NOTES

The Relation between Magneto-optic Rotation and Refractive Dispersion of Hydrocarbons

By A. Bondi

Inspection of data on the magneto-optic rotation (Verdet Constant, V) of hydrocarbons[1,2] suggested that they may be directly proportional to the refractive dispersion, $n_{\nu 1} - n_{\nu 2} = \Delta n$. The recent extensive and accurate data published by Foehr[3] make possible the quantitative comparison which is presented in Table I. It appears that $V/\Delta n$ is indeed very nearly independent of the hydrocarbon type at low molecular weights and substantially constant in the higher molecular weight range.

The greatest "exaltation" apparently occurs among the aromatic hydrocarbons, but too few measurements are available in this class of compounds to permit any valid generalization.

As a practical result this observation suggests that refractive dispersion and magneto-optic rotation may be used interchangeably. Since refractive dispersion data are usually more accessible[4,5] than Verdet constants, the ingenious scheme of (magneto-optic) hydrocarbon type analysis proposed by Foehr[3] may now be applied more extensively.

The theoretical background is contained in the Becquerel formula[6]

$$V = \gamma \frac{e}{2mc^2} \nu \frac{\partial n}{\partial \nu} \qquad (1)$$

where the universal factor $e/2$mc.[2] derives from the Larmor precession, ν = frequency of the light used, $\partial n/\partial \nu$ = refractive dispersion, γ = "anomaly" factor. The constancy of the ratio $V/\Delta n$ thus means that for hydrocarbons γ is a constant. For diamagnetic substances, according to Schütz[6]

$$\gamma = a_i + \frac{b}{2} \frac{\nu_1}{\Delta \nu_0} \quad \text{if } \nu \ll \nu_i \qquad (2)$$

where a_i = oscillator strength, ν_i = characteristic frequency of the electron transition which is active in the magneto-rotation and determines the dispersion of V (as well as of the refractivity, v. i.), $\Delta \nu_0$ = multiplet splitting shift, and b = a numerical factor of the order $-^2/_3$.[6] No data are yet available on the multiplet splitting term, $\Delta \nu_0$, of organic molecules, but it is likely to be equal for all hydrocarbons. Equation (2) therefore implies the existence of a linear relation between the oscillator strength and the characteristic frequency of the "dispersion-electron" of hydrocarbons.

As one can observe the constancy of γ within other families of organic molecules,[6] this relation should hold more widely. The lack of reliable absolute intensity data, particularly in the vacuum ultraviolet where the characteristic absorption band of the saturated hydrocarbons is located, precludes a direct test of the postulate made. The constancy of γ in spite of the wide variation in ν_i (0.8 to 2.5 × 10^{15} sec.$^{-1}$) and in a_i encountered in the range of hydrocarbons reported in Table I suggests, however, that a relationship at least similar to the proposed one exists. (A plot of the oscillator strength f_1,[7] *versus* ν_1 shows that the data lie on smoothly ascending curves, which are, however, characteristic of each family of (aromatic) hydrocarbons so tested, and not universal for all hydrocarbons as first hoped for.) The utility of Equation (2) for γ = const. consists in the possibility of expressing the refractive dispersion of hydrocarbons as a function of ν_i alone, thereby facilitating the rational treatment of this easily determined physical property.

TABLE I

COMPARISON OF VERDET CONSTANT[a] AND REFRACTIVE DISPERSION[b] OF HYDROCARBONS

Substance	$V_D \times 10^2$	$V/\Delta n$[c]	$\Delta V/\Delta n$[d]
n-Pentane	1.159	1.188	1.11
n-Decane	1.316	1.148	1.05
n-Hexadecane	1.359	1.12	1.03
11-*n*-Decyldocosane	1.423	1.12	1.01
Cyclopentane	1.238	1.08	0.96
Cyclohexane	1.247	1.05	.93
11-Cyclohexyl-*n*-heneicosane	1.440	1.12	1.00
1,1-Dicyclohexyl-*n*-heptane	1.443	1.11	0.99
Benzene	3.02	1.11	1.09
Toluene	2.726	1.065	1.11
Ethylbenzene	2.60	1.05	..
n-Propylbenzene	2.46	1.015[e]	..
p-Methylisopropylbenzene	2.30	0.986[e]	..
Diphenylmethane	3.38	1.04	..
Naphthalene	5.33	1.11	..
Methylnaphthalene	4.48	0.94[e]	1.105
Average	..	1.08 av. deviation ±0.05	..

[a] From Ref. 3. [b] From Ref. 4 and 5. [c] $\Delta n = n_{G'} - n_c$. [d] $V = V_{4359} - V_D$. [e] These scattered values may be due to inaccurate refractive dispersion data.

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(1) M. Scherer, "Pub. sci. tech. ministere de l'air," France, No. 50, (1934), p. 1-91. "Science of Petroleum," Vol. 2, London, 1938, p. 1220.

(2) S. Broersma, H. I. Waterman, J. B. Westerdijk and E. C. Wiersma, *Physica*, **10**, 97 (1943).

(3) E. G. Foehr, Ph.D. Thesis, Pennsylvania State College, 1944.

(4) R. E. Thorpe and R. G. Larsen, *Ind. Eng. Chem.*, **34**, 853 1942).

(5) W. J. C. de Kok and H. I. Waterman, *Chem. Weekblad*, **37**, 454 (1940).

(6) W. Schütz, "Magnetooptik" in Wien-Harms Handb. der Experimental physik, Vol. 16, Part 1, Leipzig, 1936, p. 80-141.

(7) From unpublished experimental data by Spectroscopic Department, Shell Development Co., Emeryville, Calif.

Since the dispersion of both the refractivity and the Verdet constant is governed by the term $\Sigma A_i/(\nu_i^2 - \nu^2)$, constancy of the ratio $\Delta V/\Delta n$ would be indicative of the fact that the electronic transitions responsible for both are identical. The data in the last column show that this expectation is essentially fulfilled, as has also been found for various aliphatic oxygen compounds.[8]

[8] W. J. Lewis and E. J. Evans, *Phil. Mag.*, **13**, 265 (1932).

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIF.

RECEIVED MAY 24, 1948

The Cryoscopic Behavior of 1,1-Dimethylcyclohexane Containing Certain Hydrocarbon Impurities[1]

BY G. L. EVANS,[2] K. W. GREENLEE, J. M. DERFER AND C. E. BOORD

A short investigation has been made concerning the cryoscopic behavior of 1,1-dimethylcyclohexane upon introduction of certain selected hydrocarbon impurities. This study was prompted by the observation that introduction of a small amount of *cis*-1,2-dimethylcyclohexane as an impurity in 1,1-dimethylcyclohexane caused an increase in the freezing point of the latter hydrocarbon, instead of the normal lowering. Although similar irregularities caused by solid solution formation have been observed in several binary hydrocarbon systems studied in detail by other workers,[3,4,5,6] it was thought that this new information would prove helpful because of the widespread reliance on cryoscopic data as criteria of purity.

The results of this investigation are summarized in Table I.

It will be noted that of the solutes used only *n*-heptane and *n*-butylcyclohexane produced normal freezing point lowering; *cis*-1,2-dimethylcyclohexane actually raised the freezing point, and the remaining solutes caused only a fraction of the normal lowering. In every case of abnormal behavior the apparent purity as calculated from the freezing point data was, of course, too high.

TABLE I

CRYOSCOPIC BEHAVIOR OF 1,1-DIMETHYLCYCLOHEXANE CONTAINING HYDROCARBON IMPURITIES

Solute (impurity)	Total mole % impurity added	Freezing point (°C.)	Observed Δt (°C.)	Expected[a] Δt (°C.)	Actual purity[b] (mole %)	Apparent purity[a] (mole %)
None added	0	−35.83 ± 0.04	....	....	99.04	...
cis-1,2-Dimethylcyclohexane	0.931	−35.66 ± .05	+0.17	−2.25	98.11	99.11
	1.97	−35.42 ± .07	+0.41	−4.79	97.07	99.21
None added	0	−35.52 ± .04	....	....	99.17	...
trans-1,2-Dimethylcyclohexane	0.648	−35.58 ± .04	−0.06	−1.57	98.52	99.15
	1.33	−35.69 ± .06	−0.17	−3.22	97.84	99.10
None added	0	−36.21 ± .03	....	....	98.88	...
trans-1,4-Dimethylcyclohexane	0.676	−37.23 ± .02	−1.02	−1.66	98.20	98.4[illegible]
	1.35	−38.39 ± .05	−2.18	−3.29	97.53	97.98
None added	0	−35.64 ± .02	....	....	99.12	...
Cyclohexane	1.26	−36.44 ± .04	−0.80	−3.05	97.86	98.79
	2.30	−37.09 ± .03	−1.45	−5.59	96.82	98.52
None added	0	−35.79 ± .03	....	....	99.06	...
2,2,3-Trimethylbutane	0.671	−35.97 ± .03	−0.18	−1.62	98.39	98.98
	1.59	−36.10 ± .05	−0.31	−3.85	97.47	98.93
None added	0	−35.58 ± .04	....	....	99.15	...
n-Heptane	0.798	−37.49 ± .02	−1.91	−1.92	98.35	98.36
	1.19	−38.36 ± .02	−2.78	−2.87	97.96	98.00
None added	0	−35.74 ± .05	....	....	99.08	...
n-Butylcyclohexane	0.643	−37.25 ± .05	−1.51	−1.54	98.44	98.45
	1.04	−38.23 ± .04	−2.49	−2.52	98.04	98.05

[a] These data were calculated from the approximate equation $\log_{10} p = 2 - (A/2.303)(t_{f_0} - t_f)$ where p = purity (actual or apparent) in mole per cent., t_{f_0} = freezing point at 100% purity t_f = experimental freezing point (actual or expected) and $A = \Delta H^\circ_m/RT_{f_0}$ in which ΔH°_m is the heat of fusion (per mole). Values for t_{f_0} (−33.54°) and A (0.0042 deg.$^{-1}$) had been given by the American Petroleum Institute Research Project 44 in Selected Values of Properties of Hydrocarbons (Circular of the National Bureau of Standards C461) Table 7z. [b] The original purity of each sample was calculated from its freezing point using the equation and data mentioned in footnote *a*, assuming that no impurity leading to abnormal behavior was already present. The subsequent (lower) purities were obtained from the original purities by subtracting the mole percentages of impurity added.

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[1] An abstract of part of a dissertation submitted by George L. Evans in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry. The investigation was sponsored by the American Petroleum Institute (Research Project 45) in coöperation with The Ohio State University Research Foundation.

[2] Present address: E. I. du Pont de Nemours and Co., Inc., Experiment Station, Wilmington, Delaware.

[3] Smittenberg, Hoog and Henkes, THIS JOURNAL, **60**, 17 (1938).

[4] Took and Aston, *ibid.*, **67**, 2275 (1945).

[5] Fink, Cines, Frey and Aston, *ibid.*, **69**, 1501 (1947).

[6] Hirschler, King and Faulconer, paper presented before the Petroleum Division at the Chicago, Illinois, meeting of the American Chemical Society, April, 1948.

The ability to form mixed crystals (solid solutions) is common to all hydrocarbons having low heats and entropies of fusion, as has 1,1-dimethylcyclohexane. Such molecules rotate in the solid phase below their melting points and possess considerable mobility of structure, enabling solute molecules of similar size and shape to be accommodated in the crystal lattice without fusion of the crystal. Solute molecules such as *n*-heptane and *n*-butylcyclohexane which would interfere with the rotation cannot be incorporated into the crystal lattice of 1,1-dimethylcyclohexane, hence, solid solution formation does not occur, and normal cryoscopic behavior is observed. The fact that abnormal behavior occurs when 2,2,3-trimethylbutane is used as the solute confirms the idea that it is the over-all size and shape of the molecule rather than its molecular species which determines whether or not a solid solution will result.

Experimental

Hydrocarbons.—The 1,1-dimethylcyclohexane and the hydrocarbons used as "impurities" were materials taken from the stock of the American Petroleum Institute Research Project 45 and were of good purity (99.0 mole % ± 0.5). When practicable, the 1,1-dimethylcyclohexane was separated from the "impurity" by fractional distillation at about 25-plate efficiency and re-used (after its freezing point had been checked) in the next determination, otherwise fresh solvent was used.

Apparatus.—The apparatus used in determining freezing points was essentially that described by Glasgow, Streiff and Rossini.[7] Temperatures were measured by means of a platinum resistance thermometer in connection with a Mueller resistance bridge (Leeds and Northrup, Type G-2). This thermometer was calibrated at the National Bureau of Standards.

Acknowledgment.—Grateful acknowledgment is made for the criticisms and suggestions of Drs. F. D. Rossini of the National Bureau of Standards and M. R. Cines of the Phillips Petroleum Company.

[7] Glasgow, Streiff and Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 16, 1948

The Reaction of Diazonium Salts with Some 2-Thiouracils

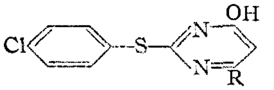
BY ELVIRA A. FALCO, GEORGE H. HITCHINGS AND PETER B. RUSSELL

Lythgoe, Todd and Topham[1] showed that pyrimidines suitably substituted in the 2,4-, 4,6- or 2,4,6-positions would undergo coupling with diazotized anilines in sodium carbonate or bicarbonate solution giving 5-phenylazo derivatives. They also investigated the structural conditions governing the coupling of pyrimidine derivatives. For this last purpose the dyes were not isolated, color being taken as an indication of coupling. They reported that 2-thiol-4,6-dihydroxy-, 2-thiol-4,6-diamino- and 2-thiol-4-hydroxy-6-methyl-pyrimidine underwent coupling.

In a recent paper Polonovski and Pesson[2] reexamined the reaction and arrived at the same general conclusions as the English authors regarding the nature of the products and the structural limitations of the reaction. They were, however, unable to couple 2-thiol-4-hydroxy-6-methylpyrimidine with diazonium salts, although they synthesized the brownish red 2-thiol-4-hydroxy-5-phenylazo-6-methylpyrimidine by condensation of thiourea with ethyl phenylazoacetoacetate.

Some time ago we examined the reactions of 2-thiol-4-hydroxypyrimidine and 2-thiol-4-hydroxy-6-methylpyrimidine with diazotized *p*-chloroaniline. When either of these compounds was allowed to react with the diazonium salt in carbonate or bicarbonate solution the following sequence of changes occurred. The solution turned pinkish red, solid separated and nitrogen was evolved. Examination of the solids revealed that they were not the expected 5-phenylazo compounds since on recrystallization from alcohol they were obtained colorless.

The product from 2-thiol-4-hydroxypyrimidine analyzed for $C_{10}H_7ON_2SCl$, while that from 2-thiol-4-hydroxy-6-methylpyrimidine gave analytical figures which agreed with the formula $C_{11}H_9ON_2SCl$. On heating with concentrated hydrochloric acid at 100° these compounds gave *p*-chlorothiophenol and uracil or 6-methyluracil, respectively. We concluded therefore that they were 2-(*p*-chlorophenylthio)-4-hydroxypyrimidine (I) and 2-(*p*-chlorophenylthio)-4-hydroxy-6-methylpyrimidine (II).



I, R = H
II, R = CH_3

The formation of *p*-chlorophenyl ethers of 2-thiolpyrimidines by this method is analogous to the formation of unsymmetrical diaryl and alkylaryl sulfides by the reaction of diazonium salts with the sodium salts of thiophenols or mercaptans.[3] In this instance the reaction proceeds *via* the diazosulfide (III) (R = alkyl or aryl). We did not isolate any product corresponding to III from the reaction of 2-thiolpyrimidines with diazonium salts. The fact that nitrogen is evolved in the cold would indicate that the 2-diazosulfides of pyrimidines are less stable than their aryl or alkyl analogs.

$$ArN_2^+X^- + RSNa \longrightarrow \underset{\text{III}}{ArN{=}NSR} \longrightarrow ArSR + N_2$$

Unfortunately Polonovski's paper, no doubt unintentionally, gives the impression that previous students of the coupling reaction have been content to observe the appearance or non-appearance of a color reaction. In fact, Todd[1] demon-

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[1] Lythgoe, Todd and Topham, *J. Chem. Soc.*, 315 (1944).

[2] Polonovski and Pesson, *Bull. soc. chim.*, [5] **15**, 688 (1948).

[3] Stadler, *Ber.*, **17**, 2675 (1884); Ziegler, *Ber.*, **23**, 2469 (1890).

strated by isolation and synthesis by alternative routes the nature of the coupling products in several instances and established the structural requirements for the occurrence of the reaction. Polonovski and Pesson have usefully extended these observations, but have failed to mention the considerable use to which the reaction already has been put in synthetic work.[4,5,6,7,8]

Experimental

2-(*p*-Chlorophenylthiol)-4-hydroxypyrimidine.—Five grams of *p*-chloroaniline in 100 ml. of *N* hydrochloric acid was diazotized with 3.0 g. of sodium nitrite at 0°. Seven and one-half grams of sodium bicarbonate was added to the solution and then the whole was added rapidly with stirring to a solution of 5 g. of 2-thiol-4-hydroxypyrimidine in 4 l. of water. When the addition of the diazonium solution was complete, 10 ml. of a 15% solution of sodium carbonate was added. The solution turned pinkish in color, some gas was evolved and a solid began to form. After standing two hours the solution was neutralized with acetic acid and the solid filtered off. The pinkish powder (5.4 g.), after recrystallization from alcohol containing a little pyridine gave colorless octahedra, m. p. 243-245°.

Anal. Calcd. for $C_{10}H_7ON_2SCl$: C, 50.4; H, 3.0; N, 11.7. Found: C, 50.4; H, 2.9; N, 11.5.

2-(*p*-Chlorophenylthio)-4-hydroxy-6-methylpyrimidine.—To a solution of 5 g. of 2-thiol-4-hydroxy-6-methylpyrimidine in 3 l. of water was added a diazonium solution prepared from 8.9 g. *p*-chloroaniline (2 moles), followed by 16.6 ml. of a 15% solution of sodium carbonate. After standing for two hours, the solution was neutralized with acetic acid and the reddish solid was filtered off (8.3 g.). After washing with warm ethanol to remove some red material the substance was recrystallized from boiling ethanol. It formed colorless rectangular prisms, m. p. 223.5°.

Anal. Calcd. for $C_{11}H_9ON_2SCl$: N, 11.1. Found: N, 11.3.

Hydrolysis of *p*-Chlorophenylthioethers with Hydrochloric Acid.—One gram of each of the above compounds was refluxed with 25 ml. of 6 *N* hydrochloric acid for three hours. Steam distillation gave *p*-chlorothiophenol in about 75% yield, m. p. 53-54°; benzoyl derivative, m. p. 74-74.5°.[9] The acid solution on evaporation gave uracil or 6-methyluracil, according to the starting material, in about 80% yield. The compounds were identified by melting points, ultraviolet absorption spectra and analyses.

Anal. Calcd. for $C_4H_4N_2O_2$: C, 42.8; H, 3.6. Found: C, 42.5; H, 3.6. Calcd. for $C_5H_6N_2O_2$: C, 47.7; H, 4.8. Found: C, 47.6; H, 4.4.

The authors are indebted to Samuel W. Blackman for the microanalyses reported here.

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[4] Baddiley, Lythgoe and Todd, *J. Chem. Soc.*, 318 (1944).

[5] Kenner, Lythgoe and Todd, *ibid.*, 652 (1944).

[6] Todd, *ibid.*, 647 (1946).

[7] King and King, *ibid.*, 731, 943 (1947).

[8] King, King and Spensley, *ibid.*, 1247 (1947).

[9] Daccomo, *Chem. Centr.*, **62**, II, 657 (1891).

THE WELLCOME RESEARCH LABORATORIES
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The Surface Area of Vermiculite

BY B. L. HARRIS

The surface area of vermiculite before and after exfoliation was measured by adsorption of nitrogen at −195° by the method of Brunauer, Emmett and Teller[1] in order to ascertain whether the area was large enough that the material might be used as a catalyst support. The area of the unexfoliated sample was measured by nitrogen adsorption and found to be 0.52 sq. m./g., giving a calculated average thickness of the platelets of 1.8 microns when the theoretical density of 2.13 is assumed. This indicates that the material was thoroughly fissured before exfoliation.

A sample of the vermiculite was exfoliated by heating for five minutes at 950°, resulting in a silvery-white accordion-like structure. The loss in weight on exfoliation was 19.6%. The surface area of this sample was 10.35 sq. m./g., giving a calculated platelet thickness of 0.091 micron. The structure of vermiculite consists of sheets of $(OH)_4Mg_6(Si, Al)_8O_{20}$ of 9.26 Å. thickness with alternate layers of 8 H_2O spaced the order of 4.8 Å.[2] It was hoped that the platelet spacing might approximate this order of magnitude, resulting in a very large surface area. The smaller area, corresponding to a thickness some 200 times as great, agrees with the conclusion of Gruner that the structure collapses above 750° and that exfoliation is mechanical, due to the formation of steam.

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[1] S. Brunauer, P. H. Emmett and Edward Teller, THIS JOURNAL, **60**, 309 (1938).

[2] J. W. Gruner, *Am. Mineral.*, **19**, 557 (1934).

DEPARTMENT OF CHEMICAL ENGINEERING
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RECEIVED JULY 28, 1948

The Interaction of Purified Antibody with Homologous Hapten. Antibody Valence and Binding Constant

BY HERMAN N. EISEN[1] AND FRED KARUSH[2]

As part of a study of the relation between protein structure and specificity we are investigating the properties of soluble complexes formed between purified antibody and homologous haptens. Rabbits were immunized with sheep serum coupled with diazotized *p*-arsanilic acid. Purified antibody, homologous to *p*-azophenylarsonic acid (R), was obtained[3] by treating pooled antisera with human erythrocyte stromata coupled with diazotized *p*-arsanilic acid (R-stromata). After several washings with 0.16 *M* sodium chloride, the antibody was eluted from R-stromata by acidification (*p*H 3.8) with acetic acid. The R-stromata was removed by centrifugation and the supernate, which contained the antibody, was neutralized. In the antibody solutions thus prepared at least 90% of the protein was specifically precipitable with R-stromata, in agreement

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[1] Research Fellow, National Institute of Health.

[2] Investigation conducted during tenure of a Fellowship in Cancer Research of the American Cancer Society, recommended by the Committee on Growth of the National Research Council.

[3] K. Landsteiner and J. van der Scheer, *J. Exp. Med.*, **63**, 325 (1936).

with the observations of Campbell, *et al.*,[4] who also prepared purified antibody by exposure to acid *p*H (3.5). Controls involving the treatment with R-stromata of normal rabbit serum, a mixture of bovine γ-globulin and purified antibody, and bovine γ-globulin alone, showed no appreciable non-specific precipitation. Protein concentrations were determined by ultraviolet absorption[5]; the validity of this procedure was assured by low R-stromata blanks, and by the characteristic shape of the absorption curves.

The binding of homologous haptenic dye *p*-(*p*-hydroxyphenylazo)-phenylarsonic acid by purified antibody was determined by equilibrium dialysis. One ml. aliquots of an antibody solution of known protein concentration (0.15%) containing buffer and salt (*p*H 7.4, 0.01 *M* PO_4, 0.16 *M* NaCl) were placed inside 0.25-in. dialysis bags. These were equilibrated against equal volumes of hapten in buffered saline whose initial dye concentrations were accurately known. The free dye concentrations in equilibrium with the bound dye were determined by measuring the spectral absorption, at 440 mμ, of the outside solutions, after suitable dilution and adjustment to strongly alkaline *p*H. The concentrations of bound dye were calculated from the values for the free equilibrium and initial dye concentrations, the former ranging from 5×10^{-6} *M* to 8×10^{-5} *M*. This calculation required a correction, due to adsorption of dye on the dialysis bag, amounting to 11% of the free dye concentration. The following (which corresponds to the third point in Fig. 1) represents a typical calculation: initial dye concentration = 3.96×10^{-5} *M*, free equilibrium dye concentration = 1.18×10^{-5} *M*, concentration of bound dye = 1.35×10^{-5} *M*, moles hapten bound per mole protein[6] (r) = 1.45.

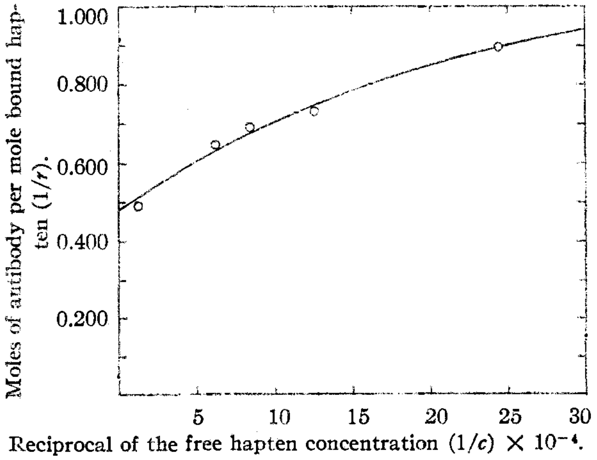

Fig. 1.

By plotting the reciprocal of moles hapten bound per mole antibody ($1/r$) against the reciprocal of free hapten concentration ($1/c$) the binding capacity is obtained from the extrapolated value of $1/r$.[7] As could be anticipated from the known heterogeneity of antibodies,[3,8] the curve obtained was not linear. In such a situation the average intrinsic association constant can be shown to be equal to the value of $1/c$ at which one-half the binding sites are occupied, if it is assumed that the variation in the free energy of binding among the various sites can be described by a Gaussian distribution function.[9] Such an assumption has been made previously by Pauling, *et al.*,[8] to describe hapten inhibition data.

The binding data obtained at room temperature (29°) with the hapten indicated above are summarized in Fig. 1. Extrapolation yields a value of 2 for the binding capacity ("valence") of the antibody, within an accuracy of 10%. The value of the intrinsic association constant is 3.5×10^5, corresponding to $\Delta F^0 = -7.7$ kcal. per mole hapten.

Antisera prepared as in these experiments by Campbell, *et al.*,[4] contained about 1.0% antibody for R-group, whereas our yields of purified antibody correspond to an initial antibody concentration in antiserum of about 0.04%. Either our antisera were far less potent than Campbell's, or the antibody removed by our purification procedure comprised only a small fraction of the total antibody present in the antiserum, in which case the above association constant would measure the average binding energy of only the most reactive antibody molecules.

Acknowledgment.—We are indebted to Professor R. Keith Cannan for the laboratory facilities so generously made available to us during the conduct of this investigation.

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[4] D. H. Campbell, R. H. Blaker and A. B. Pardee, This Journal, **70**, 2496 (1948).

[5] H. N. Eisen, *J. Immunol.*, **60**, 77 (1948).

[6] Assuming a molecular weight for rabbit antibody of 160,000

[7] I. M. Klotz, F. M. Walker and R. B. Pivan, This Journal, **68**, 1486 (1946)

[8] L. Pauling, D. Pressman and A. L. Grossberg, *ibid.*, **66**, 784 (1944).

[9] F. Karush and M. Sonenberg, *ibid.*, in press.

DEPARTMENTS OF CHEMISTRY AND MEDICINE
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RECEIVED SEPTEMBER 22, 1948

Preparation and Properties of Several Cyclohexyl-alkyl-substituted Ketene Dimers

BY CARL M. HILL AND GILBERT W. SENTER

It has been demonstrated that tertiary aliphatic amines dehydrohalogenate acid halides with the formation of ketene monomers and dimers.[1] Sauer[2] has reported the dehydrohalogenation of several fatty acid halides by tertiary aliphatic amines to yield ketene dimers.

This paper describes the dehydrohalogenation of five omega-cyclohexyl-substituted acid chlorides (of type $C_6H_{11}\cdot(CH_2)_n\cdot COCl$) by triethylamine.

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[1] Hanford and Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, New York, N. Y., 1946, pp. 138–140.

[2] Sauer, This Journal, **69**, 2444 (1947)

TABLE I

KETENE DIMERS

-Cyclohexyl, ketene dimers	B. p. °C.	B. p. Mm.	Yield,[a] %	$n^{20}D$	Formula	Analyses, % Mol. wt.[b] Found	Mol. wt.[b] Calcd.	Carbon Found	Carbon Calcd.	Hydrogen Found	Hydrogen Calcd.
,ketene	108–111	2	28	1.5001	$C_{16}H_{24}O_2$	250.7	248.4	76.68	77.36	10.08	9.74
,methyl	190–191	6	40	1.4925	$C_{18}H_{28}O_2$	281.9	276.4	78.09	78.22	10.38	10.21
β-, ethyl	115–120	2	18	1.4850	$C_{20}H_{32}O_2$	278.2	304.5	79.15	78.91	10.64	10.52
γ-, propyl	150–152 (m. p., 16–17)	1	25	1.4860	$C_{22}H_{36}O_2$	331.8	332.5	79.53	79.39	11.04	10.90
δ-, butyl	128–130 (m. p., 33–35)	1	36	....	$C_{24}H_{44}O_2$	351.6	360.5	80.46	79.88	11.56	11.18

[a] Based upon the amount of unrecovered acid chloride. [b] Determined cryoscopically.

The ketene dimers thus formed have not been previously reported.

The dimers gave a negative test with silver nitrate; positive tests with potassium permanganate, and bromine. *p*-Nitrophenylhydrazine reacted with the dimers to yield the hydrazones.

Experimental

The procedure followed in dehydrohalogenation of the the acid chlorides was similar to that reported by Sauer.[2] Equal molar quantities of acid chloride and triethylamine were allowed to react in dilute ether solution. Each dimer was isolated in its pure form by distillation under diminished pressure. A quantity of unreacted acid chloride was recovered from each experiment.

Analytical data and physical constants of the five ketene dimers are shown in Table I.

***p*-Nitrophenylhydrazones.**—The hydrazones were prepared according to the procedure described by McElvain.[3] The color of the hydrazones varied from lemon to deep orange.

Analytical data and physical properties of the hydrazones are given in Table II.

TABLE II

p-NITROPHENYLHYDRAZONES OF DIMERS

-Cyclohexyl, ketene dimer	Hydrazone	N, % Found	N, % Calcd.	M. p.,[a] °C.	Yield, %
,ketene	$C_{28}H_{34}O_4N_6$	16.29	16.21	102–103 d.	19
,methyl	$C_{30}H_{38}O_4N_6$	14.89	15.38	104–105 d.	41
β-, ethyl	$C_{32}H_{42}O_4N_6$	14.05	14.63	110–111 d.	53
γ-, propyl	$C_{34}H_{46}O_4N_6$	14.10	13.95	113–114 d.	44
δ-, butyl	$C_{36}H_{54}O_4N_6$	[b]	...	84–85	57

[a] Melting points are uncorrected. [b] Compound decomposed upon prolonged drying.

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[3] McElvain, "Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 199.

DEPARTMENT OF CHEMISTRY
TENNESSEE A. AND I. STATE COLLEGE
NASHVILLE 8, TENNESSEE

RECEIVED AUGUST 25, 1948

The Preparation and Vapor Pressure of Bromopentachloroethane; the Vapor Pressures of Heptachloropropane and Dibromotetrachloroethane

BY TAKERU HIGUCHI,[1] NOBORU ENDOW[2] AND JOHN E. WILLARD

When confronted with a need for a sample of bromopentachloroethane we were not able to find any record of its preparation in the literature. We have prepared a sample by the photobromination of pentachloroethane at elevated temperature, using a technique similar to that previously employed in this laboratory for the preparation of bromotrichloromethane from chloroform and bromine.[3] The over-all reaction is

$$C_2Cl_5H + Br_2 \longrightarrow C_2Cl_5Br + HBr$$

Eastman Kodak Co. technical pentachloroethane was washed several times with concentrated sulfuric acid, with water, with 20% potassium hydroxide solution and again with water. After drying with phosphorus pentoxide, approximately 1 mole (125 cc.) was then mixed with one mole (55 cc.) of bromine and 75 cc. of carbon tetrachloride. This mixture was illuminated by two 500-watt Mazda projection bulbs placed next to the flask which was sealed to a water-cooled reflux condenser. The heat from the bulbs was sufficient to maintain the solution at or near the boiling temperature. Since the photobromination of chloroform has been found to be inhibited by both oxygen and water, the following precautions were taken to exclude gross amounts of these substances: (a) a slow stream of nitrogen was bubbled through the solution and allowed to pass out through the condenser throughout the course of the reaction; (b) 5 g. of phosphorus pentoxide was added to the reaction flask.

Initial attempts to prepare bromopentachloroethane by this method, from mixtures of bromine and pentachloroethane without carbon tetrachloride, led to a mixture of products. Because of the possibility that this might be the result of reactions favored by the relatively high temperature of the boiling point of the pentachloroethane (155°), carbon tetrachloride was added to reduce the boiling point.

After a week of continuous illumination the reaction solution solidified on cooling. The weight of this crude product was 200 g. Following three recrystallizations from small amounts of carbon tetrachloride large white crystals were obtained which melted with decomposition in the range of 180 to 200° when heated in sealed evacuated tubes. An estimate of the molecular weight and vapor pressure was obtained from this sample by measuring the gas pressure produced in a known volume by a weighed sample as a function of temperature. This was accomplished by placing the sample in an evacuated sealed bulblet in a sidearm of an evacuated thermostated flask which was connected to an open-end mercury manometer,[4] the middle section of which was made of flexible rubber suction tubing. The sample tube was broken with a glass-enclosed magnetic hammer. By means of a leveling bulb the mercury was maintained at an index mark on the glass side arm of the flask which connected with the manometer, thus maintaining a constant gas volume as the pressure

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[1] Present address: Department of Pharmacy, University of Wisconsin, Madison, Wis.

[2] Present address: Hanford Engineer Works, General Electric Co., Richland, Wash.

[3] (a) Bohlmann and Willard, THIS JOURNAL, 64, 1342 (1942); (b) Higuchi, Ph.D. Thesis, University of Wisconsin, 1943.

[4] The apparatus used in these determinations was constructed by Norman W. Rosenberg with the aid of funds from the National Youth Administration. Details of modifications and applications are given in the Masters' degree thesis of Noboru Endow filed with the Library of the University of Wisconsin in January, 1948.

changed due to vaporization of the sample. The pressure was read as the difference in heights of the mercury columns. The connection from the flask to the manometer entered the mineral oil thermostating-bath through a bushing in the bottom of the silver-soldered copper can and the index mark was viewed through a window in the side of the can. Experiments showed that no correction was necessary for the vapor pressure of mercury, thus indicating that the time required for the mercury vapor (which was always at a lower pressure than the organic vapor) to diffuse from the narrow side arm into the flask was long compared to the time involved in the experimental measurements.

Three experiments made on the freshly purified samples believed to be bromopentachloroethane gave linear plots of the logarithm of the sublimation pressure against the reciprocal of the absolute temperature over the temperature range of about 110 to 160°. A sharp break in the curve was found in each case at the temperature of total vaporization of the sample. The average molecular weights calculated for the totally vaporized system at the break in the curve were 280, 280 and 285 as compared to the theoretical value of 281 for C_2Cl_5Br. Chemical analysis of a sample of the compound by the Carius wet oxidation method combined with the Moser–Miksh iodide metathesis method gave the results:

	Experimental	Theoretical (C_2Cl_5Br)
Bromine	27.8	28.3
Chlorine	61.2	63.2

Samples of the compound prepared by the photobromination of pentachloroethane with radiobromine of known specific activity showed a specific activity corresponding to the formula C_2Cl_5Br.

The average vapor pressure of the C_2Cl_5Br over the range tested is given by the relation $\log p = (-2.32 \times 10^3/T) + 6.33$, where p is the pressure in cm. of Hg and T is the absolute temperature.

Heptachloropropane.—A single series of measurements of the vapor pressure of $CCl_3CCl_2CHCl_2$ as a function of temperature with the apparatus described above gave a straight line plot of $\log p$ *vs.* $1/T$ for five points taken over the range of 140 to 200°. These data gave the expression $\log p = (-1.82 \times 10^3/T) + 5.11$. The sample used was obtained from the Eastman Kodak Company, which specified its melting point as 30°. The fact that the molecular weight of the sample calculated from the observed pressure at the temperature of total vaporization was 278 as compared to the theoretical value of 285 indicates that the sample was probably not highly impure. Prins,[5] Farlow[6] and Henne and Ladd[7] have reported values for the boiling point of $CCl_3CCl_2CHCl_2$ at several pressures. Their values are shown in Table I for comparison with those determined from the equation given above.

TABLE I

Pressure, mm.	Obs. b. p., other workers. °C.	B. p. from vapor pressure equation, °C.
10	110–113 (Farlow)	83
32	137–140 (Farlow)	122
43	147 (Prins)	133
90	164 (Prins)	
	163–166 (Henne and Ladd)	165

The relation of $\log p$ to $1/T$ for Farlow's data is not in agreement with that for Prins' data and neither is in agreement with our vapor pressure determinations. These latter show a consistent relationship over a 60° range under conditions of measurement which have given agreement with well established values for the vapor pressure of carbon tetrachloride and have given consistent vapor pressure and molecular weight values for a number of compounds tested.

Dibromotetrachloroethane.—A similar determination of the vapor pressure of $C_2Cl_4Br_2$ gave the expression $\log p = (-2.74 \times 10^3/T) + 7.18$ over the range from 110 to 180°. These results are in satisfactory agreement with those of Carrico and Dickinson[8] who made similar measurements from 50 to 150°. At 50° they observed a pressure of 0.4 mm. while the value calculated from our data is 0.5 mm. At 150° they found 51 mm. and our data indicate 50 mm. Following complete vaporization of the $C_2Cl_4Br_2$, the vapor was heated to 215° without more than a few per cent. decomposition over the period of about half an hour, indicating greater thermal stability than that of the C_2Cl_5Br reported above.

The work reported here was done as part of a program to which support was given by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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(5) Prins, *J. prakt. Chem.*, **89**, 414 (1914).

(6) Farlow, "Organic Synthesis," **17**, 58 (1937).

(7) Henne and Ladd, THIS JOURNAL, **60**, 2491 (1938).

(8) Carrico and Dickinson, THIS JOURNAL, **57**, 1344 (1935).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

RECEIVED JUNE 22, 1948

The Structure of Pellitorine[1]

BY MARTIN JACOBSON

The isolation from plant materials of several pungent N-isobutylamides of aliphatic unsaturated acids has been reported, namely, spilanthol (N-isobutyl-4,6-decadienamide) (I) from the flower heads of *Spilanthes oleraceae* Jacquin[2] and *S. acmella* Murr.,[3] pellitorine (the N-isobutylamide of a decadienoic acid) from the roots of *Anacyclus pyrethrum* DC.,[4] N-isobutyl-2,6,8-decatrienamide (II) from the roots of *Heliopsis longipes* (A. Gray) Blake[5]; and herculin (N-isobutyl-2,8-dodecadienamide) (III) from the bark of *Zanthoxylum clava-herculis* L.[6]

Gulland and Hopton[4] had identified pellitorine as an isomer of spilanthol, but they did not determine the positions of the double bonds in the molecule. In view of the insecticidal activity of compounds I,[3,7] II[5] and III,[6] and since preliminary tests in the laboratories of the Bureau of Entomology and Plant Quarantine had indicated that pellitorine was also insecticidal,[6] it was of considerable interest to determine the points of unsaturation in this compound, with a possible consequent correlation between insecticidal activity and molecular structure.

The procedure used in this Laboratory for isolating pure pellitorine eliminated the repeated fractional distillations found by Gulland and Hopton to be necessary for its purification. A Skelly-

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(1) Report of a study made under the Research and Marketing Act of 1946.

(2) Gerber, *Arch. Pharm.*, **241**, 270 (1903); Asano and Kanematsu, *Ber.*, **65B**, 1602 (1932).

(3) Pendse, *et al.*, *Current Sci.*, **14**, 37 (1945); Gokhale and Bhide, *J. Indian Chem. Soc.*, **22**, 250 (1945).

(4) Gulland and Hopton, *J. Chem. Soc.*, 6 (1930).

(5) Jacobson, Acree and Haller, *J. Org. Chem.*, **12**, 731 (1947).

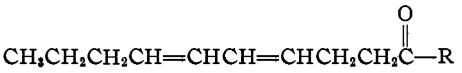
(6) Jacobson, THIS JOURNAL, **70**, 4234 (1948).

(7) Pendse, *et al.*, *J. Univ. Bombay*, **15A**, New Ser. Pt. 3, No. 20, 26 (1946).

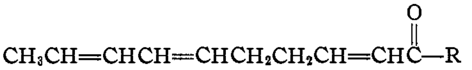
solve A extract of dry pellitory root (*Anacyclus pyrethrum* DC.)[8] was extracted with nitromethane, and the neutral fraction of the nitromethane-soluble portion was distilled. One crystallization, from Skellysolve A, of the fraction boiling at 155–165° (0.3–0.5 mm.) gave pure pellitorine in 0.14% yield, based on dry root.

Oxidation of pellitorine with alkaline permanganate resulted in the isolation of butyric, succinic and N-isobutyloxamic acids, showing that the double bonds occupy the 2- and 6-positions. Pellitorine is therefore N-isobutyl-2,6-decadienamide (IV).

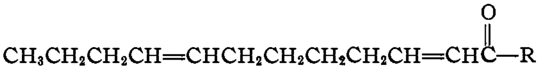
In tests[9] conducted with house flies (*Musca domestica* L.), a Deobase (refined kerosene) solution of pellitorine, used as a spray, showed paralyzing action equal to, and mortality somewhat greater than one-half that of pyrethrins tested at the same concentration.



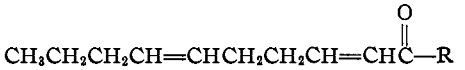
$$\mathrm{CH_3CH_2CH_2CH{=}CHCH{=}CHCH_2CH_2\overset{\overset{O}{\|}}{C}{-}R}$$ I



$$\mathrm{CH_3CH{=}CHCH{=}CHCH_2CH_2CH{=}CH\overset{\overset{O}{\|}}{C}{-}R}$$ II



$$\mathrm{CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH{=}CH\overset{\overset{O}{\|}}{C}{-}R}$$ III



$$\mathrm{CH_3CH_2CH_2CH{=}CHCH_2CH_2CH{=}CH\overset{\overset{O}{\|}}{C}{-}R}$$ IV

where R = $\mathrm{NHCH_2CH(CH_3)_2}$

Experimental[10]

Isolation of Pellitorine.—6070 g. of finely ground, dry pellitory root was extracted in a Soxhlet extractor with Skellysolve A. The solution was concentrated to *ca.* 700 ml. and extracted three times with 150-ml. and twice with 100-ml. portions of nitromethane. The combined nitromethane solution was freed of solvent under reduced pressure, the residue (27 g. of reddish-brown oil) taken up in ethyl ether, and the ether solution washed thoroughly with water, 5% hydrochloric acid solution, 5% potassium hydroxide solution, and finally with water. After being dried over sodium sulfate, the ether solution of the neutral fraction was freed of solvent completely, and the remaining 20 g. (0.33% of the bark) of viscous reddish-yellow oil solidified rapidly.

Vacuum distillation of this material, in an atmosphere of nitrogen, gave 8.5 g. of pale-yellow oil, b. p. 155–165° (0.3–0.5 mm.), which was dissolved in a small quantity of Skellysolve A, cooled in ice-salt, and filtered. The yield was 8.4 g. (0.14% based on dry bark) of colorless, feathery needles of pellitorine, m. p. 72° (lit.[4] m. p. 72°).

Oxidation of Pellitorine.—To a stirred suspension of 5 g. of pellitorine in 500 ml. of water, maintained at 70°, 18.8 g. of finely powdered potassium permanganate (equivalent to 4 moles of oxygen) was added in small portions. When the reaction mixture had become colorless, the manganese dioxide was filtered and washed thoroughly with warm water. The combined aqueous filtrates were concentrated down to 70 ml. and made acid to congo red with sulfuric acid. The solution was steam-distilled to remove the volatile acids and then extracted with ether in a continuous extractor. The ether solution was freed of solvent, and the residue was extracted with three 10-ml. portions of boiling Skellysolve B. Cooling of the hydrocarbon solution caused the separation of 2.5 g. (77%) of colorless feathery needles, m. p. 106–107°, containing nitrogen.

Anal. Calcd. for $C_6H_{11}NO_3$: N, 9.66; neut. equiv., 145. Found: N, 9.65; neut. equiv., 145.

The substance was identified as N-isobutyloxamic acid by a mixed melting-point determination with an authenic sample, m. p. 107°, prepared by the procedure of Malbot.[11]

The insoluble residue from the Skellysolve B extraction was taken up in a small amount of ethyl acetate, cooled in ice-salt mixture, and filtered. One recrystallization from a small amount of the same solvent gave 1.8 g. (69%) of colorless crystals in the form of clusters of needles, m. p. 188–189°.

Anal. Calcd. for $C_4H_6O_4$: mol. wt., 118. Found: mol. wt. (titration), 118.

The product was identified as succinic acid by a mixed melting point determination with an authentic specimen, m. p. 189°, and by preparing the *p*-phenylphenacyl ester, m. p. 208°.

The solution of steam-volatile acids obtained above was neutralized with sodium hydroxide solution, concentrated to a small volume on the steam-bath, and acidified to congo red with sulfuric acid. Steam distillation gave Duclaux values of 17.9, 15.9 and 14.6, identical with those given for butyric acid.[12]

The acid was shown to be butyric acid by evaporating the neutral solution to dryness and then preparing the *p*-phenylphenacyl ester, m. p. and mixed m. p. with an authentic sample, 81–82°.

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[8] Obtained from S. B. Penick & Co., New York, N. Y.

[9] These tests were made by W. A. Gersdorff and Miss S. F. McDuffie, of this Bureau.

[10] All melting points are corrected.

[11] Malbot, *Compt. rend.*, **104**, 229 (1887).

[12] McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 141.

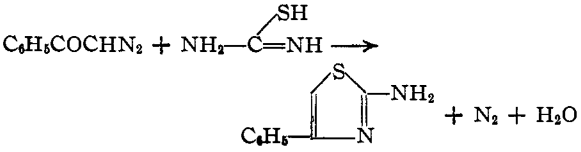
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
BELTSVILLE, MARYLAND

RECEIVED SEPTEMBER 30, 1948

The Reaction of Diazoketones with Thioamide Derivatives[1]

By L. Carroll King and F. M. Miller

Werner[2] found that the action of diazomethane on thiourea produced S-methylpseudothiourea. We have now observed that diazoketones react with thiourea and other thioamide derivatives to furnish substituted thiazoles. The reaction between diazoacetophenone and thiourea is illustrative.



The reaction is effected either by heating an intimate mixture of the reactants on the steam-bath, or by refluxing an alcoholic solution of the reaction components. The reaction in alcoholic solution is more satisfactory.[3]

Thiourea and ethyl diazoacetate react to give

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[1] For previous papers dealing with the synthesis of thiazoles, see King and co-workers: (a) THIS JOURNAL, **67**, 2242 (1945); (b) *ibid.*, **68**, 871 (1946); (c) *ibid.*, **69**, 1813 (1947).

[2] Werner, *J. Chem. Soc.*, **115**, 1168 (1919).

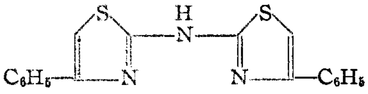
[3] A similar technique was employed for the preparation of quaternary salts from diazoacetophenone and salts of heterocyclic bases, King and Miller, THIS JOURNAL, **70**, 4154 (1948).

TABLE I

Compound	Formula	Yield, %	M. p., °C. Found[c]	M. p., °C. Reported	Composition,[h] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Amino-4-phenylthiazole	$C_9H_8N_2S$	67[a]	151–152	151–152[d]	...	...	..	..
Acetyl derivative	$C_{11}H_{10}ON_2S$		213–214	214.5–215[d]	...	...	..	..
2,4-Diphenylthiazole	$C_{15}H_{11}N_2S$	84[a]	91–92	92–93[e]	[i]	[i]	..	..
2-Amino-4-hydroxythiazole	$C_3H_4ON_2S$	34[a]	233–238, dec.	[f]	31.03	30.81	3.45	3.53
bis-(4-Phenyl-2-thiazolyl)-amine	$C_{18}H_{13}N_3S_2$	40, 78[b]	218–220	[g]	64.55	64.35	3.89	4.11
Acetyl derivative	$C_{20}H_{15}ON_4S_2$		132–133	[g]	63.16	63.45	4.25	4.14

[a] Based on the diazoketone. [b] The same compound was obtained with one or two molecular portions of diazoacetophenone, the latter giving the 78% yield, based on the dithiobiuret. [c] All melting points observed on a Fisher–Johns melting point block. [d] These compounds were compared with authentic material previously prepared in this Laboratory, reference 1.[a] [e] Hubacher, *Ann.*, **259**, 237 (1890). [f] Andreasch, *Monatsh.*, 8, 424 (1887), reported a melting point of 208° (dec.) for this material prepared by a different method. The compound from the diazoketone reaction melted in this range above. Similar results were obtained by Allen and VanAllan, "Organic Syntheses," **27**, 71 (1947). [g] Not previously reported. [h] Analysis by Miss P. Craig. [i] Calcd.: N, 5.62. Found: N, 5.69.

2-amino-4-hydroxythiazole (pseudothiohydantoin). Thiourea and thiobenzamide yield with diazoacetophenone, 2-amino-4-phenylthiazole and 2,4-diphenylthiazole, respectively. With the same diazoketone dithiobiuret gives bis-(4-phenyl-2-thiazolyl)-amine (I).[4]



I

Evidence for the structure of I lies in the method of formation, the analysis of the compound and its N-acetyl derivative, and the fact that it was unaffected by both acid and alkaline hydrolytic conditions, contrary to the known sensitivity of the thioureido group.[5] Compound I was also prepared by the action of phenacyl bromide on dithiobiuret.

Data for the compounds prepared are listed in Table I.

This investigation was supported by a grant from the Abbott Fund of Northwestern University.

Experimental

Preparation of Materials.—Diazoacetophenone was prepared as previously described.[3] Ethyl diazoacetate was prepared by the method of Curtius.[6] Thiobenzamide was prepared by suspending 60.5 g. (0.5 mole) of benzamide and 22.2 g. (0.10 mole) of phosphorus pentasulfide in 300 cc. of benzene and refluxing until the benzamide dissolved. The hot benzene solution was filtered and cooled, and the thiobenzamide collected. The material was recrystallized once from benzene m.p. 115–116°.[7] The dithiobiuret was a commercial sample, obtained through the courtesy of the American Cyanamid Company.

Preparation of the Thiazoles.—The techniques used will be illustrated by the following examples.

(a) **2-Amino-4-phenylthiazole.**—A solution of 1.46 g. (0.01 mole) of diazoacetophenone and 2.40 g. (0.012 mole) of thiourea in 20 cc. of absolute alcohol was refluxed for one hour. A portion of the alcohol was evaporated, a small amount of water and charcoal added, and the hot solution filtered and cooled. The separated material was collected and recrystallized from dilute aqueous alcohol.

(b) **bis-(4-Phenyl-2-thiazolyl)-amine.**—A solution of 2.92 g. (0.02 mole) of diazoacetophenone and 1.48 g. (0.011 mole) of dithiobiuret was refluxed for one hour in alcoholic solution. The product separated from the solution, was filtered and dissolved in excess acetone. Dilute aqueous alcohol was added and the acetone removed carefully on the steam-bath. The material crystallized on cooling and was recrystallized in the same manner.

bis-(4-Phenyl-2-thiazolyl)-amine was also prepared by refluxing 4.0 g. (0.02 mole) of phenacyl bromide and 1.50 g. (0.01 mole) of dithiobiuret in 25 cc. of alcohol for one hour. The separated material was suspended in alcohol and digested with ammonium hydroxide for one-half hour, filtered and washed with a small amount of alcohol. Recrystallization gave a material identical with that prepared above.

Acetyl Derivatives of Thiazoles.—These were prepared by the action of acetic anhydride on approximately 0.3 g. of the amino thiazole. The products were recrystallized from dilute aqueous alcohol.

Attempted Hydrolysis of I.—A solution of 0.1 g. of the material in 30 cc. of hot alcohol and 10 cc. of water was heated under reflux for three hours with 10 g. of barium hydroxide. Only the starting material was recovered, m.p. 217–218°.

Attempted acid hydrolysis performed in the same manner yielded identical results.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED AUGUST 23, 1948

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[4] The descriptive literature of the American Cyanamid Company records the reaction of chloroacetone and dithiobiuret to produce 2-thioureido-4-methylthiazole. Attempts to obtain the analogous 2-thioureido-4-phenylthiazole were not successful.

[5] Mehta and Krall, *J. Indian Chem. Soc.*, **12**, 635 (1935), report the effects of acid and basic hydrolysis of phenylthiourea.

[6] Curtius, *J. prakt. Chem.*, **38**, 401 (1888).

[7] Gabriel and Heyman, *Ber.*, **23**, 158 (1890).

The Verdet Constant of Certain Liquid Fluorocarbons

BY R. T. LAGEMANN

It is now known that certain fluorinated hydrocarbons possess some unusual physical properties. Although the density and viscosity are not particularly different from those of other liquids, the refractive index and ultrasonic velocity are both extraordinarily low. As an example, consider bis-(trifluoromethyl)-chlorononofluorocyclohexane. Here $n^{60}D$ is 1.3021,[1] only three liquids in Lange's "Handbook" have a lower value, and the ultrasonic velocity at 20° is 691.8 m./sec.,[1] also extremely low relative to other liquids. Since no values are known for the rotation of the plane of polarization of light by these liquids when placed in

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[1] Lagemann, Woolf, Evans and Underwood, THIS JOURNAL, **70**, 2994 (1948).

a magnetic field (Verdet constant), it was considered of interest to measure the Verdet constant to note if it, too, was unusual. Indeed, such was found to be the case.

The eight fluorocarbons studied are listed in Table I along with the measured values of their Verdet constants at 25° and for 5893 Å. It will be noted that the Verdet constants for these fluorinated hydrocarbons are extraordinarily low. The lowest value, that belonging to hexadecafluoroheptane, is about one-half the lowest previous value listed for any compound in the "International Critical Tables."

TABLE I

VERDET CONSTANTS OF SOME LIQUID FLUOROCARBONS AT 25° AND FOR 5893 Å[a]

Compound	Molecular weight	Density, 25°, g./cc.	Verdet constant, min./gauss-cm.
Hexadecafluoroheptane	388	1.7208	0.003500
(Trifluoromethyl)undecafluorocyclohexane	350	1.7871	,003751
bis-(Trifluoromethyl)-decafluorocyclohexane	400	1.8391	.003950
bis-(Trifluoromethyl)-chlorononofluorocyclohexane	416	1.8711	.005252
Chlorotrifluoroethylene polymer	713	1.9412	,009093
Chlorotrifluoroethylene polymer	866	1.9681	.009118
Chlorotrifluoroethylene polymer	911	1.9736	.009168
Fluorolube oil	860	2.0081	,004739

[a] The values of molecular weight and density found in this table were supplied by the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

Enough data are present in Table I to enable a calculation to be made of the molecular magnetic rotation[2] (utilizing MV/d for water at 25° and 5893 Å. as 0.2353). From this, values of the increment attributable to the fluorine atom may be made. For the cases presented here, the values vary, no doubt due to constitutive factors.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to Dr. Clifford Beck of the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee, for the loan of the compounds studied and for data concerning them. The author is also indebted to the Department of Physics of Columbia University, particularly to Dr. Lucy Hayner, for permission to use the Faraday Effect equipment.

Experimental

The measurements of the Verdet constant were made on the Faraday Effect apparatus of the Department of Physics, Columbia University. The procedures used were the same as those described by Slack[3] and the author[2] and will not be repeated here. The fluorocarbons were obtained through the courtesy of the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee, where they had been subjected to fractional distillation and their molecular weight and density measured.

EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA

RECEIVED SEPTEMBER 29, 1948

A Synthesis of Symmetric Phosphinic Acids

BY GENNADY M. KOSOLAPOFF

Michaelis and Wegner[1] were the first to employ the Grignard reaction in the synthesis of aromatic phosphinic acids under conditions which precluded the formation of by-products, by the reaction of aryl magnesium halides with N-piperidyl dichlorophosphate. Their lone paper on this subject, however, failed to state the yields obtained, although these were said to have been "good." Because of the relatively high cost of piperidine, it was thought that an equally good reagent might be found among the more available aliphatic dialkyl amines, which can be readily converted to the corresponding dichlorophosphates. This belief has been realized and excellent yields of some symmetric aromatic and aliphatic phosphinic acids have been readily attained by using N,N-diethylamine to block one reactive group of phosphorus oxychloride. The reaction, thus, may be extended to the aliphatic series, which has not been done previously.

Experimental

The yields and the properties of the products are given in the table.

SYMMETRIC PHOSPHINIC ACIDS PREPARED

Derivative	Yield, %	M. p., °C.	Equiv. weight Calcd.	Equiv. weight Found
bis-*p*-tolyl	75	131–132	......	....[1]
bis-*p*-anisyl	79	179–180	278	275
bis-*o*-anisyl	74	227–228	11.15%[a]	11.1%[a]
Di-*n*-butyl	82	70.5–71	178	176

[a] % Phosphorus.

bis-*p*-Tolylphosphinic Acid.—N,N-Diethylamidodichlorophosphate (19 g., 0.1 mole) was added during one hour to a gently refluxing solution of *p*-tolylmagnesium bromide, prepared from 34.2 g. of *p*-bromotoluene and 4.8 g. of magnesium, in 300 ml. of dry ether. After refluxing for two hours, the mixture was hydrolyzed by means of ice-water and ammonium chloride, and the organic layer was treated with 250 ml. of concentrated hydrochloric acid. Ether was distilled from the mixture and the residue was refluxed for four hours. After cooling, the product was filtered and was recrystallized from dilute ethanol It formed long colorless needles. Michaelis and Wegner[1] reported its m. p. 130–132°.

bis-*p*-Anisylphosphinic Acid.—The same procedure, using 37.4 g. of *p*-bromoanisole for the Grignard reagent, yielded this acid in the form of short colorless needles.

bis-*o*-Anisylphosphinic Acid.—The same procedure using *o*-bromoanisole gave this substance, in the form of needles; this preparation was also checked by synthesizing the product from phosphorus oxychloride and the Grignard reagent by an earlier procedure.[2] The rather unexpectedly high melting point, in comparison with the *p*-isomer, may be caused by interaction of the oxygen atom of the *o*-methoxyl group, with the PO_2H group.

Di-*n*-butylphosphinic Acid.—A procedure similar to the above was used with 57 g. of the dichlorophosphate and the Grignard reagent from 82.2 g. of *n*-butyl bromide and 14.58 g. of magnesium; the addition period was two hours and the reflux period was three hours. After hydrolysis by refluxing with hydrochloric acid, the bulk of the latter was distilled, the residue made strongly alkaline with sodium hydroxide, and the regenerated

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(2) R. T. Lagemann, *J. Polymer Sci.*, **3**, 663 (1948).

(3) F. G. Slack, *Phys. Rev.*, **46**, 945 (1934).

(1) Michaelis and Wegner, *Ber.*, **48**, 316 (1915).

(2) Kosolapoff, THIS JOURNAL, **64**, 2982 (1942).

amine was steam distilled. The crude product m. p. 66–69°, was isolated by ether extraction and converted to the corresponding chloride (for separation from possible traces of butanephosphonic acid) by warming with 51.5 g. of phosphorus pentachloride followed by distillation; b. p. 156–157° at 28 mm. Hydrolysis of the chloride with warm water and crystallization from hexane gave the pure acid in the form of long silky colorless needles. This acid was previously reported by Plets[3] who prepared it by hydrolysis of either R_2PCl_3 or R_2POCl, which were, in turn, derived from dibutylchlorophosphine; he gave m. p. 31–32° for the acid. The higher melting point of the present preparation indicates either higher purity or, possibly, an isomeric form.

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[3] Plets, dissertation, Kazan, U. S. S. R., 1938.

THE ROSS CHEMICAL LABORATORY
ALABAMA POLYTECHNIC INSTITUTE
AUBURN, ALABAMA

RECEIVED SEPTEMBER 21, 1948

Preparation and Properties of Tetramethylene Sulfones

BY MARLIN T. LEFFLER AND W. D. KRUEGER

In the course of a search for new types of chemotherapeutic agents, several cyclotetramethylene sulfones were prepared and studied. These were synthesized by the addition of amines, alcohols and mercaptans to 2,5-dihydrothiophene-1-dioxide (butadiene sulfone) in a manner similar to that described by Delfs.[1] The general formula, I, illustrates the types prepared and listed in Table I, where (X) is either –NH–, –O– or –S–, and R is an alkyl or substituted alkyl group.

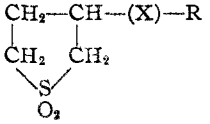
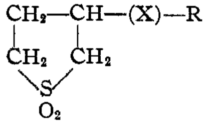

(I)

TABLE I

CYCLOTETRAMETHYLENE SULFONES,



(X)—R	M. p., °C.	Yield, %	Formula	Analyses, N, % Calcd.	Analyses, N, % Found
		Amine Hydrochlorides			
$-NHC_4H_9$-*n*·HCl	148–149	73 (base)	$C_8H_{18}ClNO_2S$	6.15	6.14
$-NHCH_2CH_2C_6H_5$·HCl	188–189	41	$C_{12}H_{18}ClNO_2S$	5.08	5.00
$-NH(CH_2)_3N(C_2H_5)_2$·2HCl	176–177[a]	77	$C_{11}H_{26}Cl_2N_2O_2S$	8.72	8.49
$-NC_5H_{10}$(Piperidino)·HCl	218–219	76 (base)	$C_9H_{18}ClNO_2S$	5.84	5.86
		Ethers			
$-O(CH_2)_2N(C_2H_5)_2$	Phosphate: 132–133 Base: B. p. 175–181 (4 mm.)	62	$C_{10}H_{24}NO_7PS$	4.20	4.31
$-SCH_2C_6H_5$	61–63	51	$C_{11}H_{14}O_2S_2$	C: 54.52 H: 5.82	54.48 5.53
$-S(CH_2)_2N(C_2H_5)_2$	HBr: 122–123	48	$C_{10}H_{22}BrNO_2S_2$	4.22	4.27

[a] Dihydrochloride precipitated by addition of excess alcoholic hydrogen chloride to an acetone solution of the base. Recrystallized from absolute alcohol.

It is of interest to note that while the addition of amines to butadiene sulfone does not generally require a catalyst, alcohols and mercaptans react best in the presence of an alkaline agent. Triton-B was found to be an effective catalyst; sodium and potassium hydroxides serve also. Worth emphasizing is the fact that strongly basic amines such as aliphatic amines, phenethylamine, etc., add readily to the double bond of butadiene sulfone but less basic amines, aniline and benzylamine for example, do not react to give any appreciable yield under similar conditions.

Through the courtesy of the Division of Chemotherapy for Tropical Diseases, National Research Council, the products described herein were tested for activity against a variety of tropical diseases. None was found to have any significant activity in amebiasis, filariasis, schistosomiasis or leischmaniasis.

We are indebted to Mr. E. F. Shelberg of the Microanalytical Department for the microchemical analyses.

Experimental

The sample of 2,5-dihydrothiophene-1-dioxide (butadiene sulfone) used in this work was furnished by the Shell Development Company under the trade name "Sulfolene."

The tetrahydrothiophene-1-dioxides listed in Table I were prepared by the following general procedures:

3-Amino Derivatives.—A mixture of 0.5 mole of butadiene sulfone and 2 moles of the primary or secondary amine was stirred and heated at 70–80° for twenty-four hours. The excess amine was then removed by distillation *in vacuo* and the residue was dissolved in 300 ml. of anhydrous ether, which solution was treated with excess dry, gaseous hydrogen chloride to form the salt. The solid salts were removed by filtration and recrystallized to constant melting point from absolute alcohol.

3-Substituted Ethers.—A mixture of 0.5 mole of butadiene sulfone, 1.0 mole of the desired alcohol and 2 to 4 ml. of Triton-B was heated at 70–80° for twenty-four hours. At the end of this time the Triton-B was neutralized with concentrated sulfuric acid and the excess of the alcohol used was removed by distillation *in vacuo*. The residue was then distilled under reduced pressure. In the case of the 3-diethylaminoethoxy derivative, the product was converted to the phosphate by the addition of a slight excess of phosphoric acid (85%) to an alcoholic solution of

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[1] Delfs, U. S. Patent 2,219,006 (1940); 2,291,798 (1942).

the base. The phosphate was purified by recrystallization from a mixture of acetone and methanol (1:4).

3-Substituted Thio-ethers.—To a mixture of 0.2 mole of butadiene sulfone, 0.2 mole of the desired mercaptan and 75 ml. of water was added slowly and with good agitation 0.4 mole of powdered sodium hydroxide. During this addition, the temperature rose to and was held at 70–80°. Stirring was continued and the temperature was maintained at 70–80° for four hours longer. Then the reaction was cooled and extracted with two 250-ml. portions of ether. The combined ether extracts were washed with 150 cc. of water and dried over anhydrous magnesium sulfate.

In the case of the benzylthio ether, the product crystallized directly from the cold ether solution. It was purified further by recrystallization from dry ether. With the diethylaminoethyl thio-ether, the base was converted to the hydrobromide by treatment of the dry ether solution with gaseous hydrogen bromide. Purification was accomplished by recrystallizing the salt from absolute alcohol.

ABBOTT RESEARCH LABORATORIES
NORTH CHICAGO, ILLINOIS
RECEIVED AUGUST 16, 1948

Thermal Exchange Experiments with Radioactive Zinc

BY LEON LEVENTHAL[1] AND C. S. GARNER

Duffield and Calvin[2] have reported an intensive study of thermal exchange reactions of copper chelate compounds in pyridine, most of which reactions proceeded at measurable rates. Other exchange experiments of the type considered here include those of Drehmann[3] on manganese(II) ions with manganese acetylacetone and manganese benzoylacetone in methanol (half-times of exchange less than one hour), Sue and Yuasa[4] on vanadyl and vanadate ions with solid vanadium 8-hydroxyquinoline and solid vanadium cupferronate (relatively slow exchange), and Johnson and Hall[5] on nickel(II) ions with various nickel chelate compounds in acetone, methyl or ethyl cellosolve (rapid to slow exchanges).

We have examined the thermal exchange reactions of zinc ions with some zinc complex compounds of the kind referred to above, partly to find conditions under which the kinetics of such reactions might be studied and partly to learn which of these zinc compounds, if any, might be suitable for use in the Szilard–Chalmers method of concentrating radioisotopes.

Complete exchange of radioactive zinc was found between dipyridine zinc acetate and the following zinc complex compounds in pyridine solution at 25° after exchange times as short as thirty seconds in each case: zinc acetylacetone, zinc acetylacetone ethylenediimine, zinc benzoylacetone ammoniate, zinc nicotinylacetone and dipyridine zinc thiocyanate. In the case of the nicotinylacetone, the exchange solution in pyridine was 0.0034 *f* in dipyridine zinc acetate and 0.0034 *f* in the zinc chelate. In all other cases, the pyridine exchange solutions were 0.01 *f* in the acetate and 0.01 *f* in the complex compound. The acetylacetone exchange was also run at 0° without any apparent difference. Thus, it appears either that rapid exchange was induced by the separation procedure utilized or, more probably, that the above zinc complex compounds are comparatively unstable with respect to ionization or displacement reactions (stability apparently comparable with that of copper salicylaldehyde, copper salicylaldehyde anil, and copper salicylaldehyde methylimine in pyridine solution[2]). If the rapid exchange was not induced, the above zinc complex compounds would not be suitable for Szilard–Chalmers separations, at least in pyridine solution.

Experimental

Radiozinc Tracer.—Several sections from a discarded copper cyclotron dee were obtained through the courtesy of Professor J. R. Richardson, to whom our thanks are hereby expressed. Since these copper parts had received lengthy deuteron and neutron bombardments and had been cooling for over a year, the principal activity in them was due to 250-day Zn^{65}, formed mainly by the reaction Cu^{65} $(d,2n)$Zn^{65}. Chemical separation and purification of the radiozinc was effected by a procedure similar to that outlined by Kamen,[6] giving a zinc fraction with the half-life and radiations characteristic of 250-day Zn^{65}.

Procedure.—Experiments were run in duplicate. All zinc compounds were synthesized and their identity established by chemical analyses. The pyridine was dried over potassium hydroxide and distilled through a column. Exchange mixtures were synthesized volumetrically from standardized stock solutions of the complex compounds and of radioactive zinc acetate in pyridine. After varying lengths of time the exchange mixtures were subjected to a separation procedure similar to that used by Duffield and Calvin[2] and consisting of the addition of water and chloroform followed by extraction of the complex compound into the chloroform–pyridine layer and of the acetate into the water–pyridine layer, re-extraction from each layer, then precipitation of zinc sulfide from the resulting extracts buffered with acetic acid–acetate mixtures. Since the zinc sulfide precipitates were found after drying to be of varying composition they were ignited to the oxide for weighing and subsequently mounted on filter paper discs. Both fractions from each experiment were counted in a reproducible geometry with a Geiger–Mueller counter and scale-of-64, the 0.45- to 1.14-Mev. gamma radiation associated with the decay of Zn^{65} being counted through a compound absorber. The total activity in each experiment was of the order of 1000 counts per minute, and corrections for decay and changes in counter efficiency (by use of a standard Zn^{65} aliquot) and for background were applied. The extent of exchange was calculated in the usual manner from the specific activities of the two fractions.

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(1) Present address: Naval Radiological Defense Laboratory, San Francisco Naval Shipyard, San Francisco 24, California.

(2) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

(3) U. Drehmann, *Z. physik. Chem.*, **B53**, 227 (1943).

(4) P. Sue and T. Yuasa, *J. chim. phys.*, **41**, 160 (1944).

(5) J. E. Johnson and N. F. Hall, THIS JOURNAL, **70**, 2344 (1948).

(6) M. D. Kamen, "Radioactive Tracers in Biology," Academic Press, Inc., New York, N. Y., 1947, p. 246.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA
RECEIVED SEPTEMBER 25, 1948

Thermal Exchange Experiments with Radioactive Chromium

BY H. E. MENKER AND C. S. GARNER

The only published work on exchange reactions of chromium compounds is the observation of

TABLE I

THERMAL EXCHANGE OF LABELLED CHROMIUM (Cr^*) BETWEEN CHROMIUM COMPOUNDS

				Activity of Separated Fractions, net c./m.:[a]			Exchange	
Ions	Composition, f.	$HClO_4$ f.	Temp. °C	Orig. act.	Orig. inact.	Std. aliq.	Time Hr.	%
$Cr(H_2O)_6^{+++}$, $Cr_2O_7^{--}$	0.010 $Cr^*(ClO_4)_3$, 0.0050 $K_2Cr_2O_7$	0.05	Rm.	4290	41	4333	72	<2
				1913	27	1952	456	<3
			45.1	2645	108	2838	72	8
				1840	129	1981	264	13
				435[b]	119[b]	530	1200	43
		2.0	Rm.	2509	23	2470	72	<2
			45.1	2534	70'	2838	72	5
Cr(III), $Cr_2O_7^{--}$	.0020 $Cr^*_2(SO_4)_3$,[c] .0020 $K_2Cr_2O_7$	[d]	25.1	310	1	354	72	<1
$Cr(OH)_4^-$, CrO_4^{--}	.010 $Cr^*(ClO_4)_3$, .010 K_2CrO_4	[e]	25.1	2713	18	2838	72	<3
$Cr(H_2O)_6^{+++}$, $Cr(SCN)_6^{---}$	.010 $Cr^*(ClO_4)_3$, .010 $K_3Cr(SCN)_6$	0.05	Rm.	1297	1	1300	72	<1
		2.0	Rm.	1363	1	1300	72	<1
$CrCl_2(H_2O)_4^+$, $Cr(SCN)_6^{---}$	.0067 Cr^*Cl_3,[c] .0067 $K_3Cr(SCN)_6$	[f]	25.2	617	3	626	24	<2
$Cr(H_2O)_6^{+++}$, $Cr(CN)_6^{---}$	.010 $Cr^*(ClO_4)_3$, .010 $K_3Cr(CN)_6$	pH 3–4	Rm.	498	275	773	72	71
$CrCl_2(H_2O)_4^+$, $Cr(CN)_6^{---}$	.0049 Cr^*Cl_3,[c] .0049 $K_3Cr(CN)_6$	[e]	25.1	501	2	...	72	<2
Cr(III), $Cr(CN)_6^{---}$	.0080 $Cr^*(OOCCH_3)_3$,[c] .0080 $K_3Cr(CN)_6$	[h]	25.1	608	38	668	96	12
$Cr(H_2O)_6^{+++}$, $Cr(C_2O_4)_3^{---}$	.010 $Cr^*(ClO_4)_3$, .010 $K_3Cr(C_2O_4)_3$	0.025	Rm.	700	0	734	72	<1
$CrCl_2(H_2O)_4^+$, $Cr(C_2O_4)_3^{---}$	.0050 Cr^*Cl_3,[c] .0050 $K_3Cr(C_2O_4)_3$	[g]	25.1	350	5	477	1	<5

[a] Statistical counting error, taken as the square root of the sum of the squares of the standard deviations of sample and of background, was 1%. [b] Analyses gave same amount of chromium in each fraction, thus showing that oxidation of chromium(III) by perchloric acid is negligible under the experimental conditions. [c] Green form. [d] H_2SO_4 (pH 2–3). [e] 3.1 f. NaOH. [f] 0.067 f. HCl. [g] 0.050 f. HCl. [h] CH_3COOH (pH 3–4).

Muxart, Daudel, Daudel and Haissinsky[1] that no appreciable exchange of radiochromium occurs between chromium(III) and dichromate ions in sulfuric acid solutions.

We have confirmed this observation and have extended the studies to exchange measurements in 2 *f* and 0.05 *f* perchloric acid and in 3.1 *f* sodium hydroxide. In addition, some exchange reactions of chromium(III) ions with hexathiocyanatochromate(III), hexacyanochromate(III), and trioxalatochromate(III) ions, respectively, have been investigated with radiochromium.

Table I summarizes the results. Appreciable exchange was observed only for Cr(III)—$Cr(CN)_6^{---}$ in low concentration of perchloric acid or acetic acid and for the pair hexaaquochromium(III) and dichromate ions in 0.05 *f* perchloric acid at 25° and 45°. In the latter case the exchange results obey approximately the exponential exchange law,[2,3] as is shown by Fig. 1. The half-time for the exchange under the stated conditions is 60 ± 6 days at 45° and greater than 430 days at 25°.

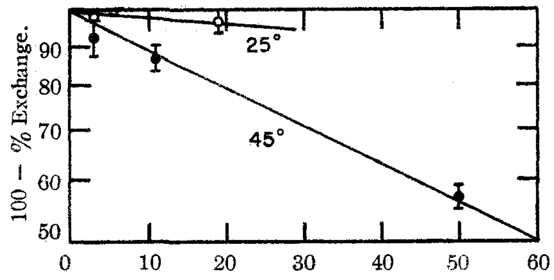

Fig. 1.—Hexaaquochromium(III)—dichromate exchange, 0.010 *f* $Cr^*(ClO_4)_3$, 0.0050 *f* $K_2Cr_2O_7$, 0.05 *f* $HClO_4$.

Experimental

Radiochromium Tracer.—Radiochromium was prepared by the Cr(*n*, γ) reaction in the Oak Ridge pile and allocated by the U. S. Atomic Energy Commission. Chemical purification gave a chromium fraction with the half-life and radiation characteristics of 27-day Cr^{51}.

Procedure.—Experiments were run in duplicate. The exchange mixtures were synthesized volumetrically from the standardized stock reagent solutions, placed inside glass-stoppered flasks immersed in a thermostated bath, and subjected to chemical separation at the end of the exchange times. In the hexathiocyanatochromate (III) and hexacyanochromate (III) exchanges separation was effected by the addition of silver nitrate to precipitate $Ag_3Cr(SCN)_6$ and $Ag_3Cr(CN)_6$, respectively. Separation in the case of the trioxalatochromate (III) exchanges was achieved by the addition of barium chloride and ethanol to precipitate $Ba_3[Cr(C_2O_4)_3]_2$. In all other cases separation was brought about by precipitation of hydrous chromium(III) oxide. Both fractions in each exchange experiment were mounted and counted, in a few cases in the form precipitated (except for drying), but in most cases as $BaCrO_4$. Samples were suction-filtered onto Whatman No. 50 paper discs held in a cylindrical glass "chimney" device, then mounted on cardboard plates for counting. The 0.33-Mev gamma radiation associated with the decay of Cr^{51} was generally used in the detection, the samples usually being counted through 108 mg./sq. cm. aluminum (to eliminate variable X-radiation) in a reproducible geometry with a Geiger–Mueller counter and scale-of-128. Corrections for decay and changes in counting efficiency (by use of a standard Cr^{51} aliquot) and for background (~19 c./m.) were made.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA
RECEIVED OCTOBER 1, 1948

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[1] R. Muxart, P. Daudel, R. Daudel and M. Haissinsky, *Nature*, **159**, 538 (1947).

[2] H. A. C. McKay, *ibid.*, **142**, 997 (1938).

[3] R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

Penicillin G as Electrolyte and Colloidal Electrolyte[1]

By J. W. McBain, Harriette Huff[2] and A. P. Brady[2]

There is disagreement concerning the state of aggregation of penicillin salts in aqueous solution. On the basis of surface tension and ultramicroscopic observations, Hauser, Phillips and Phillips[3] have reported sodium benzyl penicillinate (penicillin G) as a colloidal electrolyte. On the other hand, Kumler and Alpen[4] concluded from conductivity and surface tension measurements that both potassium and sodium salts of penicillin G are only molecularly dispersed in water. Since neither of those lines of evidence is conclusive, it seemed worth while to make other types of measurement on the solutions to decide between these opposing views. This note presents measurements of the conductivity, surface tension, freezing points, and dye solubilization at various concentrations of aqueous solutions; showing that sodium pencillin G above 0.25 m. is indeed a colloidal electrolyte, but that in lesser concentration it is an ordinary electrolyte. The authors[3,4] referred to were dealing with dilute solutions such as 0.017 mole/liter or 0.6%.

Experimental

Crystalline sodium penicillin G was kindly furnished by Bristol Laboratories, Inc., of Syracuse, New York, and according to their analysis was 96.9% G with the remainder being F, dihydro F, and K.

The conductivity was measured at 2000 cycles in an oil thermostat at 25 ± 0.005° with a Dike–Jones type bridge using an oscillograph to detect the balance point. The conductivity water was about 0.8×10^{-6} mho.

The crystalline penicillin and its solutions were stored in a refrigerator. With the exception of the solubilization measurements, all determinations were made with solutions less than six hours old and with less than half an hour at room temperature.

Results and Discussion

The results are given in Table I and plotted in Figs. 1 and 2. The freezing point results are expressed in terms of *g*, the practical osmotic coefficient, the ratio of the lowering to the ideal lowering for a uni-univalent salt. Figure 1 also includes the results of solubilization measurements both with water and with isotonic salt solution as solvents. Both freezing point and solubilization show that sodium penicillin G aggregates in concentrated solution, but the critical concentration of 0.25 m. (8.26% G) is so high that it is of little interest biologically. Solubilization experiments in the presence of isotonic salt solution

Table I

Osmotic Coefficient at 0° and Equivalent Conductivity and Surface Tension of Sodium Penicillin G Solutions at 25°

Concentration Molal	Concentration Equiv./liter	Osmotic coefficient, g.	Equivalent conductivity
0.602	0.526	0.625	36.5
.318	.294	.852	43.2
.173	.1652	.924	50.0
.0968	.0942	.950	53.5

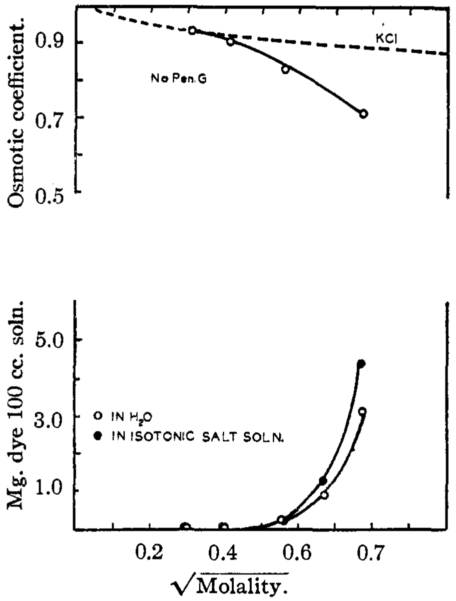

Fig. 1.—The osmotic coefficient *g* of sodium penicillin G as compared with that of potassium chloride; also its solubilizing power in water and in isotonic salt solution (0.9% NaCl).

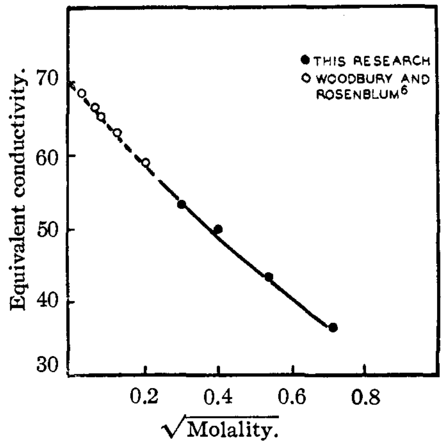

Fig. 2.—The equivalent conductivity of sodium penicillin G.

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(1) This work was carried out under a contract between the Office of Naval Research and Stanford Research Institute, under the supervision of Professor J. W. McBain.

(2) Present address: Stanford Research Institute, Stanford, California.

(3) E. A. Hauser, J. W. Phillips, and R. G. Phillips, 22nd National Colloid Symposium, Cambridge 1948; *Science*, **106**, 616 (1947); also E. A. Hauser, American Chem. Soc. Meeting, Portland, September, 1948.

(4) W. D. Kumler and E. L. Alpen, Pacific Division Amer. Assoc. Adv. Sci., Berkeley, June, 1948; *Science*, **107**, 567 (1948).

show little effect upon critical concentration. The equivalent conductivity curve shows no break or a very doubtful one at the critical concentration, as expected for this type of polycyclic compound. Bile salts and sodium abietate, both shown to be colloidal electrolytes by freezing point measurements, give no break in the conductivity curve.[5,6] The conductivity curve determined here ties in satisfactorily with the data given by Woodbury and Rosenblum,[7] converted from 30 to 25° by assuming that the salt has the same temperature coefficient as that of the sodium ion.

The surface tension of these solutions is fairly low, but relatively independent of concentration and may easily result from small amounts of impurities.

(5) J. W. McBain and S. A. Johnston, *Proc. Roy. Soc.* (*London*), **191A**, 129 (1942).

(6) I. M. Kolthoff and W. F. Johnson, *J. Phys. Chem.*, **50**, 440 (1946).

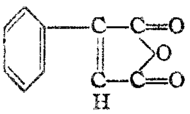
(7) D. T. Woodbury and C. Rosenblum, *J. Biol. Chem.*, **171**, 447 (1947).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIF. RECEIVED SEPTEMBER 25, 1948

A Preparation of Phenylmaleic Anhydride

BY LEONARD E. MILLER, HARLOW B. STALEY AND D. J. MANN

Although phenylmaleic anhydride (I) was first isolated in low yield as a by-product in the synthesis of phenylmalic acid by the reaction of phenylsuccinic acid with bromine and phosphorus tribromide,[1] no satisfactory procedure for the preparation of (I) has been reported.



I

When phenylsuccinic anhydride is permitted to react with N-bromosuccinimide in the presence of a catalytic amount of benzoyl peroxide, phenylmaleic anhydride can be isolated in 57–64% yield.

The use of N-bromosuccinimide as a dehydrogenating agent for several hydroaromatic compounds has been reported recently by Barnes.[2]

Experimental[3]

Phenylsuccinic anhydride,[4] m. p. 53–54°, was prepared in 78–84% yield from phenylsuccinic acid.[5]

Into a 500-ml., two-necked flask, equipped with a mechanical Hershberg stirrer (made of nichrome wire) and a condenser fitted with a drying tube, were placed 17.8 g. (0.1 mole) of N-bromosuccinimide, 8.8 g. (0.05 mole) of phenylsuccinic anhydride, 200 ml. of carbon tetrachloride and 0.1 g. of benzoyl peroxide. The reaction mixture was heated under reflux with stirring for twenty-four hours, during which time the solution became bromine-red in color and a precipitate of succinimide formed. After the mixture was cooled to room temperature, the insoluble succinimide was separated on a filter and washed with several portions of hot benzene until the washes no longer gave a positive Baeyer test with potassium permanganate (about 150 ml. of benzene were required). When cool, the combined benzene and carbon tetrachloride solutions deposited an additional small quantity of succinimide which was separated. The clear solution was concentrated by distillation to a volume of 30 ml. and was then placed in a refrigerator for two hours. The crystals of phenylmaleic anhydride which formed were separated and recrystallized from dry acetone–petroleum ether (high boiling); yield 2.1–2.3 g., m. p. 119–120° (reported, 119–119.5°[1]).

After the evaporation of the carbon tetrachloride filtrate to dryness under reduced pressure (water pump) in a two-bulb distillation apparatus, the residue was distilled under reduced pressure (1.0 mm.). At 60–70° a few drops of a yellow liquid were collected; this forerun was discarded. At 130–145° a yellow solid was collected. This material was recrystallized twice from dry acetone–petroleum ether (high boiling) (Norite) to give 2.1–2.3 g. of phenylmaleic anhydride, m. p. 119–120°. From the combined recrystallization filtrates, 0.8–1.0 g. of equally pure product was isolated. The total yield was 5.0–5.6 g. (57–64%).

The percentage yield was slightly lower (53–57%) when four times these amounts were used.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED SEPTEMBER 24, 1948

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(1) Alexander, *Ann.*, **258**, 67 (1890).

(2) Barnes, THIS JOURNAL, **70**, 145 (1948).

(3) All m. p.'s and b. p.'s are uncorrected.

(4) Verkade and Hartman, *Rec. trav. chim.*, **52**, 945 (1933).

(5) "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1941, p. 451.

Displacement-chlorination of Dimethylaminopropanol-2

BY N. L. WENDLER AND M. TISHLER

The reaction of methanesulfonyl chloride with dimethylaminopropanol-2 in an inert solvent was found to give rise to the *o*-mesylate hydrochloride (II) admixed to a greater or lesser extent with the hydrochloride of the propanolamine (I). The *o*-mesylate hydrochloride (II) could be obtained directly and in pure condition by conducting the reaction in a solvent mixture consisting of equal parts of chloroform and acetone.

The *o*-mesylate hydrochloride was titrated with one equivalent of alkali and was converted thereby to the free ester base, characterized as its picrate. When heated above its melting point for a short time the *o*-mesylate hydrochloride was converted smoothly by internal displacement into dimethylamino-2-chloropropane (III). The latter was isolated and identified as its picrate.

$$\underset{\text{(I)}}{\mathrm{CH_3CHOHCH_2N(CH_3)_2}} \longrightarrow$$

$$\underset{\text{(II)}}{\mathrm{CH_3CH(OSO_2CH_3)CH_2NH(CH_3)_2Cl}} \xrightarrow{138^\circ}$$

$$\underset{\text{(III)}}{\mathrm{CH_3CHClCH_2N(CH_3)_2}}$$

Experimental

Dimethylaminopropanol-2 *o*-Mesylate Hydrochloride.—To a stirred solution of 10.5 g. of dimethylaminopropanol-2 in 25 cc. of chloroform at 0° was added portion-wise a solution of 12.5 g. of methanesulfonyl chloride in 25 cc. of chloroform. The homogeneous solution was treated with

50 cc. of acetone and stored in the cold for twenty hours. During this time the *o*-mesylate hydrochloride crystallized. The crystals were collected, washed with cold 50% acetone-chloroform and dried in a vacuum desiccator over solid potassium hydroxide; yield 9.5–10 g. (40–45%), m. p. 126.5–128°. A small sample was recrystallized from acetone affording colorless micro-rhombs, m. p. 130–131°.

Anal. Calcd. for $C_6H_{16}O_3NSCl$: N, 6.44; Cl, 16.20; neut. equiv., 217.5. Found: N, 6.59; Cl, 16.10; neut. equiv., 226.

A sample of the *o*-mesylate hydrochloride was neutralized with aqueous potassium hydroxide at 0° and the oil which separated was extracted with ether-petroleum ether and dried over solid potassium hydroxide. The filtered solution was concentrated to dryness and the residue was converted to a picrate in ethyl acetate–ether solution. Recrystallization from ethyl acetate–ether afforded the picrate of the *o*-mesylate base as fine yellow needles, m. p. 90–91°.

Anal. Calcd. for $C_{12}H_{18}O_{10}N_4S$: C, 35.12; H, 4.39; N, 13.66; S, 7.81. Found: C, 35.39; H, 4.39; N, 13.67; S, 8.53.

Dimethylamino-2-chloropropane from *o*-Mesylate Hydrochloride.—*o*-Mesylate hydrochloride (II), 3.8 g., was sealed under vacuum in an ampule and heated in xylene vapor for four hours. The ampule was cooled. The contents were dissolved in an equal volume of water and treated with an excess of 50% aqueous potassium hydroxide solution. The oil which separated was extracted with petroleum ether, dried over solid potassium hydroxide and the solvent evaporated. The residue was converted to its picrate in ethyl acetate–ether solution and recrystallized from the same solvent as fine yellow needles, m. p. 101–103°. A mixed melting point with authentic picrate of dimethylamino-2-chloropropane was undepressed; yield 3.8–4.2 g. (70–75%).

Anal. Calcd. for $C_{11}H_{15}O_7N_4Cl$: Cl, 10.13; Found: Cl, 9.74.

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An Application of the Delépine Reaction to β-Bromopropionic Acid

BY N. L. WENDLER

A modification of the Delépine reaction[1] has been applied to β-bromopropionic acid for its conversion to β-alanine. A quaternary betaine-complex was formed between β-bromopropionic acid and hexamethylenetetramine according to a method applied by Schubert[2] to iodoacetic acid. This complex was subsequently decomposed by hydrochloric acid in ethanol to afford β-alanine in good yield and high state of purity.

$$(CH_2)_6N_4 + BrCH_2CH_2COOH \xrightarrow{HCO_3^-}$$

$$[(CH_2)_6N_4]^+{-}CH_2CH_2COO^- \xrightarrow{C_2H_5O^+H_2} H_2NCH_2CH_2COOH$$

Experimental

To a solution of 5 g. of β-bromopropionic acid[3] in 15 cc. of water and 10 cc. of ethanol was added 2.74 g. of sodium bicarbonate. After neutralization was complete, a solution of 4.57 g. of hexamethylenetetramine in 10 cc. of water was added and the resulting solution allowed to stand at room temperature for fifteen hours. At the end of this time, 50 cc. of ethanol was added to the point of faint turbidity followed by scratching, whereupon voluminous crystallization of colorless needles of the betaine-complex ensued. The crystals were chilled in ice for one to two hours and filtered, 9 g. A second crop afforded 0.5 g. yielding a total of 9.5 g. of material.

The betaine-complex (9.5 g.) was treated with 120 cc. of ethanol and 15 cc. of concentrated hydrochloric acid and refluxed for fifteen hours. The mixture was concentrated to dryness *in vacuo* at 50° and the residue extracted with several portions of ethanol. The filtered extract was concentrated to dryness and the residue boiled under reflux with 50–75 cc. of water for one-half hour. The cooled aqueous solution was treated portion-wise with an excess of silver oxide with stirring to remove chloride ion and subsequently filtered, and the filtrate saturated with hydrogen sulfide gas. The precipitated silver sulfide was removed by centrifugation followed by filtration. The colorless solution was concentrated *in vacuo* to a volume of a few cc. and diluted with ethanol to the point of crystallization. After chilling and filtering there was afforded 2.5 g. (85%) of β-alanine, m. p. 199–200° dec. A mixed melting point with known material was undepressed.

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RAHWAY, N. J.

RECEIVED SEPTEMBER 29, 1948

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[1] Delépine, *Compt. rend.*, **120**, 501 (1895).

[2] Schubert, *J. Biol. Chem.*, **116**, 444 (1936).

[3] "Organic Syntheses," Vol. IV, p. 25.

Explosive Properties of Metal Ammines[1]

BY W. R. TOMLINSON, K. G. OTTOSON AND L. F. AUDRIETH

The literature contains numerous references to the explosive nature of certain coördination compounds, but no generalization has thus far been formulated in which an effort has been made to relate chemical composition of such coördination compounds to explosive character. The experimental evidence which is presented below, together with information gleaned from the literature, demonstrates that metal compounds containing (a) coördinated ammonia and related nitrogen-containing donor molecules, and (b) coördinated and/or ionic groups of an oxidizing nature such as perchlorate, chlorate, nitrate, nitrite (or nitrato- and nitro-groups), will decompose violently under various conditions. As is known to be the case among substances classed as explosives, the sensitivity of various coördination compounds to impact, to friction, and to heat will vary widely; nevertheless, some of these same compounds can be caused to detonate when properly initiated. For this reason, due caution should be exercised in the preparation, handling and storage of compounds falling within the categories defined above.

It is significant that "metal nitrates with molecular ammonia" have been incorporated in explosive compositions containing ammonium nitrate as the principal ingredient.[2] Metallic chlorates and perchlorates containing coördinated hydrazine[3] have been found to be brisant and sensitive explosives. Other coördination compounds reported

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[1] Publication of the material contained in this paper has been approved by the Ordnance Department of the United States Army.

[2] Cook, Davis and Lawson (to E. I. du Pont de Nemours and Co.), British Patent 544,582; *cf. Chem. Abstracts*, **36**, 6804 (1942).

[3] Friederich and Vervoorst, *Z. ges. Schiess.-Sprengstoffw.*, **21**, 49, 65, 84, 103, 123, 143 (1926).

TABLE I

THE EXPLOSIVE PROPERTIES[e] OF SOME METAL AMMINES

Metal ammine[d]	Explosion temperature, °C.[c]	Impact sensitivity 2 kg. wt., cm.	Sand test-gm.			
			Power Sand crushed	Sensitivity to initiator, gm., required to cause complete explosion		
				Mercury fulminate	Lead azide	Tetryl
Hexammine chromium(III) nitrate	265	32	40.7	0.20	..	..
Hexammine cobalt(III) perchlorate	360	18	39.2	.25	..	..
Hexammine cobalt(III) iodate	355	100	14.7	.24	..	..
Hexammine cobalt(III) nitrate	295	50	35.9	.27	..	..
Hexammine cobalt(III) hexanitrocobaltate[a]	...	85	34.0	.20	..	..
Nitratopentammine cobalt(III) nitrate	310	48	35.5	.24	..	..
Chloropentammine cobalt(III) perchlorate	320	21	30.6	.20	..	..
Hexaurea chromium nitrate	265	50	3.0	..	..	..
Thiocyanatopentammine cobalt(III) perchlorate	325	55	20.1	..	..	
Dithiocyanatotetrammine cobalt(III) perchlorate	335	35	13.9	..	..	..
Dichlorodiethylenediamine cobalt(III) perchlorate	300	85	9.9	..	..	..
Dichlorodiethylenediamine cobalt(III) chlorate	320	...	13.7	..	..	..[b]
Trinitrotriammine cobalt(III)	305	44	None	..	..	..
tris-Ethylenediamine cobalt(III) nitrate	...	61	None	..	..	0.4
bis-Diethylenetriamine cobalt(III) perchlorate	325	21	39.4	..	0.07	..
Ammonium hexanitrocobaltate(III)	230	33	19.0	.30	..	..
Tetrammine copper(II) nitrate	330	19	17.2	..	..	0.19
Mercuric fulminate	...	5	21.0	..	..	..
Lead azide	335	10	18.0	..	..	..
TNT (*sym*-trinitrotoluene)	470	95	42.0	.24	..	..

[a] This compound was unstable. [b] Requires tetryl. [c] Exposure to the temperature cited causes very rapid decomposition, or explosion, in 5 seconds. [d] All oxalates, chromates, carbonates, sulfates, and non-oxygenated complexes tested were non-explosive (*e. g.*, hexammine cobalt(III) chromate, oxalate and chloride). No compounds containing explosive groupings (*e. g.*, azide) were tested. [e] For details of tests see Picatinny Arsenal Technical Report No. 1401, 18 March 1944; Bureau of Mines Technical Bulletin No. 346, "Physical Testing of Explosives" at the Bureau of Mines Explosives Experiment Station, Bruceton, Pa.

to be explosive include: hexammine cobalt(III) chlorite,[4] chlorate,[3] and perchlorate,[3,5] aquopentammine cobalt(III) chlorate and perchlorate,[5] trihydrazine cobalt(II) nitrate,[6] hexahydroxylamine cobalt(III) nitrate,[7] the tetrammineauric halides[8] and trinitrotriammine cobalt.[9] In light of the evidence available in literature, it seems quite probable that the explosions reported to have occurred during evaporation of filtrates from cobalt determinations were caused, as suggested by Broughton, Laing and Wentworth,[10] by the formation of complex nitro- or nitro-cobaltates(III).

Samples of a number of cobalt(III) and chromium(III) coördination compounds[11] were subjected to standard tests to determine explosion temperature, impact sensitivity, power and sensitivity to initiation (ease with which explosion can be effected). Results of these tests are compared in Table I with values for TNT, mercuric fulminate and lead azide, representing respectively a relatively insensitive high explosive and two very sensitive initiating agents.

The data show quite clearly that oxygenated coördination compounds, particularly those which are "oxygen balanced," vary quite widely with respect to their sensitivities to heat and impact. They represent an extremely wide range in explosive types. Since most of the compounds are capable of exploding sharply and powerfully, and in some cases with but slight provocation, they are to be considered exceedingly dangerous. Some possess sufficient sensitivity to propagate explosion under water; the use or presence of non-solvent liquids is therefore no guarantee of safety. In the absence of specific information the same considerations may be expected to apply also to other metal ammines containing oxidizing radicals such as those of silver, gold, cadmium, lead and zinc.

DOVER, NEW JERSEY

RECEIVED JULY 2, 1948

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[4] Levi, *Atti Lincei*, (5) **32**, I, 623 (1923).

[5] Salvadori, *Gazz. chim. ital.*, **40**, II, 17 (1910).

[6] Franzen and Meyer, *Z. anorg. Chem.*, **60**, 247, 274 (1908).

[7] Werner and Berl, *Ber.*, **38**, 897 (1905).

[8] Ephraim, "Inorganic Chemistry," 4 Ed., Nordeman Publishing Co., Inc., New York, N. Y., 1943, p. 311.

[9] Clark, Quick and Harkins, THIS JOURNAL, **42**, 2498 (1920).

[10] Broughton, Laing and Wentworth, *Anal. Chem.*, **19**, 72 (1947).

[11] The authors desire to acknowledge their indebtedness to Professor John C. Bailar, Jr., of the University of Illinois, for his help in furnishing many of the coördination compounds which were subjected to actual study or used for the preparation of related derivatives.

Preparation of Radioactive CO_2 from $BaCO_3$[1]

BY NORMAN ZWIEBEL,[2] JOHN TURKEVICH AND WARREN W. MILLER

To obtain the C^*O_2 from BaC^*O_3 either for introduction into a reaction system for synthesis of a

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[1] Work done at the Brookhaven National Laboratory under the auspices of the Atomic Energy Commission. The work was started by one of us (W. W. M.) while a member of the Laboratory of Nuclear Science, Massachusetts Institute of Technology.

[2] Present address: Pyridium Corporation, Yonkers, New York

labeled compound, or for transfer to a gas activity measuring device such as an ionization chamber or gas counter, it has been common practice to drop either concentrated phosphoric or sulfuric acid on the BaCO$_3$.[3] This procedure often involves the use of a stopcock in contact with concentrated acid, does not permit the ready attainment of high vacuum and may entail the formation of a crust of insoluble barium sulfate or phosphate around the active barium carbonate. In practice a still more disconcerting factor has been the spattering of the dry powder on contact with acid with the consequent sweeping of a portion of the sample out of the reaction vessel by the evolving gas. The direct thermal evolution of the C*O$_2$ from BaC*O$_3$ by roasting the dry salt in a quartz tube has also been used[4] but the temperature necessary is inconveniently high.

These difficulties may be surmounted by using a thermal reaction between dry solids to evolve the carbon dioxide. Acids such as potassium bisulfate are unsuitable as the reaction will produce water as well as carbon dioxide. Inorganic acid anhydrides such as boric oxide and the pyro salts melt at too high a temperature to be used in Pyrex apparatus. Organic anhydrides sublime under vacuum. A convenient reaction, however, is a metathetic one producing a thermally unstable carbonate such as the reaction between barium carbonate and lead chloride. Lead chloride was used because it can be readily obtained in an anhydrous state, and has a low melting point and vapor pressure. Silver chloride can also be used.

To obtain the total carbon dioxide from a barium carbonate sample, two procedures have been worked out. In the micro-procedure the weighed barium carbonate, from 5 to 200 mg., is dropped into a Pyrex test-tube with attached ground joint. Over this is layered 5 to 10 times its weight of dry powdered lead chloride, and then a wad of glass wool is pushed down on top. After attaching the tube to the vacuum system and pumping at 100°, the carbon dioxide is released by carefully melting the lead chloride with a micro burner. The reaction is known to be at least 98% complete from gas buret and activity measurements. The fusion temperature may be lowered by using a 50–50 mixture of PbCl$_2$–AgCl instead of pure lead chloride. The melt should not fill a full diameter of the reaction vessel or the latter may crack on cooling. For macro-quantities we have employed the following procedure. The two solids, one part by weight of barium carbonate and six parts by weight of lead chloride, were intimately mixed and ground together before placing the mixture in a reaction tube. The latter was connected to a standard vacuum system by means of a stopcock and a standard taper ground glass joint. The reaction mixture was pumped overnight at room temperature to a pressure of 10^{-5} mm. A tubular woven glass heating mantle was used as a heat source and the temperature was controlled by a Variac. Evolution of gas began at about 180° and each increment of temperature caused a more rapid evolution of gas which gradually decreased with time. It was found that the most convenient procedure was to raise the temperature to 400° as rapidly as possible (about twenty-five minutes) and maintain the reaction mixture at this temperature. The evolution of carbon dioxide was 65% complete in one hour from the start of heating, 80% in two hours and 96% complete in four hours. 3–9 g. of barium carbonate was employed in these experiments. Thus this reaction has been found to proceed at temperatures well below the fusion temperature and the system may therefore be used as a convenient, clean, "virtual" source of active carbon dioxide.

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK
RECEIVED AUGUST 16, 1948

(3) (a) W. G. Dauben, J. C. Reid and P. E. Yankwich, *Ind. Eng. Chem., Anal. Ed.*, **19**, 828 (1947); (b) J. T. Kummer, THIS JOURNAL, **69**, 2239 (1947); (c) J. L. Huston and T. H. Norris, *ibid.*, **70**, 1968 (1948).

(4) M. G. Inghram, Atomic Energy Commission, MDDC 60, June, 1946.

COMMUNICATIONS TO THE EDITOR

METALLIC ALUMINUM IN SOLUTION IN LIQUID AMMONIA

Sir:

It has long been generally accepted that the alkali metals, in dissolving in liquid ammonia, dissociate into alkali metal cations and free (solvated) electrons,[1] and that the latter impart the characteristic blue color to such solutions. The alkaline earth metals are known to dissolve similarly, although to a smaller extent.[2] Makishima[3] included the dissolution of electrons among electrode reactions which may occur at a cathode in liquid ammonia solutions, and Laitinen and Nyman[4] have very recently pointed out that, theoretically, all metals should be in some degree soluble in liquid ammonia. According to the hypothesis

(1) Kraus, THIS JOURNAL, **30**, 1323 (1908).

(2) Kraus, *ibid.*, **30**, 660 (1908).

(3) Makishima, *J. Faculty Eng. Tokyo Imp. Univ.*, **21**, No. 3, 115 (1938).

(4) Laitinen and Nyman, THIS JOURNAL, **70**, 3002 (1948).