 70–110° and 135–160° at 2–5 mm., averaged in twenty-six experiments, 19.6 g. and 33.5 g. The 70–110° fraction (Fraction I) consisted chiefly of 3-hydroxyisocrotonic lactone and the 135–160° fraction (Fraction II) chiefly of 2,3-dihydroxybutyric lactone; 23 and 28% of the theoretical, respectively.

Purification of the Lactone.—Fraction II gave a test for chloride ion which was due largely, but apparently not entirely, to the presence of a small amount of ammonium chloride. It was found that solution in ten parts of dry ethyl acetate (or 5 parts ethyl acetate and 2–3 parts ether) and allowing to stand overnight caused the precipitation of the salt. The salt was removed by filtration through a folded filter, and the ethyl acetate by distillation (water-bath finally at 100°)*. The residue was dissolved in water and portions of a suspension of pure silver oxide in water added until a white precipitate ceased to form. The filtered solution now failed to give a chloride ion test. The water was removed by distillation with the water pump (15–20 mm. and water-bath finally at 100°), the residue fractionated with the oil pump and the 135–160° fraction at 2–5 mm. again collected. This fraction again tested for chloride ion. The process from the point indicated by the asterisk above was repeated three or four times. While it was easy to get a product that gave only a faint test for chloride, the complete removal of the impurity required ten to fourteen repetitions of the process. Evidently chloride ion is freed during the distillations and a perfectly pure lactone can be obtained only when the source of contamination is destroyed.

The pure lactone boiled under the conditions here used (Claisen flask with long arms, oil-bath and 20 drops of distillate per minute) at 148–150° at 2–4 mm.

Anal. Subs., 0.2190, 0.2639: H_2O, 0.1234, 0.1472; CO_2, 0.3775, 0.4522. Calcd. for $C_4H_6O_3$: **H,** 5.92; **C,** 47.08. Found: **H,** 6.31, 6.24; C, 47.03, 46.82. ***Molecular weight*** determinations gave the following: 104.1, 106.9, 102.2, 104.6, average 104.4. Calculated for $C_3H_6O_3$, 102.05.

Crystallization of the Lactone.—A sample of the pure lactone in a test-tube was cooled in a carbon dioxide snow–acetone bath. Stirring of the sample and scratching of the sides of the test-tube soon caused the entire sample to solidify. This solid sample was saved for inoculation purposes. It was soon found that the lactone could be recrystallized. Thus one volume of lactone in three volumes of a one to one acetone–ether mixture was cooled to about −35° by immersion in a carbon dioxide–acetone mixture, inoculated with the solid mentioned above, and thoroughly stirred for ten minutes. The solution had then set to a pasty mass of crystals. After a half hour the mother liquor was drawn off by the insertion of a glass tube with cotton plug to the bottom of the flask and the application of suction to the tube. There was left in the flask a beautiful mass of white crystals which melted at 22.5–26°. The crystals were three times subjected to the crystallization process outlined above except that only one-half volume of acetone–ether mixture was used and the mixture of crystals and mother liquor was kept in an ice-salt mixture for one-half hour before removal of the mother liquor. The crystals still melted over the same range. They were allowed to melt and the liquid subjected to distillation at 5 mm.; the temperature rose at once to 150" and practically all of the sample distilled between 150 to 151°.

Titration. Subs., 0.2174, 0.2028: 21.38, 19.98 cc. of 0.1 N alkali (phenolphthalein). Calcd. for C_4-saccharinic acid lactone: 21.28, 19.84 cc.

The **Phenylhydrazide.**—The melting point of this compound was found to be higher than that reported by Nef (99°), and by Glatffeld and Miller (100–101°).

Apparently the pure phenylhydrazide is not always formed when the usual procedure for hydrazide formation (addition of phenylhydrazine to the lactone in ethyl acetate solution followed by short heating and letting the reaction mixture stand for several days) is followed. A product, recrystallized from ethyl acetate until the melting point no longer rose, of m. p. 105 5° was obtained by this usual procedure. Analysis of this product showed it not to be the pure phenylhydrazide (calcd. for $C_{11}H_{14}O_3N_2$: N, 13.33; found: 14.64, 14.63, 14.43). The true phenylhydrazide was obtained, however, when a mixture of 12 g. of lactone (b. p. 150–155" at 6 mm.) and 13 g. of phenylhydrazine, without solvent, was heated for two hours on the boiling water-bath and then allowed to stand for forty-eight hours; yield 13 g. Three recrystallizations from ethyl acetate yielded 7 g. of lustrous white plates with a constant melting point of 109°.

Anal. Subs., 0.1025, 0.1053: N_2, 12.25 cc. (24°, 738 mm.), 12.4 cc. (23°, 748 mm.). Calcd. for $C_{10}H_{14}N_2O_3$: N, 13.33. Found: 13.04, 13.08.

3-Hydroxyisocrotonic Acid Lactone

This lactone does not seem to have been studied extensively. Lespieau[7] prepared it by heating 2,3-dichlorobutyric acid and also[8] by the treatment of 2,3-dichlorobutyric acid with sodium carbonate. Lespieau reports the boiling point as 95–96' at 13 mm. and melting point as +4°. As mentioned above, Carré[4] reports that it was formed in his reduced pressure distillation of 2,3-dihydroxybutyric acid.

This unsaturated lactone appeared in all of our distillations of the crude 2,3-dihydroxybutyric acid. We confirmed the observation of Carré that the unsaturated lactone is not formed in the distillations of the pure 2,3-acid lactone; this latter lactone is perfectly stable once it is formed and distils at 2–4 mm. with no apparent decomposition. The unsaturated lactone must therefore be formed at some stage before the 2,3-acid has changed to its lactone.

Purification of Lactone.—About 150 g. of Fraction I (see above) was twice fractionated and the lower fractions (one-tenth of whole) discarded both times. The portion of b. p. 70–75° at 2–3 mm. pressure was cooled in a freezing mixture until about three-fourth of it was solid. The solid was separated by rapid suction filtration, melted, again partly frozen, the solid separated, etc. This process was carried out seven times; 10 g. of material which contained only 0.04% chlorine was obtained. It melted at +5°.

Anal. Subs., 0.2071, 0.1716: H_2O, 0.0925, 0.0750; CO_2, 0.3232, 0.3592. Calcd. for $C_4H_4O_2$: H, 4.79; C, 57.13. Found: H, 5.00, 4.89; C, 56.95, 57.11.

Attempts to titrate the purified lactone indicated that it contained no free acid; the first drop of 0.1 N alkali colored the solution (phenolphthalein). The results of ti-

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[7] Lespieau, *Compt. rend.*, 138, 1050 (1904); *Bull. soc. chim.*, [3] 33, 466 (1905).

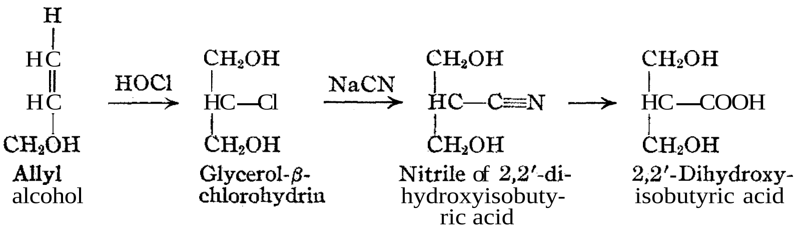
[8] Lespieau, *Compt rend.*, **141, 43** (1905); *Bull. soc. chim.*, [4] 1, 1113 (1907).

trations carried out in the usual manner (boiling out carbon dioxide after addition of excess acid) gave varying results; apparently the lactone undergoes some change in structure during titration in the hot solution.

Compound Formed **with Phenylhydrazine.**—The lactone reacts with phenylhydrazine but the yield of product is small if a solvent is used. A mixture of 14.5 g. of lactone (b. p. 75–77° at 3 4 mm.) and 22 g. of phenylhydrazine, heated for three hours on the water-bath, however, yielded (transferred with ether) 18 g. of crude product which, after repeated recrystallization from ethyl acetate, melted at 183°. Crystals from other preparations also melted at the same point. The substance was very stable (one sample did not show signs of decomposition in eighteen months) and seemed to be a characteristic derivative of 3-hydroxyisocrotonic acid. Analysis showed that it was not the simple phenylhydrazide, however; figures for carbon, hydrogen and nitrogen were all high (calcd. for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.57. Found: *C*, 68.16, 68.24; H, 6.79, 6.79; N, 17.44, 17.24).

Attempted Preparation of 2,2′-Dihydroxyisobutyric Acid

This acid has not yet been reported in the literature. As it is one of the C_4-saccharinic acids according to our definition,[9] its preparation was attempted by the process indicated below.



The experimental procedures followed for preparation and purification were exact duplicates of those outlined above for the preparation and purification of 2,3-dihydroxybutyric lactone except that the β- instead of the a-chlorohydrin of glycerol was used. Again two products were formed, a low and a high boiling product. The former was shown to be 3-hydroxyisocrotonic acid and the latter was at first thought to be the desired 2,2′-iso acid[10] mainly because of the fact that reduction of the product yielded some isobutyric acid. Further study, however, showed that if the 2,2′-iso acid was present at all, it was much contaminated by the 2,3-acid lactone. This raised the question as to the source of the 2,3-acid lactone. The most obvious explanation of the presence of the latter was that the β-chlorohydrin that had been used in the preparation work was contaminated with α-chlorohydrin. A search of the literature showed that the β-glycerol chlorohydrin prepared from allyl alcohol contains a large quantity of the α-chlorohydrin.[11] The pure α- and β-glycerol chlorohydrins

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[9] Glattfeld and Sherman, THIS JOURNAL, 47, 1742 (1925).

[10] Spieth, University of Chicago, Abstracts of Theses, Science Series, IV, 165 (1925)

[11] Smith, *Z. physik. Chem.*, 92,727 (1918); 94, 723 (1920).

were therefore prepared and these then used in the preparation procedures. Both yielded the same products, 3-hydroxyisocrotonic and 2,3-dihydroxybutyric acid lactones. This shows that the reaction between the chlorohydrins and sodium cyanide is not *a* simple double decomposition reaction. A possible explanation is that both chlorohydrins under the experimental conditions used give the same glycidol, which then adds hydrogen cyanide to form the nitrile of the 2,3-acid practically exclusively.

Pure a- and β-Glycerol Chlorohydrins.—It has long been known[12] that the α-chlorohydrin of glycerol forms a stable condensation product (isopropylidene-a-chlorohydrin) with acetone. It is also known[13] that if the two hydroxyl groups necessary for condensation with acetone are in the 1,3 (as in β-chlorohydrin of glycerol) and not the 1,2 position (as in a-chlorohydrin of glycerol), the condensation proceeds with great difficulty if at all. These facts were taken advantage of in effecting the separation of the *a*- from the β-chlorohydrin of glycerol and the purification of the two compounds. The mixture of chlorohydrins obtained by the addition of hypochlorous acid to allyl alcohol was repeatedly condensed with acetone until no more condensation occurred. The purified condensation product then yielded the pure a-chlorohydrin and the uncondensed residue the pure β-chlorohydrin of glycerol as shown below.

The only property known to us by means of which the purity of given samples of *a*- and @-chlorohydrins of glycerol can be determined is their reaction rate with alkali. In dilute aqueous solution, alkali decomposes both into glycidol but at remarkably different rates Smith[14] showed that the a-isomer is 50% decomposed in much less than one-tenth the time it takes the β-isomer to become 50% decomposed. He used the bimolecular reaction rate equation in his calculations and found that with the pure a-isomer the equation gave a fairly good "constant" but that when mixtures of a- and @-isomers were used the "constant" dropped rapidly with time. He showed, however. that the "constants" at 50% decomposition (K 50) are very good measures of purity and that K 50 for the pure a-isomer at 25° in 0.015 *N* barium hydroxide solution was 11.1 and that for the pure β-isomer about 0.81. For the work in hand it was not necessary to use 100% pure a- and @-isomers. No difficulty was experienced in obtaining samples of the two isomers that were at least 90% pure.

A mixture of 300 *g*. (K 50 = 5.26; % Cl = 36.54) of the chlorohydriu made by the method of Reed and Hurst (allyl alcohol + HOCl),[15] 200 g. of anhydrous sodium sulfate, 1200 cc. of acetone and 18 cc. of concd. sulfuric acid was introduced into a bottle which was then corked and placed in a "revolving" machine. This machine kept the sodium sulfate at all times suspended in the liquid. The machine was operated for twenty-two hours continuously, at the end of which time 75 g. of lead carbonate and 50 g. of sodium carbonate were added to the reaction mixture, the bottle put back on the machine and again rotated for six hours. The bottle was then opened, the liquid decanted and the salts washed by decantation with acetone. The acetone was removed by distillation at ordinary pressure with the water-bath finally at 100°. The residue was thoroughly extracted three or four times with low-boiling ligroin. The combined extracts were dried over sodium sulfate, fractionated at ordinary pressure, and the fraction of boiling range 145–165° saved. This was practically pure isopropylidene-a-chlorohydrin

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[12] Fischer and Pfähler, *Ber.*, 53, 1606 (1920).

[13] Speier, *ibid.*, 28,2531 (1895); Irvine, Macdonald and Soutar, J. *Chem. Soc.*, **107,** 337 (1915).

[14] Smith, *Z. physik. Chem.*, 92,717–740 (1918); 94,691–738 (1920).

[15] Reed and Hurst, J. *Chem. Soc.*, 121,989 (1922).

(209 g.). The residues insoluble in ligroin from two such experiments were now combined and put through exactly the same condensation process again; the quantities of reagents noted above were used. Again a quantity of isopropylidene-a-chlorohydrin (70 g.) and a chlorohydrin residue insoluble in ligroin were obtained. The residue was again condensed as before but proportionately smaller quantities of reagents now used. The process was repeated twice more; quantities of isopropylidene-a-chlorohydrin obtained were 60 g. and 33 g. The final crude residue weighed about 90 g. It was added to corresponding material from other runs and then fractionated with oil pump and oil-bath. Usually three or four fractionations were sufficient to give a colorless product whose boiling range was 110–114° at 3–4 mm. The yield of this purified product was about 10–15%; K 50, 0.70–0.80 and % Cl, 31.30–31.80. The combined isopropylidene-a-chlorohydrin weighed 372 g., a 45% yield. Almost half of the chlorohydrin started with is unavoidably lost in the many experimental manipulations necessary in this process.

The experiment outlined above was repeated many times. The isopropylidene-α-chlorohydrin thus prepared was twice fractionated at ordinary pressure and samples then hydrolyzed by addition of three parts of dilute sulfuric acid (0.1 to 0.15 *N*) to one part of product. The mixture was placed on the revolving machine overnight, during which time the oily condensation product completely dissolved. The sulfuric acid was quantitatively removed by means of barium hydroxide solution (an excess of base must be avoided). The reaction mixture (slightly acid) was then subjected to distillation (barium sulfate not removed) from a water-bath and with a water pump until no more distillate came over, then fractionated with oil pump and oil-bath. The product thus obtained usually boiled at about 111–114° at 7–8 mm. and had K 50 about 9 and percentage of Cl, 31.5–31.8. Repeated fractionation gave a product which was perfectly colorless and which possessed a K 50 of between 9.5 and 10.00.

Phenylurethans of a- and β-Glycerolchlorohydrins.—Rider and Hill[16] have recently prepared these compounds and report the melting points as 128–129° for the α-isomer and 133" for the 8-isomer. We prepared them from our purified products according to the directions of Rider and Hill with results as follows: 17 g. of each chlorohydrin with 13 g. of phenyl isocyanate gave 2.5 g. of crude product in the case of the a-isomer and 3 g. in the case of the 8-isomer. Recrystallization from acetone–high boiling ligroin (1 to 10) yielded finally, in the case of the a-isomer, 0.6 g. of m. p. 127–129, and, in the case of the β-isomer, 2 g. of m. p. 133–136°.

Reaction of the Pure Chlorohydrins with Cyanide.—The highly purified a- and 0-glycerol chlorohydrins prepared as indicated above were each now treated with sodium cyanide and the reaction mixtures put through the synthesis indicated above for the preparation of the 2,3-acid lactone. In each case 55 g. of the chlorohydrin was used and the corresponding quantities of reagents as used in the previous work. In the case of the 0-isomer 18 g. (35%) of product of boiling range 148–150° at 4 mm. was obtained. A sample of this titrated correctly for a dihydroxybutyric lactone (subs., 0.3274: calcd. 31.87 cc. of 0.1 N alkali; found, 31.20). It solidified when cooled with carbon dioxide, could be recrystallized from acetone–ether and melted at 22.5–25.5°. These data show that it was the lactone of 2,3-dihydroxybutyric acid. In the case of the a-isomer, 20 g of product (39%) of boiling range 146–149° at 4 mm. was obtained. It also solidified when sufficiently cooled, could be recrystallized from acetone–ether, after which it melted at 22.5–26". It titrated for a dihydroxybutyric lactone (subs., 0.2174: calcd., 21.31 cc. of 0.1 N alkali; found, 21.28 cc.). These data offer convincing evidence that the products in the two cases were identical and that both were samples of 2,3 dihydroxybutyric lactone.

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[16] Rider and Hill, THIS JOURNAL, 52,1525 (1930).

Summary

Directions are given for the preparation in about 28% yield of 2,3-dihydroxybutyric lactone from glycerol monochlorohydrin. The lactone has been obtained in crystalline form of melting range 22–26°. The phenylhydrazide melts at 109°.

A valuable by-product, 3-hydroxyisocrotonic lactone, was isolated in 23% yield. The compound which this lactone forms with phenylhydrazine (not the simple phenylhydrazide) melts at 183°.

2,2'-Dihydroxyisobutyric acid cannot be prepared by treatment of glycerol-β-chlorohydrin with sodium cyanide followed by hydrolysis. The product is 2,3-dihydroxybutyric lactone whether the α- or the β-chlorohydrin of glycerol is used in the synthesis.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES. VI. THE MECHANISM OF THE PHASE TEST

BY CATHERINE C. STEELE[1]

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The essential change in allomerization and phase test saponification in the derivatives of chlorophyll *a* is the dehydrogenation of the grouping —CHOHCO— to —COCO—, and it has now been shown that the two hydrogen atoms are removed by oxygen from the air.[2] If the phase test saponification of methyl phaeophorbide a or chlorin *e* trimethyl ester is carried out in a modified Warburg apparatus[3] the amount of oxygen absorbed can be measured. Since the products are the "unstable chlorins," the oxidation is also shown to take place in the alkaline medium, and not in the subsequent acidification nor in the conversion of the chlorins to the phaeopurpurins.

The inherent difference between Willstätter's methods of "phase test" and "hot quick" saponification, whereby he obtained either phytochlorin *g* or chlorin *e* from phaeophorbide a, is now apparent.[4] Phase test saponification is an atmospheric oxidation process: with phaeophorbide a it also opens a ring but effects only partial saponification of the methyl group,

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[1] Commonwealth Fund Fellow at Radcliffe College.

[2] A preliminary statement of these results appeared in a Communication to the Editor, THIS JOURNAL, 53, 1615 (1931), and the allomerization experiments are discussed in detail in Paper V, *ibid.*, 53, 2382 (1931). In this present paper are discussed the corresponding experiments in the phase test.

[3] Hyde and Scherp, *ibid.*, 52,3359 (1930).

[4] Willstätter and Stoll, "Investigations on Chlorophyll," translated by Schertz and Merz, Science Printing Co., 1928, p. 263.

since the product is a mixture of unstable chlorins which change to the two phaeopurpurins, one of which (7) still retains a methoxyl group.[5] Hot quick saponification of phaeophorbide *a* is an hydrolysis (or complete demethylation) process, and it is now obvious that the reason why the methyl alcoholic solution must be kept boiling during the entire process is that the alcoholic vapors above the solution eliminate practically all the air from the reaction, and hence hydrolysis is accomplished before the material has had a chance to oxidize. Conant and Moyer[6] found that in the phase test on phaeophorbide, the formation of chlorin e can be suppressed completely by substituting ethyl or n-propyl alcohol for methyl alcohol in the solution of potassium hydroxide, or by keeping the reaction mixture at $-10°$. In the latter case, hydrolysis is inhibited by the low temperature, and the oxidation has time to go to completion. In the former case it is well known that concentrated ethyl and n-propyl alcoholic alkali solutions absorb oxygen readily with the possible formation of peroxides, and therefore accelerate the oxidation in the phase test. This is borne out by the fact that, in the measurement of the oxygen absorbed in the phase test, it was found impossible to obtain an initial equilibrium in the Warburg apparatus by the use of propyl alcoholic alkali, due to its continued absorption of oxygen (see experimental portion of this paper).

Previously, several attempts to inhibit the phase test by using an atmosphere of nitrogen were made, but these were unsuccessful, owing to the minute quantity of oxygen necessary for the reaction (0.008 millimole = 0.16 cc. for 5 mg. of methyl phaeophorbide *a*). The use of oxygen absorbers was then tried; here it was found possible on a small scale to treat methyl phaeophorbide a with 25% methyl alcoholic potash in an atmosphere of nitrogen and in the presence of sodium stannite, and obtain alkali-soluble products which on methylation with diazomethane gave chlorin *e* trimethyl ester and methyl phaeophorbide a and no phaeopurpurin 7. Similarly chlorin *e* trimethyl ester gave an alkali-soluble product which on methylation gave back chlorin *e* trimethyl ester. The hydrolyzed product was apparently a monomethyl chlorin *e*, as it contained one methoxyl group.

In connection with this work, the difference in the time and optimum temperatures for the phase test on chlorin e ester and phaeophorbide *a* was noted, and led to a comparison of the rate of hydrolysis of several esters under phase test conditions (including both those which do and those which do not undergo the phase test). While these results cannot be entirely explained, we append in the following table a summary of the results obtained; the figures represent averages of several runs and are probably significant within 20%.

The usual procedure was to dissolve 5 mg. of ester in about 0.5 cc. of

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[5] Paper V, THIS JOURNAL, 53,2382 (1931).

[6] Paper III, *ibid.*, 52,3014 (1930).

pyridine and transfer it to 15 cc. of ether in a 50-cc. Erlenmeyer flask. When the solution had attained the required temperature, 1.5 cc. of 25% methyl alcoholic potash was added and the mixture stirred mechanically. It was then shaken up with water and ether, and the material in the alkaline layer transferred to fresh ether (and methylated, where the products were the unstable chlorins). The amounts of hydrolyzed and unhydrolyzed material were determined in a Zeiss comparison spectroscope. Where the two solutions were of the same material (*e. g.*, porphyrins) the ether solutions were compared directly. It was found to be immaterial whether the hydrolyzed solution was remethylated or not. Where the solutions were of different compounds, the amount of substance in mg. in each was obtained by comparison with a standard solution of the material in question.

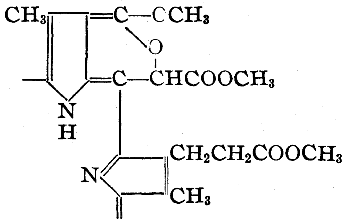
TABLE I

COMPARATIVE RATES OF HYDROLYSIS UNDER PHASE TEST CONDITIONS

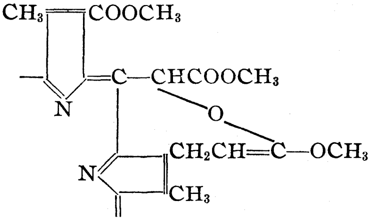
	Percentage hydrolyzed in 5 min. at −8°	30 min. at −8°	15 min. at 20°	Products
Pyrroporphyrin monomethyl ester		0	50 56	Pyrroporphyrin
Phylloporphyrin monomethyl ester		0	52 43	Phylloporphyrin
Rhodoporphyrin dimethyl ester		0	57 52	Rhodoporphyrin (spectrum)
Chlorin *a* trimethyl ester		20	100	Chlorin *a* (spectrum)
Chlorin *e* trimethyl ester		28	100	Dimethyl phaeopurpurin 7 after methylation
Dehydrophaeophorbide *a* methyl ester	87	100	100	Dimethyl phaeopurpurin 7 after methylation
Phaeophorbide *a*	51	100	100	Dimethyl phaeopurpurin 7 after methylation
Phaeophorbide *a* monomethyl ester	28	100	100	Dimethyl phaeopurpurin 7 after methylation
Phaeopurpurin 7 dimethyl ester	100	100	100	Phaeopurpurin 7 (spectrum)
Phaeopurpurin 18 monomethyl ester	100	100	100	Chlorin *a*

Pyrroporphyrin and phylloporphyrin esters contain only the propionic ester group; this apparently cannot be hydrolyzed under the phase test conditions at −8° for thirty minutes. Rhodoporphyrin ester, which has in addition a methyl group on the β-carboxyl, hydrolyzes at about the same rate. Hydrolysis under phase test conditions for five minutes at −8° of methyl phaeophorbide a, phaeophorbide a, and methyl dehydrophaeophorbide a gave the following percentages of dimethyl phaeopurpurin 7 after methylation (this represents the total alkali-soluble material): 28, 51 and 87%. Demethylation and oxidation, oxidation without demethylation, and demethylation alone are the corresponding reactions involved. These results show that the group which gives alkali solubility is a grouping which is more easily hydrolyzed than the ester groups of the porphyrins. If one considered only these results, the conclusion would be that hydrolysis of the propionic ester group is not involved in the phase test; but we know that the propionic ester group is hydrolyzed in the case of methyl phaeophorbide because the product, phaeopurpurin 7, is a monomethyl compound with the methyl group on the carboxyl directly attached to a pyrrole ring. (The proof of this follows from its pyrolysis to monomethyl chlorin f and is supported by the fact that phaeophorbide *a* also yields phaeopurpurin 7.) These results indicate that the hydrolysis of the propionic ester is not the first result of the action of alkali: it is more likely that the anhydride ring (or a lactam ring) in phaeophorbide a first opens.[5] If this is the case, no comparison can be drawn between the hydrolysis rates of the propionic ester in a neutral porphyrin and that in a compound in which a potentially acidic group has already been converted into a salt.

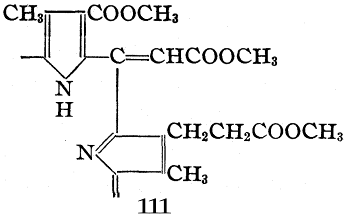
Hydrolyses of phylloporphyrin ester and methyl phaeophorbide *a* were carried out in homogeneous methyl alcoholic solution, using the same proportion of methyl alcoholic potassium hydroxide as in the phase test, and the phylloporphyrin ester was completely unhydrolyzed after thirty minutes at −8°, while the methyl phaeophorbide gave *25.5%* (compare 28% in ether) of hydrolyzed material in five minutes. The presence of a two-phase system consisting of the ether and the alcoholic layer of the potassium salt of phaeophorbide is therefore not responsible for the differences shown in Table I between the porphyrins and the phaeophorbides. The following formulas are suggested as possibilities for the trimethyl ester of chlorin *e*



I



II



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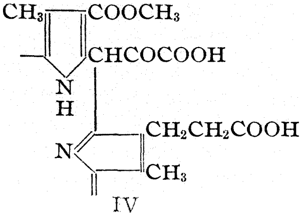
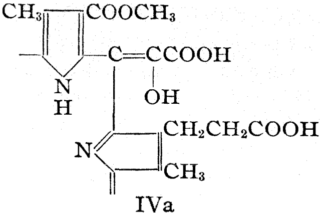
Formula II contains a more labile form for the propionic ester grouping than I or III, which require the peculiarly rapid hydrolysis of the propionic ester group as discussed above in the case of the phaeophorbide. The extraordinary rapidity with which dimethyl phaeopurpurin 7, methyl phaeopurpurin 7 and methyl phaeopurpurin 18 hydrolyze under phase test conditions (five minutes at −8°, 100% alkali soluble) is surprising. The formula for phaeopurpurin 7 must contain the grouping (IV), or the corresponding enol modification (IVa) and hydrolysis of the trimethyl ester (dimethyl phaeopurpurin 7) must again involve hydrolysis of a propionic ester group. That there is some difference in the ease of hydrolysis of the two ester groups was shown by stirring dimethyl phaeopurpurin 7 with phase test alkali at −8° for five minutes; the resulting product had a methoxyl content of 7% (calcd. for 1 (OCH_3): 4.95; for 2 (OCH_3): 9.65). It is interesting to note that although dimethyl phaeopurpurin 7 hydrolyzes under phase test conditions to phaeopurpurin 7, long standing or shaking of the dimethyl ester with phase test alkali converts it back to the unstable chlorins.



IV



IVa

The author wishes to acknowledge her indebtedness to Professor J. B. Conant for suggesting this problem.

Experimental

Absorption of Oxygen in the Phase Test.—The oxygen absorption during the phase test was demonstrated by using a modified Warburg apparatus. The use of propyl alcoholic alkali was abandoned after it was found impossible with equal volumes present to equalize the pressures in the two arms of the apparatus, due to an increasing absorption of oxygen by the alkali alone. The improved yields of phase test products by the use of propyl alcoholic alkali is therefore due to the latter acting as an oxygen absorber.[7] Equilibrium was easily obtained by using methyl alcoholic potassium hydroxide and carbon dioxide-free air.

(a) Methyl Phaeophorbide *a*.—Twenty-three cc. of 25% methyl alcoholic potash was placed in one of the bottles of the absorption apparatus, and a glass bulb having a long capillary end and containing methyl phaeophorbide a (509 mg. = 0.008 millimole) was carefully inserted in the alkali. The other bottle contained a corresponding amount of alkali to equalize the volumes. The apparatus was placed in a water-bath at 20° and shaken for ten or fifteen minutes until a constant difference in the pressure readings was obtained. The apparatus was then removed from the bath, the bulb broken by a quick shake, the apparatus replaced, and shaken continuously. Pressure readings were recorded during five-minute intervals for the first hour, subsequently at longer intervals. The number of moles of gas absorbed was calculated from a previously determined factor (1 cc. of manometer liquid = 0.0017 millimole of gas). The course of the reaction is indicated by the following figures, which give the millimoles of gas absorbed at different times: ten minutes, 0.0027; thirty minutes, 0.0046; one hour, 0.0086; one and one-half hours, 0.0102; two hours, 0.0117; two and one-half hours, 0.0129; three hours, 0.0137.

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[7] Paper III, THIS JOURNAL, 52, 3016 (1930).

That the reaction proceeds at a progressively diminishing rate is shown by the following values in 10^{-6} mole per hour for the amount of gas absorbed during successive thirty-minute intervals: 9 2, 8 0, 3 2, 3.0, 2.4, 1.6. The maximum for the rapid absorption of oxygen is in eighty-seven minutes when 0.01 millimole of oxygen has been absorbed, this corresponds to the absorption of one mole of oxygen per mole of phaeophorbide with the formation of hydrogen peroxide.

(b) Chlorin *e* Trimethyl Ester.—In an experiment with 5.92 mg. of chlorin *e* ester (=0.01 millimole), the amount of gas in millimoles absorbed at different times was as follows: ten minutes, 0.0027; thirty minutes, 0.0047; one hour, 0.0062; one and one-half hours, 0.0068; two hours, 0.0071. The rates in 10^{-6} mole per hour for the amount of gas absorbed during successive thirty-minute intervals are therefore 9.2, 3.0, 1.2, 0.6.

In a second experiment with 4 mg. of chlorin *e* ester (=0.0067 millimole) the amount of gas in millimoles absorbed was 0.0014 in ten minutes; in thirty minutes, 0.0038; in one hour, 0 0054; in one and one-half hours, 0.0065; in two hours, 0.0073. The rates in 10^{-6} millimole per hour for absorption during thirty-minute intervals is therefore 7.6, 3.2, 2.2, 1.6. The limit to the amount of oxygen absorbed is clearly one mole of oxygen per mole of chlorin *e* trimethyl ester.

In both (a) and (b) the products were the unstable chlorins, which on standing gave mixtures of phaeopurpurins 7 and 18, or on methylation with diazomethane gave dimethyl phaeopurpurin 7.

In a control experiment, phaeopurpurin 7 was used in the bulb, and no absorption was observed during 1 hour's shaking with the alkali.

Inhibition of the Phase Test

(i) Methyl Phaeophorbide a.—Twenty cc. of 25% methyl alcoholic potassium hydroxide and 1 g. of stannous chloride were placed in the long arm of a Thunberg tube, and 20 mg. of methyl phaeophorbide a was placed in the short arm. The tube was alternately evacuated and filled with nitrogen about eight times, then shaken for seven minutes. The solution was deep green in color. Water was added immediately the tube was opened, and the alkaline solution, on being shaken with ether, retained all the material. It was transferred by acidification to fresh ether, and washed with water. In one experiment the solution was methylated with diazomethane; no change in color was observed, and the product was a mixture of chlorin *e* ester (extracted with 8% acid) and of methyl phaeophorbide *a*, acid number 18. These were identified by spectrum in acid and ether; there was twice as much chlorin *e* as phaeophorbide a, and no phaeopurpurin 7 was obtained.

(ii) Chlorin *e* Trimethyl Ester.—In similar experiments on chlorin *e* ester, most of the material was alkali-soluble after fifteen minutes' shaking; the alkali solution was yellow-green. On transference to ether, methylation with diazomethane gave back the trimethyl ester of chlorin *e*, identified by acid number and spectrum in acid and ether. No phaeopurpurin 7 was obtained. Fractionation of the unmethylated solution resulted in the extraction of all the material with 5 to 6% hydrochloric acid; it had the spectrum in acid and ether of chlorin *e* but contained one methoxyl group (OCH_3: found, 5.76; calcd., 4.95).

Action of Phase Test Alkali on Esters

A few typical experiments are given below (see theoretical section of this paper for table of all the results).

Phylloporphyrin Ester.—Five mg. of ester was dissolved in pyridine, transferred to 15 cc. of ether, and 1.5 cc. of *25%* methyl alcoholic potassium hydroxide added. The mixture was stirred mechanically for fifteen minutes at 20°; then, after addition of water and ether, the alkaline layer was separated and acidified in the presence of fresh ether. The two ether solutions were compared in the spectroscope and gave the ratio hydrolyzed:unhydrolyzed material:: 19.6:20. The volumes of the two solutions were measured and the ratio became 19.6×95 cc.:20×87 cc. The percentage of hydrolyzed material is therefore 51.7%. The hydrolyzed fraction was methylated with diazomethane, washed and dried. On comparing it again with the unhydrolyzed ester the ratio was 20×46 cc.:19.2×50 cc., and the percentage hydrolyzed was 49.6.

Methyl Phaeophorbide a.—(i) Five mg. of ester dissolved in pyridine and transferred to ether was cooled to −8° in an ice–salt bath and 1.5 cc. of methyl alcoholic potassium hydroxide added. The mixture was stirred for five minutes, then water and ether were added. The alkaline layer was acidified under fresh ether and immediately methylated with diazomethane to convert the unstable chlorins to dimethyl phaeopurpurin 7. This was compared with a standard solution of dimethyl phaeopurpurin 7 (50 mg. per liter) and the amount determined was 1.11 mg. The original ether solution containing the unhydrolyzed material was compared with a standard solution of methyl phaeophorbide a. The amount obtained was 2.8 mg.; hence the percentage of hydrolyzed material was 28%.

(ii) Five mg. of ester in pyridine was added to 15 cc. of methyl alcohol in a 50-cc. flask, the solution was cooled to −8° and stirred for five minutes with 1.5 cc. of 25% methyl alcoholic potassium hydroxide. Water and ether were added and the alkaline layer was washed several times with ether, then acidified under fresh ether. This was methylated, and was found to contain 1.2 mg. of dimethyl phaeopurpurin 7. The percentage of unhydrolyzed material was 25.5.

Phaeophorbide a.—Five mg. of phaeophorbide a in pyridine and ether was stirred for five minutes at −8° with 1.5 cc. of 25% methyl alcoholic potassium hydroxide. Water and ether were added, the alkaline layer rapidly acidified under fresh ether, and the product methylated. A fractionation with 14% hydrochloric acid removed the dimethyl phaeopurpurin 7 and this was compared with a standard solution. The amount found was 2.4 mg. The residue from the fractionation, which consisted of unphased phaeophorbide, was washed, dried and compared with a standard solution of methyl phaeophorbide a. The amount was 2.3 mg.; hence the percentage of phaeophorbide phased was 51.

Methyl Dehydrophaeophorbide a.—Five mg. in pyridine–ether was stirred with alkali for five minutes at −8°. The alkaline layer was acidified under fresh ether and the solution methylated. It was compared with a standard solution of dimethyl phaeopurpurin 7, and contained 1.2 mg. The original ether, containing unhydrolyzed material, was compared with a standard solution of methyl dehydrophaeophorbide a (15 mg. per liter). It contained 0.6 mg.; hence the percentage hydrolysis was 87%.

Summary

1. The phase test on chlorophyll derivatives involves oxidation by atmospheric oxygen. The amount absorbed was measured in the case of methyl phaeophorbide *a* and chlorin e trimethyl ester.

2. This oxidation can be prevented by the use of sodium stannite with an atmosphere of nitrogen.

3. A comparison of the rates of hydrolysis under "phase test" conditions of various esters in the "*a*" series is given.

CAMBRIDGE. MASSACHUSETTS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS. IX. THE ADDITION OF HYPOCHLOROUS AND HYPOBROMOUS ACIDS TO VINYLACRYLIC ACID

BY IRVING E. MUSKAT AND LESLIE HUDSON

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In a recent paper Muskat and Northrup[1] have developed a theory to interpret the addition reactions of conjugated systems. This theory is based on the supposition that conjugated systems differ from non-conjugated systems only in so far as the former may exhibit 1,3-rearrangement, while the latter cannot exhibit this phenomenon. It further assumes that the addition of both components of the addendum to an ethylenic double bond does not occur simultaneously but rather, as has been suggested by Stieglitz,[2] that the essential feature is the attraction of the positive substituting group to the negative carbon valences irrespective of complete saturation. By the application of this theory these authors have shown that in the halogenation of vinylacrylic acid a 1,3-rearrangement is not possible and consequently only 3,4-halogenation can occur. This is in accord with the work of Muskat, Becker and Lowenstein,[3,4] who have shown that in the chlorination and bromination of vinylacrylic acid only 3,4-addition products are formed. As a corollary to the mechanism proposed by these authors, the hypohalous acids should add to vinylacrylic acid in exactly the same manner as do the halogens. The work reported in this paper was undertaken to test this point and contains the results of an investigation on the addition of hypochlorous and hypobromous acids to vinylacrylic acid.

Thiele[5] proved that vinylacrylic acid is reduced, by means of sodium amalgam in alkaline medium, in the 1,4-positions, and not in the 1,2-positions as claimed by Doebner.[6] Ingold and Burton[7] have shown that if vinylacrylic acid is reduced by means of sodium amalgam in acid medium, then 18% of the vinylacrylic acid is reduced in the 1,2-positions while the remainder is reduced in the 1,4-positions. Muskat and Knapp[8] have recently shown that vinylacrylic acid is hydrogenated catalytically in the 3,4-positions. These last investigators have proposed a theory to interpret these varying reduction reactions of conjugated systems.

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[1] Muskat and Northrup, THIS JOURNAL, 52, 4043 (1930).

[2] Stieglitz, *ibid.*, 44, 1304 (1922).

[3] Muskat, Becker and Lowenstein, *ibid.*, 52, 326 (1930).

[4] Muskat and Becker, *ibid.*, 52, 812 (1930).

[5] Thiele, *Ber.*, 35, 2320 (1902).

[6] Doebner, *ibid.*, 35, 1136 (1902).

[7] Ingold and Burton, *J. Chem. Soc.*, 2022 (1929).

[8] Muskat and Knapp, *Ber.*, 64, 779 (1931).

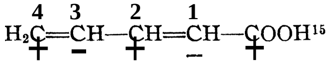
Kohler and Butler,[9] while studying the relative ease of 1,4- and 1,6-addition, showed that sodium malonic ester combines with the esters of vinylacrylic and sorbic acids to give 1,6-addition products, while phenylmagnesium bromide reacts with the same esters to give first the corresponding ketones, which react further to give 1,4-addition products.

Muskat, Becker and Lowenstein[10] have studied the chlorination and bromination of vinylacrylic acid and found that both chlorine and bromine are absorbed in the 3,4-positions. They also found that 3-chloro- and 3-bromovinylacrylic acids absorb chlorine and bromine, respectively, in the 3,4-positions. These are the only addition reactions of vinylacrylic acid that have been reported in the literature.

Mokiewsky[11] was the first investigator to study the addition of hypohalous acids to conjugated systems.[12] He prepared the dichlorohydrin and dibromohydrin of isoprene but did not determine the structure of these compounds. Muskat and Grimsley[13] have made a detailed study of the addition of hypochlorous and hypobromous acids to phenylbutadiene. They have found that these acids are added to phenylbutadiene in the 3,4-positions to give 3-hydroxy-4-chloro-1-phenylbutadiene and 3-hydroxy-4-bromo-1-phenylbutadiene, respectively. They also prepared the dichlorohydrin and dibromohydrin of phenylbutadiene.

Braun[14] recently attempted to add hypochlorous acid to vinylacrylic acid and reported that "vinylacrylic acid is easily oxidizable with hypochlorous acid." However, he did not isolate any products. In our investigation we had no difficulty in preparing and isolating crystalline monohalogenhydrins and dihalogenhydrins of vinylacrylic acid.

The addition of hypochlorous acid to vinylacrylic acid was first studied. It was found that vinylacrylic acid very readily absorbs one molecule of hypochlorous acid to form a monochlorohydrin, m. p. 71–74°. The structure of the monochlorohydrin was determined by ozonization. Six monochlorohydrins are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the relative positions of the Cl and OH groups.



$$\overset{4}{\underset{+}{H_2C}}{=}\overset{3}{\underset{-}{CH}}{-}\overset{2}{\underset{+}{CH}}{=}\overset{1}{\underset{-}{CH}}{-}\underset{+}{COOH}^{15}$$

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[9] Kohler and Butler, THIS JOURNAL, 48, 1036 (1926).

[10] Muskat, Becker and Lowenstein, *ibid.*, 52, 326, 812 (1930); see also Farmer and Healy, J. *Chem. Soc.*, 130, 1060 (1927)

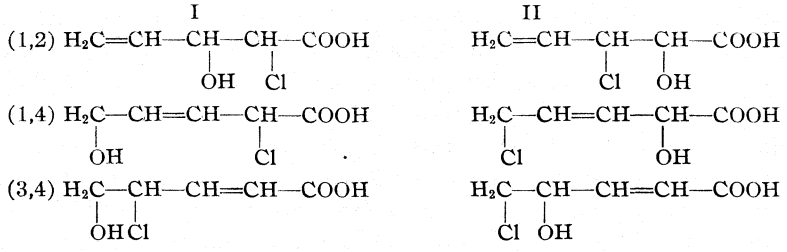
[11] Mokiewsky, J. *Russ. Phys.-Chem. Soc.*, 30,885 *(1898).*

[12] We refer here to conjugated systems of carbon atoms C=C—C=C but not to those containing the carbonyl group in conjugation with an ethylene linkage, such as C=C—C=O.

[13] Muskat and Grimsley, THIS JOURNAL, 52,1574 (1930).

[14] Braun, *ibid.*, 52, 3188 (1930).

[15] The plus and minus signs do not imply a complete transfer of an electron from



I

(1,2) $H_2C{=}CH{-}\underset{OH}{CH}{-}\underset{Cl}{CH}{-}COOH$

(1,4) $\underset{OH}{H_2C}{-}CH{=}CH{-}\underset{Cl}{CH}{-}COOH$

(3,4) $\underset{OH}{H_2C}{-}\underset{Cl}{CH}{-}CH{=}CH{-}COOH$

II

$H_2C{=}CH{-}\underset{Cl}{CH}{-}\underset{OH}{CH}{-}COOH$

$\underset{Cl}{H_2C}{-}CH{=}CH{-}\underset{OH}{CH}{-}COOH$

$\underset{Cl}{H_2C}{-}\underset{OH}{CH}{-}CH{=}CH{-}COOH$

However, since in all of its addition reactions hypochlorous acid reacts as if it has the electronic structure $\overset{-}{HO}\,\overset{+}{Cl}$, and since the electronic structure of vinylacrylic acid has been shown to be $\overset{+}{CH_2}{=}\overset{-}{CH}{-}\overset{+}{CH}{=}\overset{-}{CH}{-}\overset{+}{C}OOH$,[4] it seems altogether probable that the structure of the monochlorohydrin is represented by series I rather than by series II.

On ozonizing the vinylacrylic acid monochlorohydrin it was possible to isolate oxalic acid as one of the oxidation products. This proves that hypochlorous acid adds to vinylacrylic acid in the 3,4-positions to give the chlorohydrin $CH_2OH{-}CHCl{-}CH{=}CH{-}COOH$.

On distilling the monochlorohydrin under reduced pressure, decomposition occurred with the elimination of water. A lower-boiling fraction distilled over but it was not possible to identify any definite products.

An ethereal solution of the monochlorohydrin was treated with phosphorus pentoxide. Water was eliminated, as could be easily seen, by the warming of the solution and the appearance of the phosphoric anhydride. A polymer was obtained which appeared to be the polymer of 3-chlorovinylacrylic acid but no definite proof could be obtained.

The monochlorohydrin of vinylacrylic acid readily absorbs a molecule of hypochlorous acid to form a dichlorohydrin, m. p. 143°. Its structure was not determined but it most probably had the structure $CH_2OH{-}CHCl{-}CHOH{-}CHCl{-}COOH$.

The addition of hypobromous acid to vinylacrylic acid was then studied. It was found that vinylacrylic acid readily absorbs one molecule of hypobromous acid to form a monobromohydrin, m. p. 92–93'. The structure of the monobromohydrin was determined in a manner entirely analogous to that used for the chlorohydrin. The isolation and identification of oxalic acid as one of the oxidation products of the bromohydrin proved that it also was a 3,4-addition product of vinplacrylic acid.

Vinylacrylic acid bromohydrin readily absorbs a molecule of hypobromous acid to form a dibromohydrin, m. p. 148–149". Its structure was not determined but it most probably had the structure $CH_2OH{-}CHBr{-}CHOH{-}CHBr{-}COOH$.

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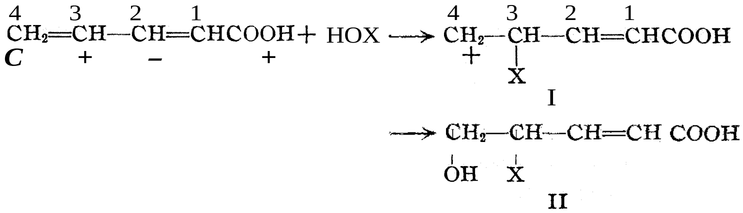
one atom to another. They indicate merely a displacement of the pair of valence electrons from the central position.

The addition of the hypohalous acids to vinylacrylic acid in the 3,4-positions therefore confirms the theory of Muskat and Northrup[1] regarding the addition reactions of conjugated systems. The first step in the addition of $\overset{-}{H}\overset{+}{O}\overset{+}{X}$ to vinylacrylic acid, is the addition of the positive halogen X^+ to the 3-carbon atom to give the intermediate I.



$$\begin{array}{l} \overset{4}{\underset{C}{CH_2}}{=}\overset{3}{\underset{+}{CH}}{-}\overset{2}{\underset{-}{CH}}{=}\overset{1}{\underset{+}{CH}}COOH + HOX \longrightarrow \overset{4}{\underset{+}{CH_2}}{-}\overset{3}{\underset{\underset{X}{|}}{CH}}{-}\overset{2}{CH}{=}\overset{1}{CH}COOH \quad \text{I} \\ \longrightarrow \underset{\underset{OH}{|}}{CH_2}{-}\underset{\underset{X}{|}}{CH}{-}CH{=}CH\ COOH \quad \text{II} \end{array}$$

This intermediate cannot undergo a 1,3-rearrangement, and the negative hydroxyl group must therefore add to the terminal carbon atom to give the 3,4-addition product, II.

Experimental Part

Vinylacrylic Acid Chlorohydrin.—Vinylacrylic acid was prepared according to the method of Muskat, Becker and Lowenstein,[3] by the condensation of acrolein with potassium bisulfite and treatment of the resulting addition product with malonic acid. Hypochlorous acid was prepared according to the method of Reformatsky,[16] by passing chlorine into a finely divided suspension of mercuric oxide in water at about −5°. The hypochlorous acid was distilled under reduced pressure to free it from dissolved mercuric salts. A 3–5% solution of hypochlorous acid, free from chlorine, was used in these experiments.

Vinylacrylic acid in chloroform solution was treated with one mole of a dilute hypochlorous acid solution. The hypochlorous acid must be added very slowly and under continuous stirring and cooling in an ice-bath; otherwise, the reaction becomes too violent. The hypochlorous acid is absorbed almost instantaneously. The reaction mixture was then extracted several times with chloroform, in which vinlyacrylic acid is very soluble but the chlorohydrin of vinylacrylic acid is insoluble. The water solution was then thoroughly extracted with ether, the ethereal solution dried over anhydrous sodium sulfate, and the ether removed by vaporization. A yellowish oil remained which crystallized on standing. The crystals were brought onto a porcelain suction filter and thoroughly washed with a chloroform–benzene (3–1) solution. The crystals melted at 71–74". The chlorohydrin is soluble in water, alcohol, acetone, glacial acetic acid, ethyl acetate, pyridine, ether, benzene and toluene. It is insoluble in ligroin, chloroform and carbon tetrachloride.

Anal. Calcd. for $C_5H_7O_3Cl$: Cl, 23.56. Found: Cl, 23.70, 23.59. Calcd. for $C_5H_7O_3Cl$: mol. wt., 150.5. Found (by acid–base titration): mol. wt., 156.0.

The vinylacrylic acid chlorohydrin, dissolved in water, was subjected to ozonization for twenty-four hours. The process of ozonization and the method of working up the oxidized fractions are amply described by Muskat and Becker.[4] It was possible to isolate oxalic acid from the ozonization products, which proved that hypochlorous acid had added to vinylacrylic acid in the 3,4-positions. A number of ozonizations were made,

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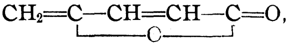
[16] Reformatsky, *J. prakt. Chem.*, 40,396 (1889).

using glacial acetic acid as the solvent for vinylacrylic acid. In every case oxalic acid was the only product that was isolated.

A portion of the vinylacrylic acid chlorohydrin was distilled under reduced pressure. Decomposition occurred with the elimination of water. A lower boiling fraction (100–130° under 12 mm. pressure) distilled over, from which a small amount of a solid, m. p. 137–141°, was isolated. It appeared to be the γ-lactone,  $\mathrm{CH_2{=}C{-}CH{=}CH{-}C{=}O}$ (ring closed through O), which was obtained by the distillation of the dichloride and dibromide of vinylacrylic acid. However, this was not verified.

An anhydrous ethereal solution of the chlorohydrin was shaken with phosphorus pentoxide. The reaction mixture became quite warm and the phosphorus pentoxide became sticky and gave all the indications of having taken up water from the chlorohydrin. The solution was filtered, and the ether was removed by vaporization. A solid remained which appeared to be the polymer of 3-chlorovinylacrylic acid. However, this could not be verified.

$$\mathrm{CH_2OH{-}CHCl{-}CH{=}CH{-}COOH} \xrightarrow[\text{agent}]{\text{dehydrat.}} \mathrm{CH_2{=}CCl{-}CH{=}CH{-}COOH}$$

A number of efforts were made to chlorinate the vinylacrylic acid chlorohydrin, but with no success. Only a small amount of chlorine seemed to be absorbed. This fact is of interest since the 3,4-dichloride of vinylacrylic acid would not absorb chlorine to form the tetrachloride of vinylacrylic acid.[4]

Vinylacrylic Acid Dichlorohydrin.—Vinylacrylic acid chlorohydrin, in water solution, was treated with one mole of a dilute hypochlorous acid solution. Absorption took place fairly readily and the solution became warm. The water solution was extracted a number of times with ether. The ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by vaporization. A yellowish oil remained which crystallized on standing. The crystalline mass was triturated with a small amount of ether and filtered by means of suction. Snow white crystals remained on the filter. The pure crystals melted sharply at 143°. The dichlorohydrin is very soluble in alcohol, acetone and hot water; moderately soluble in ether; and insoluble in ligroin, benzene, chloroform and carbon tetrachloride.

Anal. Calcd. for $\mathrm{C_5H_8O_4Cl_2}$: Cl, 34.936. Found: Cl, 34.89, 34.62. Calcd. for $\mathrm{C_5H_8O_4Cl_2}$, mol. wt., 202.98. Found (by acid–base titration): mol. wt., 205.99.

Vinylacrylic Acid Bromohydrin.—Vinylacrylic acid was treated with one mole of a dilute hypobromous acid solution. Its method of preparation is identical with that described for the preparation of the chlorohydrin. It is essential in this preparation that the hypobromous acid be distilled under reduced pressure to free it from dissolved mercuric salts. The bromohydrin may easily be recrystallized from benzene. The pure bromohydrin melts at 92–93°. It is very soluble in ether, alcohol, glacial acetic acid; somewhat soluble in hot benzene, chloroform, carbon tetrachloride, water; and insoluble in cold benzine and ligroin.

Anal. Calcd. for $\mathrm{C_5H_7O_3Br}$: Br, 40.99. Found: Br, 40.94, 40.78.

The vinylacrylic acid bromohydrin, in water solution, was subjected to ozonization and the ozonide thus formed was worked up in a manner entirely analogous to that described for the chlorohydrin. It was possible to isolate oxalic acid as one of the oxidation products which was identified by its melting point and the melting point of a mixture with a sample of known origin. It was not possible to obtain even the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds formed by the 1,2- or 1,4-addition of hypobromous acid.

Vinylacrylic Acid Dibromohydrin.—Vinylacrylic acid bromohydrin, in ethereal solution, was treated with one mole of a dilute hypobromous acid solution. Its method of preparation is identical with that described above for the dichlorohydrin. The pure crystalline dibromohydrin melts at 148-149°. It has approximately the same solubilities as the monobromohydrin.

Anal. Calcd. for $C_5H_8O_4Br_2$: Br, 54.76. Found: Br, 54.84.

Summary

1. Vinylacrylic acid absorbs hypochlorous and hypobromous acid in the 3,4-positions to form 3-chloro-4-hydroxyvinylacrylic acid and 3-bromo-4-hydroxyvinylacrylic acid, respectively.

2. Vinylacrylic acid chlorohydrin absorbs a molecule of hypochlorous acid to give a dichlorohydrin. In the same way vinylacrylic acid bromohydrin absorbs a molecule of hypobromous acid to give a dibromohydrin.

3. These addition reactions of vinylacrylic acid are found to be in perfect agreement with the general theory on the addition reactions of conjugated systems as previously developed.

CHICAGO, ILLINOIS

NOTES

A Simplified Method of Preparation of Alpha Amino Acid Amides.[1]—It has been generally recognized by investigators of the chemistry of alpha amino acids that good yields of the amides of these acids are difficult to obtain. Fischer,[2] Koenigs[3] and Bergell[4] were leaders in this field of work. The Fischer method and that of Koenigs for obtaining the amides consists in treatment of the alpha amino acid esters with liquid ammonia in sealed tubes at room temperature for from ten days to three months. Bergell, Heintz,[5] and others obtained the amides by treatment of the alpha halogen fatty acid esters or amides with alcoholic ammonia at fairly high temperatures. The yields of amides obtained by the use of these methods were not particularly satisfactory.

The authors undertook the preparation of certain alpha amino acid amides as a preliminary to the study of the chemistry of their biuret reactions[6] A simplification of the older methods for obtaining the amides was accomplished. The esters of glycine, d-alanine and dl-leucine were treated separately in a shaking device with methyl alcohol which had been saturated previously with ammonia at 0°. The reactions were allowed

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[1] The contents of this paper were reported at the National Meeting of the American Chemical Society held at Cincinnati, September, 1930.

[2] E. Fischer, "Untersuchungen über Aminosauren, Polypeptide und Proteine," Julius Springer, Berlin, 1906.

[3] E. Koenigs and B. Mylo, *Ber.*, 41, 4427 (1908).

[4] P. Bergell and T. Brugsch, *Z. physiol. Chem.*, *67*, 97 (1910).

[5] W. Heintz, *ibid.*, 64, 348 (1910).

[6] Mary M. Rising and C. A. Johnson, *J. Biol. Chem.*, 80, 709 (1928); Mary M. Rising, J. S. Hicks and G. A. Moerke, *ibid.*, 89, 1 (1930).

to proceed at room temperature for a number of hours, and the excess of alcohol and ammonia was then removed under reduced pressure, the amides remaining in the form of white crystals, or as oils which solidified when placed in the refrigerator. This treatment of the esters named produced the amides in good yield. Table I shows at a glance the conditions used by us and the advantages of this plan as compared with the methods and results of previous workers. Glycine amide[7] and d-alanine amide were purified by solution in chloroform and reprecipitation from this solution by means of dry ether. dl-Leucine amide was purified by recrystallization from benzene. The glycine amide, d-alanine amide and dl-leucine amides obtained by us melted at 67–68° (uncorr.), 71–72° (uncorr.) and 105–106° (uncorr.), respectively.

TABLE I

THE PREPARATION OF ALPHA AMINO ACID AMIDES

	Present method		Previous methods	
Amide	Conditions	Yield	Conditions[8]	Yield, %
Glycine amide	Glycine ester (20 g.), CH_3OH satd. with ammonia (300 cc.), shaking 20 hrs.	(8 g.) 55.7%	Liquid ammonia, bomb, 10 days	33
d-Alanine amide	Alanine ester (3.5 g.), CH_3OH satd. with ammonia (60 cc.), shaking 50 hrs.	(2.6 g.) 83.7%	Liquid ammonia, bomb, 1 mo.	53
dl-Leucine amide	Leucine ester (4.9 g.), CH_3OH satd. with ammonia (75 cc.), shaking 80 hrs.	(3.6 g.) 88.5%	Liquid ammonia, bomb, 3 mo.	80–85

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PETER S. YANG
MARY M. RISING

RECEIVED MAY 15, 1931
PUBLISHED AUGUST 5, 1931

The Reaction of Acetophenone Derivatives with Sodium Hypochlorite.—It has long been known that acetophenone, when treated with sodium hypochlorite, is changed into benzoic acid. Likewise benzalacetone is decomposed into cinnamic acid.[1] The literature, however, gives very little information regarding the general scope of this procedure for the synthesis of aromatic acids.

The lowered cost of aluminum chloride provides an inexpensive method for the synthesis of certain acetophenone derivatives by means of the Friedel–Crafts reaction. The oxidation of these derivatives with sodium hypochlorite is, however, restricted to compounds which do not contain

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[7] During the preparation of glycine amide some glycine anhydride separated and was removed from the reaction mixture at the conclusion of the reaction by filtration.

[1] Noyes, "Organic Chemistry for Laboratory," Chemical Publishing Co., Easton, Pa., 1920, p. 99.

reactive groups such as nitro or free hydroxyl groups. The results with various derivatives are shown in the following table.

Compound	Observed m. p., acid, °C.	Given[a] m. p., acid, °C.	Yield of acid, %
Acetophenone	121	121	85
4-Methoxyacetophenone	180–183	184	90
4-Chloroacetophenone	234–236	236	93
4-Bromoacetophenone	250–251	250–251	91
4-Methylacetophenone	171–175	176–177	96
3-Nitroacetophenone	.....	140	0
3,4-Dimethylacetophenone	160–162	163	92
3-Methyl-4-methoxyacetophenone	190–192	192–193	92
2-Methyl-4-methoxyacetophenone	175	175	90
Resacetophenone		199	0
Nitroresacetophenone		215	0
p-Hydroxyacetophenone	.....	158	0

Five to 10 gram samples were used in each case.

[a] From Richter "Lexikon" and Beilstein.

Compounds which are not easily halogenated may be treated by passing chlorine slowly into a suspension of the compound in sodium hydroxide solution. Those which easily react with halogens, such as *p*-methoxyacetophenone, may be treated by adding a cold alkaline hypochlorite solution to a methyl alcohol solution of the compound. The latter solvent may frequently be used to increase the solubility of the acetophenone derivative and thereby increase the speed of the reaction. A considerable excess of hypochlorite must be used to ensure complete reaction. At the end of the reaction acetone or sulfur dioxide was added to destroy the excess halogen before the solution was acidified. The free chlorine is easily detected by adding a few drops of the solution to a solution of potassium iodide. Hypochlorite proved much more efficient and convenient than the hypobromite or iodite. With the latter reagents the reaction was much slower and less complete. Furthermore, the separation of bromoform or iodoform from the reaction was often difficult. The general procedure used may be illustrated as follows.

p-Chlorobenzoic Acid.—Five grams of p-chloroacetophenone was dissolved in 25 cc. of methyl alcohol and 50 cc. of 20% sodium hydroxide was then added to the solution. Chlorine was passed into the solution while stirring rapidly. The cloudy solution soon began to clear as the temperature rose to about 80°. More alkali was added from time to time until a total volume of 100 cc. had been used. When the solution was practically clear, the chlorine addition was stopped and the solution stirred for about fifteen minutes longer. A small amount of acetone was added to react with the excess chlorine. The solution was treated with a small quantity of Norite and filtered. Upon acidifying with hydrochloric acid the organic acid was precipitated. The product was practically pure, but was further purified by reprecipitating it from dilute sodium hydroxide. The yield was 93%, m. p. 234–236°.

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M. E. CUPERY

RECEIVED JUNE 18, 1931
PUBLISHED AUGUST 5, 1931

Correction. Para-Nitrophenyl Carbamyl Chloride and Para-Nitrophenyl Isocyanate.—In a recent paper it was stated that the product of the action of phosgene on *p*-nitraniline was p-nitrophenyl carbamyl chloride.[1] While this is the primary product of the reaction mixture, it has been found that after recrystallization from hot carbon tetrachloride as recommended in the procedure, the final purified product is then free from halogen and is p-nitrophenyl isocyanate, m. p. 57.° The analysis given is incorrect. Determination of the nitrogen by the micro Dumas method gave the following results.

Anal. Subs., 3.322 mg.: N_2 gas, 0.577 cc. at 31° and 744 mm. Calcd. for $C_7H_4O_3N_2$: N, 17.07. Calcd. for $C_7H_5O_3N_2Cl$: N, 13.97. Found: N, 17.09.

The purified product with m. p. 57° is therefore p-nitrophenyl isocyanate[2] and is the reagent from which the urethans were prepared. It is evident that the *p*-nitrophenyl carbamyl chloride lost hydrogen chloride during the recrystallization from boiling carbon tetrachloride.

CONTRIBUTION FROM THE
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W. H. HORNE
R. L. SHRINER

RECEIVED JULY 6, 1931
PUBLISHED AUGUST 5, 1931

COMMUNICATIONS TO THE EDITOR

INTERATOMIC FORCES IN BINARY ALLOYS

Sir:

Under this title, N. W. Taylor has recently published [THIS JOURNAL, 53, 2423 (1931)] a test of Langmuir's theory of non-electrolyte solutions which seems to me unfortunate in three respects. Following Hildebrand and Sharma [*ibid.*, **51**, 467 (1929)], he has confused Hildebrand's definition [*ibid.*, **51**, 66 (1929)] of a "regular solution," for which at constant composition T log a_1/N_1 is independent of the temperature, with that of a "symmetrical system," for which at constant temperature log $(a_1/N_1)/N_2^2$

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[1] Shriner and Cox, THIS JOURNAL, 53, 1601 (1931).

[2] This has also been noted by van Hoogstraten, Doctor's Dissertation Rijks University, Leiden, June 30, 1931.

is independent of the composition. His method of comparison is to compare one quantity calculated by means of an extrapolation with another calculated by an integration from a few experimental points and involving the first extrapolation and also a second one. He considers that the agreement with Langmuir's equation supports Langmuir's assumptions, but he does not give a comparison with the equations of Heitler and of Van Laar.

The test can be made directly with the experimental data, and the accompanying table shows the comparison for cadmium–lead alloys [Taylor, *ibid.*, 45, 28 (1923)]. The results for the other alloys, which are essentially the same, are omitted for the sake of brevity. The solutions appear not to be "regular," but the values of T log a_1/N_1 decrease with increasing temperature somewhat more than the irregularities of the individual measurements. They are constant enough to make the use of their average in the comparison which follows preferable to the use of the measurements at any one temperature, even though the temperatures are not the same for all the compositions.

I have discussed elsewhere [Chemical Reviews, 8, 321 (1931)] the various theories as to the relation of the change in free energy to the composition. Heitler's theory gives "symmetrical systems" or T log $a_1/N_1 = \alpha N_2^2$ (1); Langmuir's theory gives T log $a_1/N_1 = \beta S_1[N_2S_2/(N_1S_1 + N_2S_2)]^2$ (2); Van Laar's theory and the more general theory I proposed give T log $a_1/N_1 = \gamma V_1[N_2V_2/(N_1V_1 + N_2V_2)]^2$ (3). The S's are the molecular (or molal) surfaces, and the V's the corresponding volumes, and α, β and γ are constants. The comparison of these three equations is given in the last three rows of the table, with constants calculated for the most dilute

Cadmium–Lead Alloys

N_1	0.786	0.696	0.584	0.509	0.401	0.293	0.269	0.155	0.123
N_2^2	.046	.092	.173	.241	.359	.500	.534	.714	.769
$\left(\dfrac{N_2S_2}{N_1S_1 + N_2S_2}\right)^2$	.064	.123	.220	.296	.421	.562	.594	.759	.806
$\left(\dfrac{N_2V_2}{N_1V_1 + N_2V_2}\right)^2$	.074	.141	.246	.325	.453	.591	.623	.779	.823
T log a_1/N_1									
427°		56		123			244		328
436°	31		92		172			298	
466°						222			
476°		58		122			245		325
484°	32		95		169				
544°		54		117		219	239		318
572°		54		115			237		317
Av.	31	55	93	119	170	220	241	298	322
Eq. 1	19	39	72	101	150	210	224	299	322
Eq. 2	26	49	88	118	168	225	238	304	322
Eq. 3	29	55	96	127	177	231	244	305	322

alloys. Although the physical theories are quite different, the resulting equations do not differ greatly for molecules so similar in size as these metals. The agreement of equation (1) with the experiments is distinctly poorer than that of the other two equations, but the difference between these two is too small to choose between them, and either one checks the measurements almost within the experimental error. The results with the other alloys are equally indecisive. In fact, I know of no measurements, in systems for which the agreement might be significant, which agree distinctly better with the equation of Langmuir than with that of Van Laar, or *vice versa*. The choice of theory must rest on a more fundamental analysis, a further contribution to which I hope to publish shortly.

CONTRIBUTION NO. 266
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
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CAMBRIDGE, MASSACHUSETTS
GEORGE SCATCHARD

RECEIVED JULY 1, 1931
PUBLISHED AUGUST 5, 1931

THE FORMATION OF HYDROGEN PEROXIDE FROM HYDROGEN AND OXYGEN

Sir:

I have recently reported [THIS JOURNAL, 52, **5106–5110** (1930)] that hydrogen peroxide is formed, along with water, when hydrogen–oxygen mixtures at atmospheric pressure are passed through a Pyrex reaction tube at 500–550°. Thermodynamic data [Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 496] indicate that the peroxide cannot have been formed via water

$$H_2 + {}^1/_2\, O_2 \longrightarrow H_2O \qquad (1)$$

$$H_2O + {}^1/_2\, O_2 \longrightarrow H_2O_2 \qquad (2)$$

but must have been produced directly

$$H_2 + O_2 \longrightarrow H_2O_2 \qquad (3)$$

Since hydrogen peroxide dissociates to give water, the question arises as to whether all the water formed passes through the peroxide stage, or whether a part comes direct from the elements.

An attempt was made to answer this by determining the ratio of peroxide to water formed under conditions leading to successively lower total conversions. If hydrogen peroxide were the only primary product, one should obtain something approaching pure peroxide in the limit. As the experimental results were on the whole inconclusive, it seems unnecessary to report them in full. However, a representative set of data may be of interest.

The data of the table refer to experiments in which $19H_2{:}1O_2$ mixtures were passed through a spherical Pyrex reaction vessel of 4.3 cm. diameter. The gases passed from flowmeters to traps cooled to −79°, then through the reaction bulb and then through a weighing U-tube also cooled to −79.° Total product was determined by weighing; the peroxide was then titrated with 0.05 N potassium permanganate; and water was obtained by difference.

Temp. °C.	Approx. heating, sec.	Part press. in off-gas in 0.001 atm. H_2O_2	H_2O	Ratio H_2O_2/H_2O	H_2 reacting, %
550	0 5	0 068	0.37	0.18	0.046
550	1	.21	1.7	.12	.20
540	1	.19	0.76	.25	.10
530	1	.056	0 21	.27	.028

In spite of the extremely small total conversions (less than 0.2% H_2), the best result obtained was one mole of peroxide to four moles of water. The possibility of independent, direct formation of water from the elements is thus by no means excluded.

DEPARTMENT OF CHEMISTRY
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PRINCETON, N. J.
ROBERT N. PEASE

RECEIVED JULY 10, 1931
PUBLISHED AUGUST 5, 1931

SURFACE REACTIONS OF ATOMS AND RADICALS

Sir:

Recently we[1] have found that water vapor, dissociated in a discharge tube, will oxidize carbon monoxide to carbon dioxide. Since atomic oxygen is not very effective in causing this oxidation we are led to believe that the carbon dioxide is formed as the result of a reaction involving the hydroxyl radical. Assuming that this is the case, we can use the oxidation of carbon monoxide as a test for OH and in this way determine whether it is affected by certain catalytic surfaces.

By observing the effect of different catalysts on the yield of carbon dioxide, we have found that a dehydrogenation catalyst is inefficient in causing the H + OH combination while a dehydration catalyst is quite efficient. This result is in accord with the work of Taylor and Lavin[2] and shows, as might be expected, that a strictly dehydrogenation catalyst is only effective in causing the recombination of hydrogen atoms.

In light of the fact that we are able to observe the oxidation of carbon monoxide after practically all of the hydrogen atoms have been removed (by the dehydrogenation catalyst) it seems that we have here a method for the separation of H and OH.

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G. I. LAVIN
W. F. JACKSON

RECEIVED JULY 16, 1931
PUBLISHED AUGUST 5, 1931

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[1] Lavin and Jackson, THIS JOURNAL, 53, 383 (1931).

[2] Taylor and Lavin, ibid., 52, 1910 (1930).

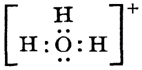
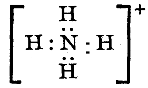
THE ROLE OF HYDROGEN BONDS IN CONDUCTION BY HYDROGEN AND HYDROXYL IONS

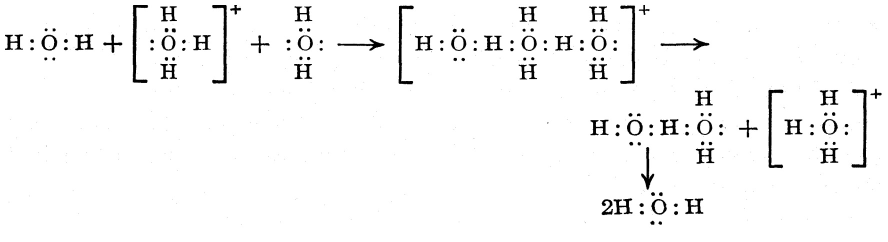
Sir:

The abnormally high conductance of hydrogen and hydroxyl ions in water solution is well known.' To account for this it has been proposed[2] that "an interchange takes place between the ions and the solvent molecules with the result that the mean path over which these ions travel is reduced in proportion to the effective diameter of the solvent molecules which are concerned in this interchange^{M}—a modification of Grotthuss' chain theory of conduction.

Against this hypothesis it has been pointed out[1] that similar abnormally high conductances would be expected for solvent ions in solvents such as ammonia, whereas this is not the case. Recourse is then had to the assumption that the abnormal speeds of the solvent ions in water are due to their relatively low hydration.

I shall attempt to show now that the concept of "hydrogen bonds," first proposed by me in 1919 and shortly thereafter independently by Latimer and Rodebush, furnishes a satisfactory mechanism for chain conduction by the solvent ions in water but not in ammonia.

Let us assume, for simplicity, that hydrogen ions are  $\left[\begin{matrix} & \mathrm{H} & \\ \mathrm{H}: & \ddot{\underset{\cdot\cdot}{\mathrm{O}}} & :\mathrm{H}\end{matrix}\right]^{+}$ in water and  $\left[\begin{matrix} & \mathrm{H} & \\ \mathrm{H}: & \ddot{\underset{\cdot\cdot}{\mathrm{N}}} & :\mathrm{H} \\ & \mathrm{H} & \end{matrix}\right]^{+}$ in ammonia. The hydrogen kernels are held quite tightly to the oxygen and even more tightly to the nitrogen. In the case of H_3O^+ the force holding each hydrogen will be greatly decreased if another hydrogen, say in an H_2O molecule, approaches the lone pair in the oxygen valence shell. If at the same time an oxygen lone pair in another water molecule should approach one of the H_3O^+ hydrogens, that hydrogen might well be transferred to this second water molecule, making it an H_3O^+ ion. Diagrammatically



Such a mechanism is obviously impossible with NH_4^+ ions, for no lone pairs are available to aid in the "loosening" of the NH bonds.

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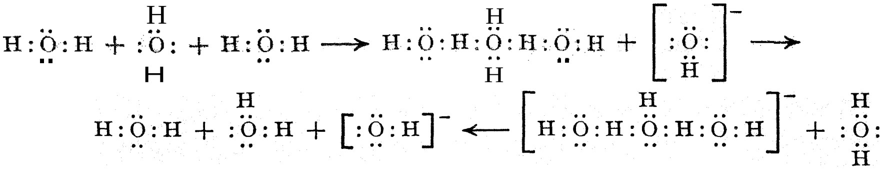
[1] Cf. Kraus, "Properties of Electrically Conducting Systems," The Chemical Catalog Co., Inc., New York, 1922, p. 206.

[2] Lumsse. Thesis, Clark University, 1920.

Analogously, an OH– ion can remove a hydrogen from a water molecule if the oxygen in the latter has around it three other hydrogens



Although one might postulate hydrogen bonds between NH3 molecules so as to produce nitrogen atoms surrounded by four hydrogens, these hydrogens would be more tightly held than each of four hydrogens surrounding an oxygen (NH_4^+ is more stable than OH_4^{++}) and apparently they cannot easily be removed by NH_2^- ions.

It seems likely, moreover, that N : H : N bonds are not readily formed. ((: F : H : F :)– is quite stable; O : H : O bonds are weaker but common in crystals and probably in liquid water and temporarily during many reactions, whereas no examples whatever of N : H : N or C : H : C bonds are known to me.) If so, this in itself suffices to account for the lack of abnormally large conductances of NH_4^+ and NH_2^- in ammonia.

The conductance data for other solvents also seem to be in agreement with the ideas here expressed, but I shall not now take the space to discuss them.

DEPARTMENT OF CHEMISTRY
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MAURICE L. HUGGINS

RECEIVED JULY 15, 1931
PUBLISHED AUGUST 5, 1931

HEXAFLUORODISILANE

Sir:

Up to the time of the present writing the only binary fluoride of silicon that has been identified definitely is the tetrafluoride, SiF_4. Methods leading to the formation of so-called subfluorides, several of which have been reported, have failed when repeated by later experimenters. Nevertheless, the presumption remained that binary fluorides other than the tetrafluoride should be capable of existence, since certain of the corresponding compounds of carbon have been isolated.

We have now succeeded in preparing hexafluorodisilane, Si_2F_6, by gently warming hexachlorodisilane with anhydrous zinc fluoride, followed by condensation and fractionation of the products. The substance is gaseous under ordinary conditions of temperature and pressure, but may be condensed to a snow white solid, melting at –18.5° under 780 mm. pressure.

The vapor pressure of the substance has been determined from –79 to –4°; the pressure becoming 760 mm. at –19°. Gas density determinations upon the same product lead to the molecular weight 173.8 (calcd. for Si_2F_6, 170.1). Inasmuch as the product has been shown to be quite pure, not only by the rectilinear character of the vapor pressure curves when log p is plotted against $1/T$, but also by the observed sharpness of the melting point, and by the absence of any appreciable amounts of chloride, we feel that there can be little doubt concerning the actual composition of the substance.

When in contact with moist air or water, the substance is instantly hydrolyzed, the products formed including hydrogen, hydrofluoric acid, "silico-oxalic acid"—or 1,2-bis-(oxy-oxo)disilane—silicic and fluosilicic acids, the proportions of the several substances varying with experimental conditions. The quantitative study of this hydrolysis, which will also make possible the analysis of the original substance for silicon and fluorine, is now in progress, and will be described in the detailed account of this investigation in a later issue of THIS JOURNAL.

It may be added that the analogous preparation of hexafluoroethane, C_2F_6, by the interaction of zinc fluoride with hexachloroethane, has failed to give satisfactory results at ordinary pressure.

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WALTER C. SCHUMB
E. LEE GAMBLE

RECEIVED JULY 25, 1931
PUBLISHED AUGUST 5, 1931

THE DECOMPOSITION OF PYROSULFURYL CHLORIDE, A HOMOGENEOUS UNIMOLECULAR REACTION

Sir:

According to the literature, given to date in Mellor's "Treatise on Inorganic and Theoretical Chemistry," Vol. X, p. 683, pyrosulfuryl chloride, $S_2O_5Cl_2$, decomposes at its boiling point and above at a rate which should be convenient for study. The molecule is sufficiently large that one might expect, in accord with present theories, that the decomposition might be unimolecular. The vapor phase decomposition has been investigated, and found to be homogeneous and unimolecular.

The reaction has been followed by the pressure-increase method in a Pyrex bulb, both empty and when filled with glass tubing. The pressure approximately doubles during the reaction, which is considered to be one yielding SO_3 and SO_2Cl_2, and which, at 179° has a half-time of seven minutes in the empty bulb. When the surface is increased four times by packing, the half-time is approximately fifteen minutes.

Other temperatures are now being used, and the reality of the apparent decrease in rate with increased surface is being studied. The full report of the experiments will be submitted as soon as possible.

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DOUGLAS G. HILL

RECEIVED JULY 27, 1931
PUBLISHED AUGUST 5, 1931

NEW BOOKS

Radioelements and Isotopes: Chemical Forces and Optical Properties of Substances. By KASIMIR FAJANS, University of Munich. The George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University. The McGraw-Hill Book Company, Inc., 370 Seventh Ave, New York, 1931. x + 125 pp. Illustrated. 15.5 × 23.5 cm. Price, $2.50.

This volume, for the most part, contains the subject-matter of Professor Fajans' lectures given in the spring of 1930 at Cornell University as George Fisher Baker Non-Resident Lecturer. The systematic discussions of Radioactivity and of Isotopes given in these lectures have been omitted as they are covered fully in other publications of the author.

Part I of this volume is devoted to The Origin of the Actinium Series and the Stability of Isotopes; Part II to Chemical Forces and Optical Properties. Part II is much the longer and is particularly useful as a presentation in brief and convenient form of the important researches of Professor Fajans upon these subjects.

Both in content and in physical appearance this volume maintains the high standard of excellence characteristic of the earlier volumes of this series.

ARTHUR B. LAMB

Atlas der physikalischen und anorganischen Chemie. Die Eigenschaften der Elemente und ihrer Verbindungen in graphischer **Darstellung** auf 29 **Tafeln.** (Atlas of Physical and Inorganic Chemistry. The Properties of the Elements and their Compounds Graphically Illustrated on 29 Charts.) By PROF. DR. A. VON ANTROPOFF and DR. M. VON STACKELBERG, University of Bonn. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1929. 64 pp. 19 figs. 29 × 36 cm. Price, RM. 40, cardboard, KM 42, cloth binding

This Atlas consists of a collection of 29 charts, each 11 by 14 inches and provided with a key printed in English, German and Spanish. These charts cover the important physical and chemical properties and the distribution of the elements. An explanatory text in German of 64 pages containing many tables and diagrams accompanies the charts.

This Atlas should be very useful to the teacher in presenting vividly the numerical data characteristic of the chemical elements, and to the professional chemist as a means of quick and ready reference.

ARTHUR B. LAMB

Introduction à l'étude de la mécanique ondulatoire. (An Introduction to the Study of Wave Mechanics.) By Lours DE BROGLIE, Maître de Conférences à la Sorbonne Libtairie Scientifique Hermann et Cie., 6, Rue de la Sorbonne, Paris, France, 1930. xvi + 292 pp. Illustrated. 16 X 25 cm. Price, unbound, 85 fr.; bound, 95 fr.

Wave mechanics from its beginning has been a many-sided science, and the side to which de Broglie has contributed, and which he writes about, is the connection of wave mechanics with classical mechanics. For that aspect of the subject, the present book gives a very complete and readable discussion. On the other hand, the specific problems of atomic and molecular dynamics for which wave mechanics has proved so valuable are treated to only a very slight extent by de Broglie. For this reason, the book is less likely to appeal to a chemist or experimental physicist than many other works which have appeared. On the other hand, the reader interested in analytical mechanics will enjoy the clear account of the relation of wave mechanics to the methods of Lagrange, Hamilton and Jacobi, a relation which is made the basis of the author's treatment. The discussions of wave packets, of the uncertainty principle, and of various other branches of the subject are valuable. The book is, however, mathematical throughout, and could hardly be read with profit except by one who already had some familiarity with the subject.

JOHN C. SLATER

Handbook of Chemical Microscopy. Vol. II. Chemical Methods and Inorganic Qualitative Analysis. By ÉMILE MONNIN CHAMOT, B.S., Ph.D., Professor of Chemical Microscopy and Sanitary Chemistry, Cornell University, and CLYDE WALTER MASON, A.B., Ph.D., Assistant Professor of Chemical Microscopy, Cornell University. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1931. ix + 411 pp. Illustrated. 15 × 23.5 cm. Price, $4.50.

In Volume II, "The inclusive field of 'microchemistry,' which comprises all chemical procedures dealing with small amounts of material, is discussed only as regards those portions of it which involve microscopical qualitative reactions." After two introductory chapters which give clear and detailed descriptions of the necessary technique, the specific tests used in the detection of the various elements are discussed, under the groups of the periodic table. In addition to the detailed description of the procedure by which the various crystalline products are obtained, and to the verbal description of the products themselves, excellent photomicrographs of the characteristic crystals are given. The reviewer regrets that the optical constants of these various characteristic crystals are not given; the need of such constants is often felt, and they may be of positive aid in the identification of poorly formed crystals. A curious slip was found on page 156: in the thallium alums it is the alkali, not the aluminum, that is replaced by thallium, hence it is incorrect to state that "Its analogy to aluminum is shown by its property of forming alums." The discussion of the detection of anions is especially good. The "Handbook of Chemical Microscopy" will be found an indispensable aid to those who use the microscope in chemical problems; and the clear exposition of the technique given therein should greatly increase the number of those who make use of these rapid and satisfying methods.

GEORGE W. MOREY

Berl-Lunge **Taschenbuch für** die anorganisch-chemische **Grossindustrie.** (Berl-Lunge Handbook of Inorganic Industrial Chemistry.) Edited by E. BERL, Ph.D., Professor of Industrial and Electrochemistry at the Technical High School of Darmstadt. Seventh, revised, edition. Second part, Nomograms, Verlag von Julius Springer, Linkstrasse **23–24,** Berlin W **9,** Germany, **1930. 31** tables, with legends and descriptions. **23.5** X **31** cm. Price, **RM.** 37.50.

This publication consists of thirty-one unbound nomographic charts which are designed to be useful in the control laboratories of manufacturers or users of inorganic heavy chemicals. The charts are well printed and will doubtless permit interpolations and interpretations of the observed data with greater speed and less danger of blunders than by the use of tables or computations.

GRINNELL JONES

The Terpenes. Vol. **I.** The Simpler Acyclic and Monocyclic Terpenes and their Derivatives. By J. L. SIMONSEN, D.Sc., F. I. C., Professor of Chemistry, University College of North Wales. The Macmillan Co., **60** Fifth Ave., New York, **1931.** xv + **420** pp. **14** X **22.5** cm.

The author states in his preface that, while the constituents of the various essential oils have been adequately dealt with in the English language by Parry, "The Chemistry of the Essential Oils," and by Finnemore, "Essential Oils," with the exception of Brooks' monograph, "The Non-Benzenoid Hydrocarbons," which covers a somewhat wider field, no book is available which deals with the chemistry of the terpenes.

In order to supply this deficiency the author has written this work. Special attention has been directed to the methods used in the determination of constitution and synthesis.

The author has traced the development of the views on the constitution of the various terpenes in a clear and pleasing manner, and with adequate references.

Where further research is desirable he has so indicated, and his comments are valuable and to the point and show a broad knowledge of his subject. Structural formulas have not been spared, and the student of terpene chemistry will find no difficulty in following the trend of thought.

The work is well written and will be of value to those interested in this fascinating field of organic chemistry.

Very few errors in printing were noted.

E. K. NELSON

The Carbon **Compounds.** A Textbook of Organic Chemistry. By C. W. PORTER, Professor of Chemistry in the University of California. Second revised edition. Ginn and Company, **15** Ashburton Place, Boston, Massachusetts, **1931.** ix + 469 pp. Illustrated. **15.5** × 24 cm. Price, $4.00.

The latest edition of this well-known text is not only revised but is, to a very large extent, rearranged and rewritten. In almost all cases the changes have been in the direction of simplification and clarification.

"In this edition the structure of sucrose has been revised on the basis of the researches of Haworth and his associates. Thyroxine and two other amino acids have been added to the list of the hydrolysis products of proteins. The discussion of Robertson's theory of protein salt formation has been replaced by a statement setting forth the views of Osborne, Cohn, Vickery and Schmidt. Dissociation constants of acids and bases have been added."

In addition to these major changes and additions all the tables of constants have been revised according to the latest data. The two indexes have been combined in one. The Questions and Problems have been almost entirely changed and have been somewhat expanded.

Very few adverse criticisms can be made. The carbon tetrahedron on page 15 is wrongly constructed. The explanation of the Geneva system of naming substances with complex side chains remains unsatisfactory. Occasional loose statements creep in, like that on page 92 regarding the hydrolysis of cyanides.

The author has taken full advantage of the opportunity to improve an already excellent text.

FRANK C. WHITMORE

Jahrbuch der organischen Chemie. (Yearbook of Organic Chemistry.) By Professor Dr. JULIUS SCHMIDT, Stuttgart. Vol. 16, 1929. Verlag von Franz Deuticke, Vienna, Austria, 1931. xvii + 299 pp. 17 × 26 cm. Price, M. 30, unbound: M. 33, bound.

The sixteenth annual report on Organic Chemistry deals with the publications of 1929. The material is organized in the same manner as in previous reports but the new volume is somewhat larger, mainly because it contains an additional chapter which deals with "glucosides, resins and organic colloids." Author and publisher are evidently making a praiseworthy effort to have these reports appear more promptly.

E. P. KOHLER

The Development of Physiological Chemistry in the United States. By RUSSELL H. CHITTENDEN, Professor of Physiological Chemistry in the Sheffield Scientific School of Yale University, 1882–1922. American Chemical Society Monograph Series. Published by The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1930. 427 pp. 15.5 × 23.5 cm. Price $6.00.

Professor Chittenden has undertaken the difficult task of writing an account of *a* half-century's progress in this country in the field of physiological chemistry. The task is difficult because it is not always possible with our perspective to distinguish between progression and retrogression, between the important and the unimportant. Nevertheless this monograph will be a valuable source of information to the advanced student, to the teacher and to that future historian who will write a critical review of science in this era.

It is particularly fitting that Professor Chittenden should be the author of such a monograph. The lead taken by his laboratory in the study of physiological chemistry is indicated by the fact that of the twelve chapters, No. 10 and significant parts of six others deal with researches at New Haven. The author points out that Yale has had 93 successful candidates for the degree of Ph.D. in physiological chemistry up to 1927 and of these, 57 hold or have held important positions in American universities or medical colleges.

One can make few criticisms of a specific character. In view of the author's association with Osborne it is surprising to read (p. **93)** that zein "constitutes nearly one-half of the maize kernel." A statement that smacks of radio science appears on p. 151 where reference is made to Reichert's 600 photomicrographs of hemoglobin crystals "coming from the blood of every conceivable species of animal." Presumably because the literature references, with but few exceptions, terminate with 1927, no reference is made to Fiske's work on phosphocreatine. Many will be disappointed because of the decision to confine the monograph to the United States. If the author, like our scientific societies, had disregarded the Canadian boundary he would not have excluded that happy patriarch of physiological chemistry in America, A. B. Macallum.

D. B. DILL

The Vitamins. By H. C. SHERMAN, Mitchill Professor of Chemistry, Columbia University, and S. L. SMITH, Senior Chemist, Office of Experiment Stations, United States Department of Agriculture. American Chemical Society Monograph Series. Second edition. The Chemical Catalog Company, Inc., 419 Fourth Avenue, at 29th Street, New York, 1931. 575 pp. Illustrated. 15.5 X 23.5 cm. Price, $6.00.

To those interested specifically in the field of nutrition, Dr. Sherman's book presents in available form excellent abstracts of the most important investigations. Many chemists wish to obtain a survey of this field and Dr. Sherman has most carefully, and in his usual unbiased critical manner, presented a well classified, chronological review of the fundamental contributions in the field of vitamins. The large number of citations makes the book exceedingly valuable as a reference book and as an aid to research.

It is believed that the excellent subdivisions of each chapter will enable students to classify, for the first time, the problems in the respective fields. It is unfortunate that the nomenclature was not definitely standardized. To those not directly concerned in vitamin research, a critical correlation of the various researches would be helpful. The evidence more recently published indicating the presence of several new factors in yeast, wheat and casein deserves a fuller discussion.

This book differs greatly from his first edition. It consists of **336** pages of text, 184 pages of literature containing over 3000 citations. Eighteen pages are devoted to author index and **24** to subject index. **A** number of excellent photographs are included. No illustrations on vitamin D are given. The original chapter on B is divided into two chapters, vitamin B and vitamin G. There is an excellent chapter on vitamin E **and** also one on vitamin D. The chapter on "Vitamins in the Problem of Food Supply," has been omitted and the material combined with the other chapters.

CHARLES N. FREY

BOOKS RECEIVED

June **15, 1931–July 15. 1931**

A. E. VAN ARKEL AND J. H. DE BOER. "Chemische Bindung als elektrostatische Erscheinung." Deutsche von den Verfassern autorisierte Ausgabe von Li Klemm und Wilhelm Klemm. Verlag von S. Hirzel, Konigstrasse **2,** Leipzig C **1,** Germany. **320** pp. M. **15,** unbound; M. **17,** bound.

MAX BLOCH. "Über einige Gesetzmassigkeiten im Schaffen hervorragende Chemiker." Verlag Chemie, G. m. b. H., Corneliusstrasse **3,** Berlin W 10, Germany. **56** pp. **M. 3.50.**

MAX BOËTIUS. "Über die Fehlerquellen bei der mikroanalytischen Bestimmung des Kohlen- und Wasserstoffes nach der Methode von Fritz Pregl." Verlag Chemie, G. m. b. H., Corneliusstrasse **3,** Berlin W **10,** Germany. **113** pp. RM. **7.**

ROBIN CHARLES BURRELL. "Chemistry for Students of Agriculture and Home Economics." McGraw-Hill Book Company, Inc., **370** Seventh Ave., New York. **459** pp. **$3.50.**

J. C. COLBERT. "A Shorter Course in Organic Chemistry." The Century Co., **353** Fourth Ave., New York. **352** pp. **$3.60.**

SVEN FAGERBERG. "Die Kathodophosphoreszenz der seltenen Erden in Kalciumoxyd." Inaugural Dissertation, Uppsala, **1931.** Almqvist & Wiksells Boktryckeri-A.-B. Uppsala, Sweden. **58** pp.

GEORG GRASSER. "Kurzes Lehrbuch der Chromgerbung. Ein Leiffaden für Praktiker und Theoretiker." Verlag von Ferdinand Enke, Stuttgart, Germany. **223** pp. RM. **15,** unbound; RM. **16.50** bound.

JOSEF F. HEUBERGER. "Reaktionskinetische Studien an der spontanen Kohlensäureabspaltung der Nitroessigsaure." Inaugural Dissertation, Uppsala, **1928.** Almqvist & Wiksells, Boktryckeri-A.-B., Uppsala, Sweden. **119** pp.

WALTER HÜCKEL. "Theoretische Grundlagen der organischen Chemie." Akademische Verlagsgesellschaft m. b. H., Schlossgasse **9,** Leipzig C **1,** Germany. Vol. I, **410** pp. M. **22,** unbound; **M. 24,** bound. **Vol. II, 352** pp. M. **18,** unbound; M. **20,** bound.

K. IMHOFF. "Der Ruhrverband." Dritte Auflage. Carl Heymanns Verlag, Berlin **W 8,** Germany. 66 pp.

EDVIN JÖNSSON. "Absorptionsmessungen im Langwelligen Rontgengebiet und Gesetze der Absorption." Inaugural Dissertation, Uppsala, **1928.** Almqvist & Wiksells Boktryckeri-A.-B., Uppsala, Sweden. **102** pp.

I. M. KOLTHOFF. "The Colorimetric and Potentiometric Determination of pH. Outline Electrometric Titrations." John Wiley and Sons, Inc., 440 Fourth Ave., New York. **167** pp. **$2.25.**

LEONARD B. LOEB. "The Nature of a Gas." John Wiley and Sons, Inc., **440** Fourth Ave., New York. **153** pp. **$2.50.**

DARWIN O. LYON. "Das periodische System in neuer Anordnung mit Tabellen uber Funfzehn physikalische Konstanten in Anordnung nach der Ordnungszahl der Elemente und nach der Grosse der Konstanten." Second edition. Verlag Franz Deuticke, Helferstorferstrasse **4** (Schottenhof), Wien **1,** Austria. **40** pp. + tables and diagrams. M. 8, unbound; M. 10, bound.

THOMAS P. MCCUTCHEON, HARRY SELTZ AND J. C. WARNER. "General Chemistry, Theoretical and Descriptive." Second edition. D. Van Nostrand Company, Inc., **250** Fourth Ave., New York. **533** pp. **$3.50.**

JAMES F. NORRIS. "Principles of Organic Chemistry." Third edition. McGraw Hill Book Company, Inc., **370** Seventh Ave., New York. **595** pp. **$3.00.**

PAUL NYLÉN. "Studien iiber organische Phosphorverbindungen." Inaugural Dissertation, Uppsala, **1930.** Almqvist & Wiksells Boktryckeri-A.-B., Uppsala, Sweden. 239 pp.

FRITZ OHL. "Die Kunstseiden. Nitrat-, Azetat-, Ather-, Viskose und Kupferkunstseide." Dr. Max Janecke Verlagsbuchhandlung, Leipzig, Germany. **211** pp. RM. **7.80.**

HERMANN RINDE. "The Distribution of the Sizes of Particles in Gold Sols Prepared According to the Nuclear Method." Inaugural Dissertation, Uppsala, **1928.** Almqvist & Wiksells Boktryckeri-A.-B., Uppsala, Sweden. **225** pp.

ARNE TISELIUS. "The Moving Boundary Method of Studying the Electrophoresis of Proteins." Inaugural Dissertation, Uppsala, **1930.** Almqvist & Wiksells Boktryckeri-A.-B., Uppsala, Sweden. **107** pp.

O. TUNMANN. "Pflanzenmikrochemie. Ein Hilfsbuch beim mikrochemischen Studium pflanzlicher Objekte." Zweite vermehrte und verbesserte Auflage, bearbeitet von Dr. L. Rosenthaler. Verlag von Gebriider Borntraeger, Schoneberger Ufer 12a, Berlin, Germany. **1047** pp. RM. **75,** unbound; RM. **78.** bound.

BRUNO WAESER. "Alkalien und Erdalkalien in Ausgewahlten Kapiteln." Verlagsbuchhandlung Theodor Steinkopff, Residenzstrasse *32,* Dresden-Blasewitz, Germany. **196** pp. RM. **13.50,** unbound; RM. **15,** bound.

ROGER J. WILLIAMS. "An Introduction to Organic Chemistry." Second edition. D. Van Nostrand Co., **250** Fourth Ave., New York. **585** pp. **$3.50.**

"Gmelius Handbuch der anorganischen Chemie." **8** Auflage. Heransgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer **59:** Eisen. Teil B, Lieferung 4. Verlag Chemie, G. m. b. H., Corneliusstrasse **3,** Berlin 'W **10,** Germany. **216** pp. M. **35;** subscribers, M. **28.**

"Gutachten iiber die Bildung einer Wassergenossenschaft 'Weisse Elster.' " Erstattet von Dr. Ing. Imhoff und Obering. Fries. Druck von Th. Reismann-Grone, G. m. b. H., Essen, Germany. **39** pp. + diagrams.

"Métodos de Análisis de Aguas Potables, Liquidos Cloacales, Aguas Residuales y Lodos Cloacales que ha Adoptado el Laboratorio de la Institución." Segundo edición. Obras Sanitarias de la Nación. Imprenta O. S. N., Buenos Aires, Argentina, S. A., 1929. 108 pp.

"Mineral Resources of the United States, 1928." By Frank J. Katz, Chief Engineer, Division of Mineral Statistics. From Superintendent of Documents, Government Printing Office, Washington, D. C. Part I, Metals. 910 pp. $1.50. Part II, Non-Metals. 801 pp. $1.25.

"Physics of the Earth. IV. The Age of the Earth." Bulletin No. 80 of the National Research Council. By the Subsidiary Committee on the Age of the Earth. Published by the National Research Council of the National Academy of Sciences, Washington, D. C. 487 pp. $4.50.

"A Quarter Century of Learning, 1904–1929." As Recorded in Lectures Delivered at Columbia University on the Occasion of the One Hundred and Seventy-Fifth Anniversary of Its Founding. Columbia University Press, 2960 Broadway, New York. 382 pp. $3.50.

"Quicksilver." By C. N. Schuette. From Superintendent of Documents, Government Printing Office, Washington, D. C. 168 pp. $0.45.