Acetic acid, run on a column under the identical conditions, had the same threshold volume as the acid in the second zone. This acid was positively identified as acetic by Duclaux numbers; known acetic acid—6.45, 7.1, 7.2; acetic acid from wilforgine—6.5, 7.1, 7.3.

The water layer of the first zone was evaporated to a small volume and then acidified with a drop of concentrated hydrochloric acid, but there separated only a few small crystals which either melted or sublimed at 112° (hot stage). The ultraviolet spectrum of the remaining mother liquor was identical with that of 3-furoic acid (Fig. 5).

In a subsequent experiment 0.2984 g. of wilforgine was saponified. Its saponification equivalent was 107.6 (7.97 equivalents of acid per mole). After repetition of the procedure described above 10.8 mg. of pure 3-furoic acid was isolated from the first zone by repeated recrystallizations from water. An additional 13.6 mg. of less pure material was recovered from the mother liquors. The isolated acid and the authentic sample melted at 120–120.5° (in sealed tube to prevent sublimation), and the mixed melting point showed no depression. The ultraviolet spectrum in water was identical with that of the authentic sample (Fig. 5). The ultraviolet spectra of the sodium salts, formed by the addition of the theoretical quantity of alkali, were also identical (Fig. 5). After drying for several days over phosphorus pentoxide, the acid was analyzed.

Anal. Calcd. for $C_5H_4O_3$: C, 53.57; H, 3.60; neut. equiv., 112. Found: C, 53.40; H, 3.97; neut. equiv., 109.

Saponification of Wilfortrine.—32.50 mg. of wilfortrine was saponified as above. The saponification equivalent was determined to be 108.9 (8.02 equivalents of acid per mole). After acidification to congo red with sulfuric acid, the solution was steam distilled exhaustively. The distillate required 1.785 ml. of 0.1242 *N* sodium hydroxide (5.96 equivalents of steam volatile acid per mole). By difference there were 2.06 equivalents of steam non-volatile acid per mole.

Identification of Volatile Acids in Wilfortrine.—The titrated volatile acids were separated and analyzed as described above for wilforgine. The first zone required 0.735 ml. of 0.0512 *N* alkali (1.01 equivalents of acid per mole). The second zone required 3.505 ml. of 0.0512 *N* alkali (4.82 equivalents of acid per mole). The acid in the second zone was identified as acetic in the same manner as described above; Duclaux numbers—6.6, 7.1, 7.3.

On another lot of 0.1545 g. of wilfortrine the saponification equivalent was determined to be 108.7 (8.04 equivalents of acid per mole). From this lot 12.2 mg. of crude 3-furoic acid was isolated, which was purified and identified as above.

BELTSVILLE, MD.

RECEIVED OCTOBER 29, 1951

NOTES

Acetylenic Compounds from Fungi

BY MARJORIE ANCHEL

During the past few years, there have been isolated in this Laboratory, from culture liquids of different species of *Basidiomycetes*, several antibiotic substances which have in common an ultraviolet absorption spectrum of striking and unusual form. The spectra show a series of five to seven sharp maxima in the region of 205 to 360 mμ, giving a characteristic "finger" effect when plotted.

The first compounds of this type isolated and studied spectrophotometrically were obtained from the culture liquids of three different species of *Basidiomycetes: Poria tenuis*, *P. corticola* and an unidentified species.[1,2] These compounds are remarkable not only because of their striking absorption spectra, but also because of their extreme instability.[3] At that time the only naturally occurring compounds described in the literature as having both similar spectra and similar behavior were the polyene fatty acids.[5]

In 1950,[6] a most interesting series of papers from the laboratory of N. A. Sörensen appeared, in which the isolation of polyacetylenic compounds from several genera of *Compositae* was reported, and their ultraviolet absorption spectra presented.[8] The spectra of these compounds resemble closely those of the compounds isolated from *Basidiomycetes*. In correspondence with Dr. Sörensen, we mentioned this similarity and sent him data on the ultraviolet spectra of our compounds. From these spectra, Dr. Sörensen identified our compounds as polyacetylenes. He pointed out to us that according to the rule of Hausser, Kuhn and Seitz[9] concerning the frequency differences of absorption maxima of polyenes and polyacetylenes (about 44 and about 63 f., respectively), our compounds must belong to the latter class. He further made detailed comparisons of the maxima of our compounds with those of acetylenic compounds isolated in his laboratory, as well as some synthesized in the laboratory of E. R. H. Jones,[10] in Manchester. From the near-identity of these, Dr. Sörensen has suggested the presence in our compounds of several specific groupings to which the spectra might be attributed.

In the following tables, the wave lengths of the maxima of the compounds from the *Basidiomycetes* are compared with those of the acetylenic compounds from the laboratories of Dr. Sörensen and Dr. Jones, and the responsible groupings suggested

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(1) M. Anchel, J. Polatnick and F. Kavanagh, *Arch. Biochem.*, **25**, 208 (1950).

(2) F. Kavanagh, A. Hervey and W. J. Robbins, *Proc. Nat. Acad. Sci.*, **36**, 1, 102 (1950).

(3) Biformin[4] also, in view of its behavior (instability and silver salt formation) and of the ultraviolet absorption spectrum[1,4] of a crude preparation, probably belongs to this class of compounds.

(4) W. J. Robbins, F. Kavanagh and A. Hervey, *Proc. Nat. Acad. Sci.*, **33**, 176 (1947).

(5) K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., Chapter 5.

(6) The first paper in this series was published in 1941.[7] It described the isolation of a highly unsaturated ester to which an acetylenic structure was assigned, tentatively. Due to lack of facilities, spectrophotometric studies were not made.

(7) N. A. Sörensen and J. Steue, *Ann.*, **549**, 80 (1941).

(8) (a) R. T. Holman and N. A. Sörensen, *Acta Chem. Scand.*, **4**, 416 (1950); (b) T. Bruun, C. M. Haug and N. A. Sörensen, *ibid.*, **4**, 850 (1950); (c) N. A. Sörensen and K. Stavholt, *ibid.*, **4**, 1080 (1950); (d) K. Stavholt and N. A. Sörensen, *ibid.*, **4**, 1567 (1950); (e) N. A. Sörensen and K. Stavholt, *ibid.*, **4**, 1575 (1950).

(9) K. W. Hausser, R. Kuhn and G. Seitz, *Z. physik. Chem.*, **29B**, 391 (1935).

(10) E. R. H. Jones, unpublished data.

TABLE I

Compound	Maxima, mμ					Solvent	Ref.
cis-α,β-Dihydromatricaria acid $(CH_3{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH_2CH_2{-}COOH)$	215	239	251.5	265.5	282.2	Hexane	[a]
trans-α,β-Dihydromatricaria acid	215	239	252.0	265.5	282.0	Hexane	[a]
$CH_2{=}CH{-}C{\equiv}C{-}C{\equiv}CH$	...	236	248	262	277	95% EtOH	[b]
$CH_3{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}CH$	...	238	251	264	280	95% EtOH	[b]
Nemotin $({-}C{=}C{-}C{\equiv}C{-}C{\equiv}C{-})$[d]	207	236	248	262	276	Water	[c]
Nemotinic acid	208	237	249	263	277	Water	[c]
Nemotin (ν of maxima)		1271.2	1209.7	1145.0	1087.0	f.	
(Δν)			61.5	64.7	58	f.	
Nemotinic acid (ν of max.)		1265.8	1204.8	1140.7	1081.1	f.	
(Δν)			61.0	64.1	59.6	f.	

[a] Laboratory of Sörensen.[11] [b] Laboratory of E. R. H. Jones.[10] [c] New York Botanical Garden.[1,2] [d] Grouping suggested by Dr. Sörensen.

TABLE II

Compound	Maxima mμ							Solvent	Ref.
Compound $C_{12}H_{10}O$ from *Artemisia vulgaris* (probably an ene-triyne)	231.0	242.5	257.7	272.5	289.0	308.1	328.6	Hexane	[a]
Nemotin A (alkali conversion product of Nemotin) $({-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{=}C{-})$[d]	231	242	257.8 (shoulder)	272	289	307	328	Phosphate buffer (*p*H 7)	[b]
Compound from *Clitocybe diatreta* (not analyzed)[e] $({-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{=}C{-})$[d]	230	240	...	270	285	303	323	95% ethanol	[c]
Nemotin A (ν of maxima)	1298.7	1239.7		1102.9	1038.1	977.2	914.6	f.	
(Δν)		59			64.8	60.9	62.6	f.	
Compound from *Clitocybe diatreta* (ν of maxima)	1304.3	1250.0		1111.1	1052.6	990.1	928.2	f.	
(Δν)		54.3			58.5	69	61.9	f.	

[a] Laboratory of Sörensen.[8e] [b] New York Botanical Garden.[1,2] [c] New York Botanical Garden.[12] [d] Grouping suggested by Dr. Sörensen. [e] This compound was obtained in amounts insufficient for satisfactory purification. In different preparations the positions of the maxima above 300 mμ varied by 2 or 3 mμ.

TABLE III

Compound	Maxima, mμ					Solvent	Ref.
cis-Lachnophyllum ester $(CH_3{-}CH_2{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH{-}COOCH_3)$	224.0	Inflexion	277.0	291.1	308.8	Hexane	[a]
trans-Lachnophyllum ester	223.5	256.8	271.0	287.2	305.3	Hexane	[b]
Compound from *Clitocybe diatreta* (tentative formula, $C_{17}H_{12}N_2O_6$) $({-}C{\equiv}C{-}C{\equiv}C{-}C{=}C{-}COOR)$[d]	225	260	275	291	310	95% Ethanol	[c]
Compound from *Clitocybe diatreta* (ν of maxima)	1333.3	1153.8	1090.9	1030.9	967.7	f.	
(Δν)			63.1	60.0	63.2	f.	

[a] Laboratory of Sörensen.[8b,e] [b] Laboratory of Sörensen.[8b] [c] New York Botanical Garden.[12] [d] Grouping suggested by Dr. Sörensen.

TABLE IV

Compound	Maxima, mμ						Solvent	Ref.
$R{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}COOH$	....	....	272	288	307	328	95% Ethanol	[a]
Agrocybin $({-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}COOR)$[c]	216	224	269	286	304	325	95% Ethanol	[b]
Agrocybin (ν of maxima)	1388.9	1339.3	1115.2	1048.9	986.8	923.1	f.	
(Δν)		49.6		66.3	62.1	63.7	f.	

[a] Laboratory of E. R. H. Jones.[10] [b] New York Botanical Garden.[12] [c] Grouping suggested by Dr. Sörensen.

by Dr. Sörensen as probably common to both are indicated.

At least two other compounds with this characteristic absorption spectrum have been found in culture liquids of *Basidiomycetes*. These are being studied.

Besides the compounds already referred to, other examples of naturally occurring di- or polyacetylenes so far reported are described in the Annals of the Ministry of Agriculture of the Dutch East Indies in 1907, one by Wiljams, Smirnow and Goljmov[13] in 1935, and one by Castille[14] in 1939. The first two of these were obtained from plants of Compositae, the third from boleko nuts. It is of interest that these highly unstable compounds occur both in higher plants and in fungi.

Acknowledgment.—The author wishes to express

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(11) P. K. Christensen, unpublished data.

(12) M. Anchel, unpublished data.

(13) W. W. Wiljams, V. S. Smirnow and V. P. Goljmov, *J. Gen. Chem.* (*U. S. S. R.*), **5**, 1195 (1935).

(14) A. Castille, *Ann.*, **543**, 104 (1940).

her gratitude to Dr. Jones and Dr. Sörensen for reading the manuscript, and for making available their unpublished data.

THE NEW YORK BOTANICAL GARDEN
BRONX PARK
NEW YORK, N. Y.
RECEIVED OCTOBER 29, 1951

Non-exchange of Radiocyanide and Radiosulfide Ions with Aqueous Thiocyanate Ion[1]

BY ARTHUR W. ADAMSON AND PHILLIP S. MAGEE

The exchange reactions of $C^{14}N^-$ and $S^{35=}$ ions with thiocyanate ion have been investigated with essentially negative results.

Experimental

The $KC^{14}N$ solution was prepared from $BaC^{14}O_3$ by the method of Adamson,[2] and that of Na_2S^{35} by the addition of sulfate-free BaS^{35}.[3] The exchange experiments were carried out by mixing the appropriate solutions in small centrifuge tubes which were then sealed. Those containing sulfate were sealed in a nitrogen atmosphere.

After the elapse of the desired time, the separation of radiocyanide and thiocyanate ions was carried out by the precipitation of zinc cyanide. The zinc cyanide was purified by reprecipitation and then treated by the distillation and sample preparation method previously reported.[4] The separation of radiosulfide and thiocyanate ions was accomplished by precipitation of cadmium sulfide. The cadmium sulfide was subjected to a fairly elaborate purification before being counted, in order to remove coprecipitated thiocyanate ion. The samples of zinc cyanide or of cadmium sulfide were counted with a mica end window counter (2 mg./cm.^{2} window) and with an atmospheric pressure flow counter, respectively.

Approximate corrections for self absorption were made.

TABLE I

EXCHANGE OF RADIOCYANIDE WITH THIOCYANATE IN AQUEOUS SOLUTION

$(KSCN) = 0.19\,f$; $(KC^{14}N) = 0.59\,f$

*p*H	Temp., °C.	Exchange time, hr.	Exchange,[a] %
11.10	24	140	0.80
12.70	24	334	.61
12.70	60	170	.26
14.0	24	187	.65
14.0	60	163	.10
0.5	24	160	2.26

[a] Defined as in reference 5.

The data given in Table I are representative of the rather larger total amount of results obtained, and indicates no measurable exchange, with the possible exception of the system at *p*H 0.5. The results with radiosulfide agree with those reported in this issue by Heisig and Holt[5] in that no exchange was found in solutions 0.3 *f* in KSCN and 0.05 *f* in Na_2S at room temperature, after 204 hours at *p*H 12.6, and after 554 hours at *p*H 13.4.

These findings of negligible exchange are in accord with the difficulties of formulating potential mechanisms. Thus, the fact that the free energy for the primary dissociation of thiocyanate into sulfur and cyanide ion is positive by 16 kcal.[6] is in agreement with the fact that this path does not lead to exchange.

An alternative mechanism, in the case of the cyanide-thiocyanate system, might be considered to be an exchange of sulfur through the intermediate $NCSCN^{-2}$, but one is confronted with the impossibility of writing a structure for this species without exceeding the octet on carbon or invoking an improbable imide formulation for the cyanide group. It is noteworthy, however, that the analogous intermediate $O_3SSSO_3^{-4}$ has been proposed for the measurable exchange between sulfite and thiosulfate.[7] Here, however, structures of some *a priori* plausibility can be written since it is not unreasonable to exceed the octet on sulfur. Somewhat similar considerations serve to rationalize the lack of exchange of sulfide and thiocyanate, in contrast to the measurable exchange of sulfide with thiosulfate.[7]

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA
RECEIVED JULY 31, 1951

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[1] These investigations were carried out under contract N6onr23809 between the University of Southern California and the Office of Naval Research.

[2] A. W. Adamson, THIS JOURNAL, **69**, 2564 (1947).

[3] The tracers were obtained from the Atomic Energy Commission.

[4] A. W. Adamson, J. P. Walker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[5] G. E. Heisig and R. Holt, *ibid.*, **74**, 1597 (1952).

[6] W. M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, Inc., New York, N. Y., 1938, p. 128.

[7] D. P. Ames and J. E. Willard, THIS JOURNAL, **73**, 164 (1951).

The Kinetics of the Thermal Decomposition of Aluminum Borohydride[1]

BY RICHARD S. BROKAW AND ROBERT N. PEASE

Schlesinger, Sanderson and Burg[2] have observed that as the temperature is raised aluminum borohydride ($Al(BH_4)_3$) decomposes yielding hydrogen and solid products. This research was undertaken in order to obtain more detailed information as to the nature of the pyrolysis. Preliminary observations[3] of pressure–time curves at temperatures of 150° and higher showed the initial slopes of such curves to be proportional to the initial aluminum borohydride pressure, suggesting that the decomposition is essentially a first order process. Products were hydrogen and inhomogeneous solid products containing varying amounts of hydrogen.

Since both aluminum borohydride and the solid products yield hydrogen on heating it is not possible to calculate the aluminum borohydride pressure as a function of time from the total pressure. Instead, borohydride was run into a thermostated reaction bulb[4] to the desired pressure, and the clock started. After a predetermined time the thermostat was removed and the reaction bulb rapidly cooled to room temperature. A pressure reading was made, and then the hydrogen evolved was pumped off at liquid nitrogen temperature. On warming again to room temperature the pressure of undecomposed borohydride was measured, and from this the pressure at the reaction temperature was calculated. From a series of such runs for different time intervals the disappearance of aluminum borohydride as a function of time was determined. That the condensible residue was in fact undecomposed aluminum borohydride was established by observing (a) on exhaustive decomposition at 450–600° (by heating in the luminous flame of a torch) about 5.6–5.9 volumes of hydrogen are obtained both with the condensible gaseous residue and with aluminum borohydride and (b) if the residues from several runs are returned to the re-

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[1] (a) Taken from a thesis submitted by Richard S. Brokaw in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. (b) The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coördinated by Project Squid, Princeton University. (c) We wish to acknowledge the assistance of Dean H. S. Taylor, who has general supervision of this project. (d) Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] H. T. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940).

[3] E. J. Badin and P. C. Hunter, unpublished work.

[4] The apparatus was the one used in studying the reaction of aluminum borohydride with olefins: see Brokaw and Pease, THIS JOURNAL, **72**, 3237 (1950).

action bulb they decompose at the same rate as aluminum borohydride.

The initial decomposition rate for 1000 seconds at 159° was found to be unaffected by the nature of the flask surface (either clean or coated with solid products in various stages of decomposition). Furthermore, this rate was the same in the presence of added hydrogen. Half-lives were about 6500 seconds at 159° and 450 seconds at 189°.

The borohydride pressure as a function of time may be expressed by the equation

$$P_{\mathrm{Al(BH_4)_3}} = P_{0\mathrm{Al(BH_4)_3}}\,[ae^{-k_it} + (1 - a)e^{-k_ft}] \quad (1)$$

where

$P_{\mathrm{Al(BH_4)_3}}$ = pressure of aluminum borohydride at time t
$P_{0\mathrm{Al(BH_4)_3}}$ = initial pressure of aluminum borohydride
a = constant $1 > a > 0$
k_i, k_f are constants

In Table I the experimental results are summarized in terms of the constants of equation (1). The runs at 159° and 85 mm. initial pressure were performed in a reaction vessel packed with glass beads so that the area–volume ratio was increased by a factor of about twelve, and it is seen that the rate is unaffected.

TABLE I

Temp., °C.	Initial $\mathrm{Al(BH_4)_3}$ pressure (mm.)	a	k_1(sec.$^{-1}$)	k_f(sec.$^{-1}$)
159	110.0	0.127	1.68×10^{-3}	8.51×10^{-5}
	85.0	.146	....	8.25×10^{-5}
	57.5	.125	1.4×10^{-3}	7.88×10^{-5}
189	85.0	.406	4.48×10^{-3}	6.33×10^{-1}

In the hope of determining the number of hydrogen atoms split off in the initial stage of the reaction plots of pressure of hydrogen evolved divided by pressure of borohydride decomposed *versus* time at 159 and 189° were made. These plots were very steep near the origin and it was only possible to conclude that not more than three hydrogen atoms are lost in the initial process.

The differential equations for successive first order reactions with reversible steps have been solved by Rakowski.[5] For such systems expressions similar in form to equation (1) are obtained. However, one would expect that the reverse of the reactions in which hydrogen is split off should be second order and should show a dependence on the hydrogen pressure, yet such an effect is not observed.

It is to be concluded, therefore, that while equation (1) adequately describes the aluminum borohydride concentration as a function of time, the mechanism of the reaction may be determined only when the nature and concentrations of the intermediate species become known.

[5] Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
RECEIVED NOVEMBER 24, 1951

Condensation of Lactones with Benzene

BY ROBERT V. CHRISTIAN, JR.

Eijkman[1] studied the reaction of benzene and its homologs with a few aliphatic lactones in the presence of aluminum chloride. For example, γ-valerolactone with benzene gave γ-phenylvaleric acid in unspecified yield.[1a] The ready availability of several simple, aliphatic lactones suggested an examination of this reaction as a means for the synthesis of certain aryl-aliphatic acids.

It was found that the $\mathrm{AlCl_3}$ catalyzed condensation of benzene with the appropriate lactone yielded γ-phenylbutyric acid, γ-phenylvaleric acid and δ-phenylvaleric acid in yields of 44, 61 and 51%, respectively. Significantly, no isomerization of the side chain took place and the phenyl radical was attached at the position of the alcohol function in the parent hydroxy acid. A competing reaction was the further alkylation of the initially formed product to yield polyfunctional acids. This could probably be minimized by a suitable choice of reaction conditions.

Lactide did not condense with benzene in the presence of aluminum chloride even upon heating at 70–80°. In the case of β-propiolactone the principal reaction seemed to be destruction of the lactone by the aluminum chloride and the expected β-phenylpropionic acid was not isolated in quantities sufficient to permit conclusive identification.

Experimental

The condensations were carried out in flasks equipped for reflux and mechanical stirring. The temperature during the early stages of the reaction was held below 45° by varying the rate of addition of the last component and by external cooling with water when necessary.

γ-Phenylbutyric Acid.—To a stirred solution of 43 g. (0.5 mole) of γ-butyrolactone (Cliffs Dow Chemical Co., Marquette, Michigan) in 100 g. of benzene, 93 g. (0.7 mole) of powdered aluminum chloride was added in small portions. After 4 hours 100 ml. of benzene was added and the mixture was allowed to stand overnight at room temperature. Subsequent to heating in a water-bath for an hour, the mixture was hydrolyzed with ice and hydrochloric acid. Distillation of the benzene layer gave 36 g. (44%) of white crystals of b.p. 120–125° (1 mm.). Crystallization from methanol and water yielded material whose melting point, 48–49°, was undepressed when mixed with authentic γ-phenylbutyric acid. Approximately 30 g. of higher boiling material was not examined further.

γ-Phenylvaleric Acid.—To a stirred suspension of 50 g. (0.38 mole) of aluminum chloride in 60 g. of benzene, there was added dropwise 30 g. (0.3 mole) of γ-valerolactone (Monsanto Chemical Co., St. Louis, Missouri). After being heated in a water-bath for 30 minutes, the mixture was hydrolyzed as before. Distillation of the benzene layer gave 32.5 g. (61%) of colorless liquid boiling at 123–126° (0.5 mm.).

That the substance was γ-phenylvaleric acid was confirmed by conversion to 4-methyl-1-tetralone[2] from which the known solid semicarbazone[2,3] was obtained in the usual manner. The heretofore undescribed *p*-bromophenacyl ester was also prepared. It crystallized from dilute methanol as white leaflets melting at 76°. *Anal.* Calcd. for $\mathrm{C_{19}H_{19}O_3Br}$: Br, 21.3. Found: Br, 21.1.

In other experiments, the residue remaining after distillation of γ-phenylvaleric acid was esterified with ethanol. The resulting material had boiling point 165–169° (0.5 mm.), $d^{25}{}_4$ 1.0212, $n^{25}\mathrm{D}$ 1.4914. Analysis indicated that it was probably diethyl γ,γ′-phenylenedivalerate. *Anal.* Calcd. for $\mathrm{C_{20}H_{30}O_4}$: MR_D, 94.62; sapn. equiv., 167; C, 71.9; H, 9.04 Found: MR_D, 94.84; sapn. equiv., 169, 171; C, 72.2; H, 9.37.

δ-Phenylvaleric Acid.—Aluminum chloride (33.4 g., 0.25 mole) was added in portions to a stirred solution of 20 g. (0.20 mole) of δ-valerolactone (prepared in quantitative yield from δ-hydroxyvaleraldehyde[4] by oxidation with per-

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[1] (a) J. F. Eijkman, *Chem. Weekblad*, **1**, 421 (1904); (b) J. F. Eijkman, *ibid.*, **2**, 229 (1905); **4**, 191, 727 (1907).

[2] M. C. Kloetzel, THIS JOURNAL, **62**, 1708 (1940).

[3] F. Mayer and G. Stamm, *Ber.*, **56**, 1424 (1923); J. von Braun and A. Stuckenschmidt, *ibid.*, **56**, 1724 (1923).

[4] G. F. Woods, Jr., *Org. Syntheses*, **27**, 43 (1947).

acetic acid) in 150 ml. of benzene. After the mixture had stood overnight at room temperature it was heated at 100° for an hour and then hydrolyzed in the usual way. The benzene layer was distilled to yield 18 g. (51%) of solid boiling at 130–140° (2 mm.). Crystallization from petroleum ether (b.p. 35–45°) gave colorless crystals of m.p. 58–59°; this was unchanged by mixture with authentic δ-phenylvaleric acid.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WICHITA
WICHITA 14, KANSAS

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Exchange between the Tris-(5,6-dimethyl-1,10-phenanthroline) Complexes of Iron(II) and -(III)[1]

BY LOIS EIMER AND A. I. MEDALIA

Exchange reactions which proceed *via* transfer of an electron are of interest as a simple, symmetrical class of oxidation–reduction reactions. Uncertainties as to the states of complexing, which arise in studying simple ions, may be avoided by studying complexes of known structure, such as the phenanthroline complexes of iron(II) and -(III).

In undertaking such a study, an experimental survey was first made of seven commercially available phenanthrolines and analogs. It was established[2] that the most suitable compound for such a study, from the standpoint of the stability of both the ferrous and ferric forms in aqueous acid, is 5,6-dimethyl-1,10-phenanthroline, with which therefore all further work was conducted.

Experimental.—The 5,6-dimethyl-1,10-phenanthroline was used as obtained from the G. F. Smith Chemical Co. The red ferrous complex (designated as ferroin-5,6) was prepared by complexing of ferrous iron with 5–10% excess of the phenanthroline at *p*H 8.5–9.0; the blue ferric complex (ferriin-5,6), by oxidation of ferroin-5,6 with lead dioxide in 1 *N* sulfuric acid, followed by filtration through sintered glass to remove PbO_2 and $PbSO_4$. These compounds have been prepared with inactive iron; and with samples of radioactive iron of both low and high activity (Fe^{55}), which were obtained from Oak Ridge and then purified by extraction, fumed with sulfuric acid, and reduced with sulfur dioxide under the conditions suggested by Marti and Conde.[3] All water used was purified in a continuous quadruple Pyrex still.

Two methods of separation have been developed: (1) The ferroin-5,6 is precipitated as the perchlorate in 50% perchloric acid and is collected on a glass frit, the ferriin-5,6 remaining in solution. The precipitate is counted on the frit after drying 48 hours in a vacuum desiccator. (2) The ferroin-5,6 is extracted with a solution of camphorsulfonic acid (0.013 *f*) in chloroform, the ferriin-5,6 remaining in the aqueous phase.

The extraction method can be used at lower concentrations than the precipitation method; however, a lower limit is set by the reduction of ferriin-5,6 by impurities in the chloroform. Of several methods which were investigated for purification of the chloroform, the following gave the best results: analytical reagent grade chloroform was washed at 0° with several portions each of water, concentrated sulfuric acid, 0.1 *f* sodium bicarbonate, and water, in succession; then dried with potassium carbonate, and distilled over calcium hydride in a nitrogen atmosphere. The product was collected in a chilled receiver and stored under nitrogen at 5°. Ethylene dichloride showed some promise as an alternative solvent but its use was not fully investigated.

Ferriin-5,6 remaining in the aqueous phase after extraction has been reduced by passage of sulfur dioxide for 30 seconds; after addition of carrier (inactive ferroin-5,6, 5 × 10^{-4} *f*) the ferroin-5,6 was precipitated by addition of Na_2CdI_4 (0.02 *f*) at 0° and filtered through S&S #756 paper placed on a glass frit. The paper was dried at 110°, mounted and placed under an end-window G-M tube filled with 71.5 cm. of argon and 2.5 cm. of ethyl acetate, for counting.

Several methods have been investigated[2] for recovery of active iron from the chloroform extracts of ferroin-5,6. Satisfactory results were obtained by a procedure involving the following steps: evaporation of the extract in a silica dish, ignition at 500°, solution in boiling 0.6 *f* HCl, reduction with hydroxylamine hydrochloride, and re-formation of ferroin-5,6 in acetate buffer followed by addition of carrier, precipitation, filtration and counting as above.

Exchange Experiments with 4.2 × 10^{-4} *f* Solutions.—Mixtures were prepared at 0° of 2 cc. each of active and inactive ferroin-5,6 and ferriin-5,6 as shown in Table I. About five seconds were required for mixing. Six cc. of 70% perchloric acid at 0° was added and the mixture was shaken for one minute and then filtered. Filtration required approximately one minute. The precipitate was counted and in some cases the filtrate was treated with sulfur dioxide and the ferroin-5,6 thus formed was also precipitated as the perchlorate, filtered and counted. Results are given in Table I.

TABLE I

EXCHANGE OF 4.2 × 10^{-4} *f* SOLUTIONS IN 1 *N* SULFURIC ACID AT 0°

Total count on initially active species: 420 c./min.

Initially active species	c./min. ferroin-5,6 fraction	c./min. ferriin-5,6 fraction
Ferriin-5,6	198	...
Ferriin-5,6	204	...
Ferroin-5,6	185	183
Ferroin-5,6	194	249

Total activity of the ferroin-5,6 was determined by perchlorate precipitation; and of the ferriin-5,6 by reduction with sulfur dioxide followed by perchlorate precipitation. Completeness of precipitation of ferroin-5,6 and completeness of recovery of the ferriin-5,6 in the filtrate were checked spectrophotometrically.

It appears from the results in Table I that complete exchange took place in the experiments.

Exchange Experiments with 2.2 × 10^{-5} *f* Solutions.—Four cc. of a solution of camphorsulfonic acid (0.013 *f*) in chloroform was placed in a 30-cc. separatory funnel and chilled to 0°. To this were added simultaneously 2 cc. each of ferroin-5,6 and ferriin-5,6 at 0°, each 4.4 × 10^{-5} *f* before mixing. The separatory funnel was immediately stoppered and shaken for ten seconds; the chloroform was then drained off, and both phases were worked up as described above. Results are given in Table II.

TABLE II

EXCHANGE OF 2.2 × 10^{-5} *f* SOLUTIONS IN 1 *N* SULFURIC ACID AT 0°

Initially active species	c./min. in ferroin fraction	c./min. in ferriin fraction	Sum of fractions	Total on original ferroin solution	% of activity recovered
Ferroin-5,6	4350	4000	8350	8190	102
Ferroin-5,6	. .	3820	. .	8190	. . .
Ferriin-5,6	3980	3910	7890	8190	97
Ferriin-5,6	3780	3780	7560	8190	93
Blank (Ferriin-alone)	950	6720	7670	8190	94
Ferroin-5,6	4380	3400	7780	7750	100
Ferroin-5,6	4200	3890	8090	7750	104
Ferriin-5,6	3900	3880	7780	7750	100
Ferriin-5,6	3990	3720	7710	7750	100
Blank (Ferriin-alone)	620	6520	7140	7750	92

Reasonably good recovery was obtained in all experiments (between 92 and 104%). Reduction of ferriin-5,6 by the

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] L. Eimer and A. I. Medalia, BNL-1022.

[3] F. B. Marti and F. L. Conde, *Anal. Chim. Acta*, **3**, 547 (1949).

camphorsulfonic acid–chloroform amounted to about 10%. Within the over-all experimental error of about 10% the activity in both fractions was the same, and there was no definite evidence for greater recovery of activity in the initially active than in the initially inactive species. We therefore conclude that, using an extraction technique of separation, complete exchange is found between ferroin-5,6 and ferriin-5,6 within 15 seconds at 0°, at concentrations of $2.2 \times 10^{-5} f$ in each species.

We are grateful to Dr. R. W. Dodson for his guidance and stimulation.

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, LONG ISLAND, N. Y. RECEIVED NOVEMBER 21, 1951

The Ammonia Induced Decomposition of Nitric Oxide

BY CHARLES P. FENIMORE[1] AND JOHN R. KELSO

A means of catalyzing the sluggish decomposition of nitric oxide is suggested by reaction (A) which occurs in the thermal decomposition of nitrous oxide.[2]

$$O + N_2O \longrightarrow 2NO + 36.6 \text{ kcal.} \qquad (A)$$

The suggestion we draw from (A) is that its reverse might go if the unfavorable energy change could be overcome. If the oxygen atom could react with a particle, X, to form a labile oxide of dissociation energy, q, then the following scheme might permit the desired catalysis.

$$\begin{gathered} 2NO + X \longrightarrow N_2O + XO + (q - 36.6) \text{ kcal.} \\ XO + NO \longrightarrow NO_2 + X + (71 - q) \\ NO + N_2O \longrightarrow NO_2 + N_2 \\ 2NO_2 \longrightarrow 2NO + O_2 \end{gathered}$$

For if q lies between 37 and 71 kcal., the first two steps would be exothermal and, perhaps, relatively fast. The last two steps describe the catalytic decomposition of nitrous by nitric oxide and are known to be consistent with that process.[2] Since an N–O single bond possesses an energy in the desired range, we hoped that ammonia or some intermediate derived from ammonia might catalyze the decomposition of nitric oxide.

Experimental

Premixed ammonia and nitric oxide were heated in a spherical quartz vessel of 523-cc. volume. Both gases were distilled and were spectroscopically pure (infrared spectra). In a few runs in which hydrazine was used, the hydrazine was twice distilled from barium oxide.

The reacting gas was sampled by opening the quartz vessel to an evacuated bulb which was fitted with a manometer and a very small freezing appendix. The condensible gases, including oxygen in the presence of excess nitric oxide, were frozen with liquid nitrogen and the permanent gas measured. This was infrared inactive, hydrogen and oxygen free by analysis, and therefore all nitrogen.

A small amount of nitrous oxide was identified in the condensible portion by its infrared spectrum. The nitrous oxide was found only in partially reacted mixtures and disappeared toward the end of the catalytic decomposition.

Results

At temperatures at which pure nitric oxide is decomposed only very slowly, the ammonia induced decomposition of a constant initial pressure of nitric oxide, which is always in excess, is characterized by: (1) The yield of nitrogen, $(N_2)_\infty$, is proportional to the square root of the initial concentration of ammonia, $(NH_3)_0^{1/2}$.

(2) The half-time of the evolution of nitrogen is independent of $(NH_3)_0$.

TABLE I

DECOMPOSITION OF NO, NH_3 MIXTURES AT 700 MM. INITIAL PRESSURE[a]

T, °C.	(NH_3), %	$(N_2)_\infty/(NH_3)_0^{1/2}$, mm.$^{1/2}$	$\frac{1}{2}$ time, min.
702	5	44	19
	2.5	41	17
	1.0	42	18
	0.5	43	18
725	2.5	34	9.0
	1.0	35	8.5
	0.5	35	9.0
740	2.5	28	4.4
	1.0	28	4.6
755	2.5	32	3.2
	1.0	30	3.2

[a] All pressures measured at reaction temperature.

These findings are proved by the data in Table I and illustrated by the typical curves in Fig. 1.

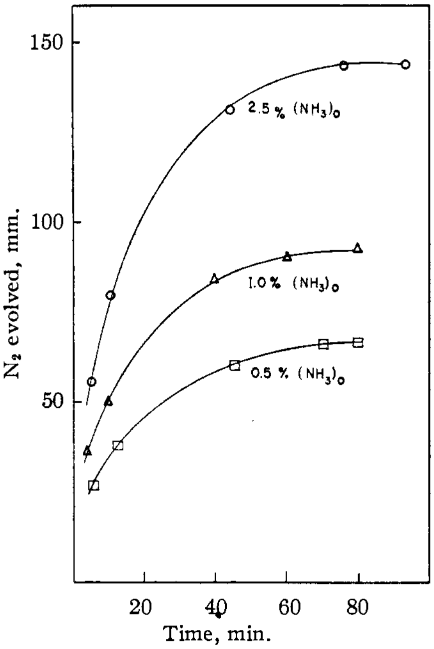

Fig. 1.—Evolution of N_2 from 700 mm. NO + NH_3 at 725°. Initial % of NH_3 is marked on each curve.

With varying initial pressures of nitric oxide, we find the data given in Table II, typical curves in Fig. 2.

(3) At 700 and 900 mm. pressure, the half-time of the evolution of nitrogen varies roughly inversely with the square of initial nitric oxide. On the initial reaction, rate varies roughly directly with this quantity.

(4) The yield of nitrogen at a fixed pressure is approximately independent of the initial nitric oxide concentration as long as this is in excess. This conclusion is not obvious from Fig. 2, but note in Table II that the low yield of nitrogen obtained

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[1] General Electric Research Laboratory, The Knolls, Schenectady, New York.

[2] F. F. Musgrave and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **135A**, **23** (1932).

TABLE II

DECOMPOSITION OF NO, NH_3 MIXTURES AT VARYING NO CONCENTRATIONS[a]

T, °C.	Reactants, mm. NH₃	Reactants, mm. NO	$(N_2)_\infty$, mm.	½ Reaction time, min. obsd.	½ Reaction time, min. calcd.	$k_a = 10_5$
702	17.5	882	182	9.0	9.5	19
		682	172	17.0	17.0	
		482[b]	140	24.0	36.0	
		482	174			
725	3.5	896	82	5.5	5.5	36
		696	67	9.0	9.0	
740	7.0	893	84	2.5	2.6	74
		693	76	4.6	4.5	
755	17.5	882	158	1.8	1.9	104
		682	132	3.2	3.2	
		682[b]	152	3.4	3.2	

[a] All pressures measured at reaction temperatures. Half-reaction time calculated from

$$t_{\frac{1}{2}}(\text{calcd.}) = \frac{2}{k_a[(NO) - 2(N_2)_\infty]}\left[\frac{1}{[2(N_2)_\infty - (NO)_0]}\ln\left\{\frac{(NO)}{2[(NO)_0 - (N_2)_\infty]}\right\} - \frac{(N_2)}{(NO)_0[(NO)_0 - (N_2)_\infty]}\right]$$

[b] The reactants for the last runs at 702 and 755° contained added N_2 to give an initial pressure of 900 mm.

from 482 mm. nitric oxide at 702° can be raised almost to the yield from 882 mm. nitric oxide by the addition of inert gas to give the same initial pressure. The effect is observed at 755° also.

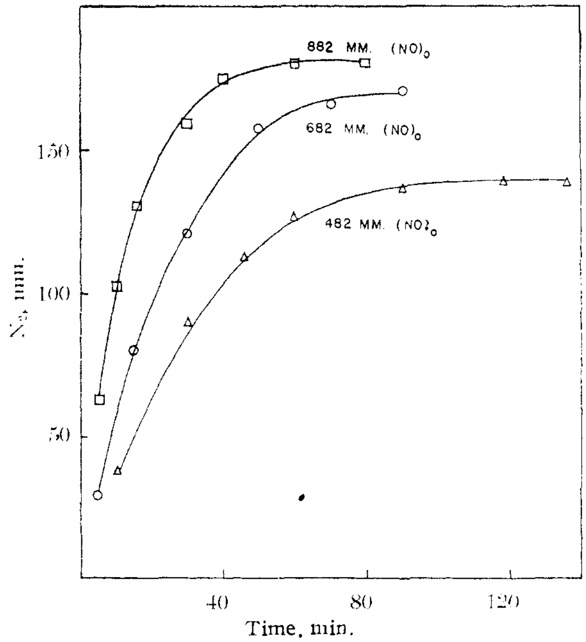

Fig. 2.—Evolution of N_2 from NO, NH_3 mixtures at 702° containing 17.5 mm. NH_3 initially. Initial NO pressure is marked on each curve.

The rate equations

$$-\frac{d(NH_3)}{dt} = k_a(NH_3)(NO)^2$$

$$\text{and } \frac{d(N_2)}{dt} = k_b(NH_3)^{\frac{1}{2}}(NO)^2$$

are consistent with our observations. Because then $(N_2)_\infty = (2k_b/k_a)(NH_3)_0^{\frac{1}{2}}$, characteristics (1) and (4), and $t_{\frac{1}{2}}$ = approximately $2\ln2/k_a \cdot (NO)_0^2$, characteristics (2) and (3) (more exactly, $t_{\frac{1}{2}}$ is given in the footnote to Table II). But other choices of exponents in the rate equations will not give these relations.

An obvious interpretation of the one-half order ammonia dependence of the rate of formation of nitrogen is that ammonia itself is not the catalytic agent, but that two catalytic particles arise from each ammonia molecule consumed in a rate determining reaction. An inert gas effect in increasing the yield of nitrogen is then explicable because of the possibility of diffusion of the catalytic particles to the vessel wall and their destruction there.

The catalytic particles might be NH_2 radicals, and since the thermal decomposition of hydrazine to NH_2 is first order and homogeneous, in part, above 650-700°,[3] we looked into the possibility of inducing the decomposition of nitric oxide by hydrazine at 800°. The higher temperature was chosen to increase the fraction of hydrazine decomposing unimolecularly in the gas phase. This reaction is not clean: nitrogen (but less than the moles of hydrazine taken) is formed at room temperature when hydrazine is mixed with nitric oxide, and the slow decomposition of nitric oxide is appreciable in our apparatus at 800°. It is scarcely worthwhile to tabulate the yields. Nitric oxide is decomposed by 0.2–1.0% hydrazine at 800° and gives nitrogen in yields comparable to those obtained with the same amount of ammonia at 700–750° although the reaction with hydrazine is less reproducible. We conclude from the runs with hydrazine, rather as we began, that the catalytic framents might be, but need not necessarily be, NH_2 radicals.

The foregoing data are insufficient to illuminate the mechanism. If one identifies X with NH_2 in the four equations set down in the introduction to this paper, assumes that NH_2 radicals are generated two for every ammonia molecule consumed in a reaction 1st order in ammonia and 2nd order in nitric oxide, and supposes that the radicals are destroyed two at a time in the gas phase, then one can arrive at rate equations agreeing with those deduced above. But the values of k_a in Table II give a temperature dependence of the consumption of ammonia corresponding to an activation energy of 70 ± 5 kcal./mole. This large activation energy suggests that the formation of NH_2 radicals cannot be both termolecular and relatively fast and so the question of mechanism must be left open.

(3) M. Szwarc, *Proc. Roy. Soc.* (*London*), **198A**, 267 (1949).

BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MD. RECEIVED JULY 13, 1951

The Reaction of Some Aryllithium Compounds with Epichlorohydrin

BY HENRY GILMAN, BURT HOFFERTH AND JULIAN B. HONEYCUTT

In connection with the synthesis of some alkamine ethers,[1] it was of interest to prepare a series of aromatic secondary alcohols by the action of

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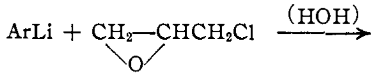
(1) B. Hofferth, Doctoral Dissertation, Iowa State College, 1950.

aryllithium reagents upon epichlorohydrin.[2] Accordingly, phenyl-, *p*-tolyl-, 1-naphthyl- and *p*-dimethylaminophenyllithium were treated with epichlorohydrin to give satisfactory yields of the corresponding arylpropylene chlorohydrins.

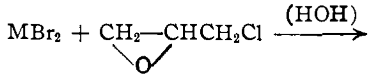


$$\text{ArLi} + \underbrace{\text{CH}_2\text{—CHCH}_2\text{Cl}}_{\text{O}} \xrightarrow{\text{(HOH)}} \text{ArCH}_2\text{CHOHCH}_2\text{Cl} \quad (1)$$

The reaction of 9-fluorenyllithium under like conditions did not produce an isolable product.

Similar reactions employing Grignard reagents have been carried out with epichlorohydrin to give generally unsatisfactory conversions to the desired products. The best yield of 1-chloro-3-phenyl-2-propanol prepared from phenylmagnesium bromide was 18.2%.[3] Yield data were not given in reports of authors employing *p*-tolylmagnesium bromide[4] and 1-naphthylmagnesium bromide.[3c] The product, 1-chloro-3-(*p*-dimethylaminophenyl)-2-propanol, which was prepared from *p*-dimethylaminophenyllithium has not been reported.

It has been shown previously[5] that the low yields of substituted chlorohydrins prepared from the less reactive organometallic compounds resulted from competition between reaction (1) and reaction (2) where M is a metallic cation capable of coordination with ether oxygen.



$$\text{MBr}_2 + \underbrace{\text{CH}_2\text{—CHCH}_2\text{Cl}}_{\text{O}} \xrightarrow{\text{(HOH)}} \text{BrCH}_2\text{CHOHCH}_2\text{Cl} \quad (2)$$

With phenylcadmium chloride,[6] for example, the only material isolated after 13 hours of reaction at room temperature was a dense liquid believed to be a mixture of glycerol bromochlorohydrin and glycerol dichlorohydrin.

The opening of the oxide ring by lithium bromide present in phenyllithium solutions may be responsible for the low yields obtained under ordinary conditions, since equivalent quantities of phenyllithium and epichlorohydrin at ether-reflux temperature gave only 9.8% of 1-chloro-3-phenyl-2-propanol. When initially lower temperatures and longer reaction periods were employed the yield was raised to 67%.

Experimental

All boiling points are uncorrected. The following example is typical of the procedures used to prepare three other chlorohydrins, the properties of which are reported in Table I.

TABLE I

SOME 3-ARYL-1-CHLORO-2-PROPANOLS

Ar–	Yield, %	B.p., uncor. °C.	Mm.	n^{20}D	d^{20}_{20}	Chlorine, % Calcd.	Found
p-$CH_3C_6H_4$–	42	140–143	12	1.5366	1.126	19.22	19.30
1-$C_{10}H_7$–	43	180–182	0.2	1.6189	1.236	16.09	15.86
p-$(CH_3)_2NC_6H_4$–	38	36–38	0.13	1.5208	1.023	17.78	17.99

1-Chloro-3-phenyl-2-propanol.—Epichlorohydrin (0.44 mole) in 60 ml. of anhydrous ether was placed in a 500-ml. three-necked flask fitted with a nitrogen inlet tube, mechanical stirrer and dropping funnel. The flask and contents were cooled to −78° in a Dry Ice–trichloroethylene-bath and 290 ml. (0.44 mole) of phenyllithium were added during a period of one-half hour. The mixture was stirred at −78° for 1.5 hours and then the bath was allowed to warm slowly to 0°.

The hydrolysis[7] was carried out in dilute sulfuric acid containing crushed ice. The ether layer was separated and washed successively with water, sodium carbonate solution and water. Subsequent to the drying of the extract over anhydrous sodium sulfate, the ether was removed by distillation. The product was distilled at 132–142° (13–17 mm.) to yield 50.5 g. (67.4%) of distillate having n^{20}D 1.5426. The 3,5-dinitrobenzoate melted at 119.5–120.5°. The reported n^{25}D and m.p. are 1.5470 and 120–121°, respectively.[3a]

In another preparation 0.18 mole of phenyllithium was treated with 0.18 mole of epichlorohydrin under similar conditions. The yield was 36.6 g. (66.2%) of product having b.p. 125–127° (11–12 mm.), n^{20}D 1.5420 and d^{20}_4 1.155.

Anal. Calcd. for $C_9H_{11}ClO$: Cl, 20.80. Found: Cl, 20.70.

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[2] For a discussion of the mechanism of the opening of oxide rings, see S. Winstein and R. B. Henderson in R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 27–42.

[3] (a) C. F. Koelsch and S. M. McElvain, THIS JOURNAL, **52**, 1164 (1930); see also (b) E. Fourneau and M. Tiffeneau, *Bull. soc. chim. France*, [4] **1**, 1227 (1907), and (c) E. Fourneau, J. Tréfouel and J. Tréfouel, *ibid.*, [4] **43**, 454 (1928).

[4] R. R. Read, H. Lathrop and H. L. Chandler, THIS JOURNAL, **49**, 3118 (1927).

[5] (a) I. Ribas and E. Tapia, *Anales soc. españ. fís. quím.*, **28**, 636, 691 (1930) [*C. A.*, **24**, 4265 (1930)] and (b) J. K. Magrane and D. L. Cottle, THIS JOURNAL, **64**, 484 (1942).

[6] Prepared by the addition of a small excess of fused and pulverized cadmium chloride to a solution of phenylmagnesium bromide.

[7] Color Test I should be negative before hydrolysis. See H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

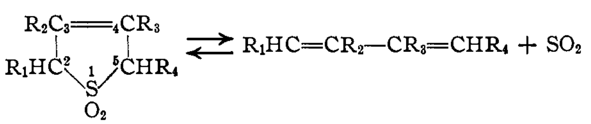
THE CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED NOVEMBER 3, 1951

Thermal Dissociation of 3-Phenyldihydrothiophene-1-dioxide

BY OLIVER GRUMMITT AND HELEN LEAVER

A comparison of the rates of thermal dissociation of the cyclic sulfones of butadiene, piperylene, isoprene, 1,3-dimethylbutadiene and 2,3-dimethylbutadiene to the diolefin and sulfur dioxide has



shown that this reaction is facilitated by 2-methyl substitution and is hindered to a smaller degree by 3-methyl substitution.[1] In extending this study to sulfones of arylbutadienes it was found that *cis*- and *trans*-1-phenyl-1,3-butadiene did not add sulfur dioxide to give either a cyclic sulfone or a polysulfone.[2] The sulfone of 2-phenyl-1,3-butadiene[3] was selected next.

While undertaking to prepare 2-phenyl-1,3-butadiene from methylethylphenylcarbinol by dehydration, bromination and debromination according to Backer and Strating,[3] the more convenient synthesis of Price, *et al.*, based on the condensation of α-methylstyrene, formaldehyde and acetic acid to 2-phenyl-4-acetoxy-1-butene and thermal de-

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[1] O. Grummitt, A. E. Ardis and J. Fick, THIS JOURNAL, **72**, 5167 (1950).

[2] (a) O. Grummitt and F. J. Christoph, *ibid.*, **73**, 3479 (1951); (b) O. Grummitt and J. Splitter, Organic Division, A.C.S. Meeting, Chicago, Illinois, September 5, 1950.

[3] H. J. Backer and J. Strating, *Rec. trav. chim.*, **53**, 525 (1934).

TABLE I

SPECIFIC REACTION VELOCITY CONSTANTS AND DERIVED DATA

Sulfone of	Temp., ± 0.02°	Av. k min.$^{-1}$ × 10^3	Detns.	Av. % dev.	Temp. for equal dissociation rates,[a] °C.	$\Delta E^{\ddagger b}$	$\Delta S^{\ddagger c}$	$\Delta F^{\ddagger d}$	Freq. fac.[e]
2-Phenyl-1,3-butadiene	138.8	3.72	2	0.5	150.4	43.5 ± 2.0	27 ± 4.9	32.1	7 × 10^{18}
	142.8	5.74	2	0.8					
	146.4	9.70	2	4.1					
Butadiene	115.1	6.26	4	2.7	124.7	33.6 ± 0.5	8.9 ± 1.2	30.1	7 × 10^{14}
	125.2	16.7	2	1.0					
	129.1	24.2	2	1.0					
Isoprene	108.8	1.35	1		131.2	34.6 ± 0.5	9.9 ± 1.2	30.6	1 × 10^{15}
	115.7	2.81	2	1.6					
	125.0	8.70	2	2.4					
	135.5	23.6	2	0.5					

[a] k = 15.8 × 10^{-3} min.$^{-1}$. [b,d] kcal./g. mole. [c] Entropy units. [e] Sec.$^{-1}$.

composition of this ester became available.[4] This readily gave the hydrocarbon in 34% yield and from this the sulfone was obtained in 50% yield, m.p. 131.3–131.8° (cor.).

The technique of carrying out the thermal dissociations and the calculation of the results were the same as used earlier.[1] The specific reaction velocity constants, heats of activation, etc., are summarized in Table I. The plot of the log of the undissociated sulfone *vs.* time at the various temperatures and the plot of log k *vs.* the reciprocal of the absolute temperature gave satisfactory straight lines. For comparison the corresponding data for butadiene and isoprene are included.

The greater stability of the sulfone of 2-phenyl-1,3-butadiene, as indicated by the higher values for $\Delta E^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta F^{\ddagger}$, compared to isoprene sulfone which in turn is somewhat more stable than butadiene sulfone, shows the stabilizing influence of the 3-phenyl group. While a reasonable explanation was offered for the facilitated dissociation of the sulfone due to the 2-methyl group,[1] there is no apparent explanation for the stabilizing influence of the 3-methyl group and the even greater effect of the 3-phenyl group in terms of the conventional strain theory or of inductive or electromeric effects.

These results suggest that related cyclic compounds containing the C_6H_5—C=C grouping should be stabilized and should form more readily. For example, phenylmaleic acid should more readily dehydrate to the anhydride than does maleic acid to maleic anhydride. This has already been observed in case of the methyl- and dimethylmaleic anhydrides, but there does not appear to be published information on phenylmaleic anhydride. A point of difference between the dissociation of the 2-phenylbutadiene sulfone and the other sulfones is the presence of liquid phenylbutadiene which does not distil rapidly from the unreacted sulfone, as do the more volatile butadiene and isoprene. This liquid phenylbutadiene might exert a solvent effect on the undissociated sulfone. The effect seemed to be a minor one however since the changing concentration of sulfone with time should alter the rate of dissociation. This was not observed.

From our work on the Backer and Strating synthesis of 2-phenyl-1,3-butadiene[3] two points are noteworthy: (1) the intermediate methylethylphenylcarbinol is more efficiently dehydrated in the presence of phosphoric acid than with alum, (2) the dehydrobromination of the intermediate phenylbromobutene, which had been done earlier over barium chloride at 380°, cannot be done with molten potassium hydroxide at 180° or with sodium amide.

Experimental

2-Phenyl-1,3-butadiene Sulfone.—The preparation of the hydrocarbon[4] started with purified Dow α-methylstyrene, b.p. 69–71° at 27 mm., n^{24}D 1.5368. The condensation with formaldehyde and acetic acid of 284 g. (2.5 moles) of α-methylstyrene gave 273 g. (1.44 moles) of 2-phenyl-4-acetoxy-1-butene, b.p. 149–154° at 15 mm., n^{25}D 1.5221, 57.5% yield. Pyrolysis through a tube 70 cm. long and 20 mm. inside diameter packed with 1/4" Berl saddles at 500–550° gave a 34% yield of 2-phenyl-1,3-butadiene, b.p. 55–64° at 15 mm., n^{20}D 1.5489. The maleic anhydride adduct melted 105–105.2°; lit. gives 105–105.5°.[3]

A mixture of 70 g. (1.1 moles) of liquid sulfur dioxide, 22 g. (0.17 mole) of 2-phenyl-1,3-butadiene and 1.1 g. of phenyl-β-naphthylamine was allowed to stand in a pressure bottle at room temperature for 36 hours and then heated on the steam-bath for 15 hours. After the excess sulfur dioxide had evaporated the crude sulfone was crystallized twice from a 1-1 mixture of 95% ethanol and water to give 16.8 g. (49%), m.p. 131.3–131.8°; lit. gives 132.5–133.5°.[3]

Addendum to Backer and Strating.[3]—Methylethylphenylcarbinol, b.p. 85.5–87.8° at 4 mm., n^{25}D 1.5173, d^{24}_4 0.9844, was prepared from ethylmagnesium bromide and acetophenone. The physical constants checked closely with the literature values.[5] Dehydration to 2-phenyl-2-butene in the presence of alum gave 40–50% yields, lit. gives 64%.[3] With phosphoric acid the yield was increased to 81%: to 27 g. of 85% phosphoric acid in a 100-ml. three-necked flask fitted with a thermometer, dropping funnel and condenser set for distillation was added 101 g. of carbinol at about one drop per second so that the temperature of the reaction mixture was held at 205–210°.[6] The mixture was heated for one hour after the addition. The distillate was dried and redistilled to give 72 g., 81% of product boiling 60.2–66° at 4–5 mm., n^{25}D 1.5327.

Bromine analyses were run on the intermediates for 2-phenyl-1,3-butadiene since these were not reported. Addition of bromine to the 2-phenyl-2-butene by the method described[3] gave a 97% yield of crude dried dibromide.

Anal. Calcd. for $C_{10}H_{12}Br_2$: Br, 54.7. Found: Br, 56.3.

Dehydrobromination with alcoholic potassium hydroxide as described gave an 89% yield of crude dried product; n^{25}D 1.5454.

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[4] C. C. Price, F. L. Benton and C. J. Schmidle, THIS JOURNAL, **71**, 2860 (1949); H. O. Mottern, U. S. Patent 2,335,691 (Nov. 30, 1943). We are grateful to Dr. Price and his co-workers for allowing us to use this method before its publication.

[5] A. Klages, *Ber.*, **35**, 3507 (1902).

[6] Patterned after the dehydration of cyclohexanol to cyclohexene of W. M. Dehn and K. E. Jackson, THIS JOURNAL, **55**, 4285 (1933).

Anal. Calcd. for $C_{10}H_{11}Br$: Br, 37.8. Found: Br, 31.1.

A second treatment with base reduced the bromine content to 27.4%. One more step did not change this.

The removal of more than the one atom of bromine in the first step, as indicated by the analysis, might arise from the mixture of products starting with the presence of some 2-phenyl-1-butene along with 2-phenyl-2-butene in the original olefin[8] which in turn would lead to mixtures of dibromides and monobromides in which the ease of hydrogen bromide removal would vary with structure.

When the monobromide of 31.1% bromine content was treated with molten potassium hydroxide under the conditions used for the preparation of phenylacetylene from β-bromostyrene,[7] the product failed to give the expected adduct with maleic anhydride. With excess sodium amide in liquid ammonia or ether solution for reaction times as long as 6.5 hours the removal of bromine from the monobromide was incomplete. The greatest dehydrobromination obtained in several experiments was about 20% of the calculated. The product contained no phenylbutadiene according to a reaction with maleic anhydride.

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[7] J. C. Hessler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 438.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND 6, OHIO
RECEIVED NOVEMBER 12, 1951

Addition of Hydrogen Chloride to 1-Phenyl-2-methyl-1-propene

BY ROSS H. HALL, R. G. PYKE AND GEORGE F WRIGHT

It is well-known that the addition of hydrogen chloride to styrene forms exclusively 1-phenyl-1-chloroethane. In the same manner 1-phenylpropene-1 is converted to 1-phenyl-1-chloropropane[1] in high purity. Since the homologous 1-phenyl-2-methyl-1-propene had not been examined in this manner we treated it with hydrogen chloride and were able to isolate only one product, 1-phenyl-2-methyl-2-chloropropane. The mode of addition is thus opposite to those characteristic of the lower homologs and is similar to the hydrohalogenation of 2-methyl-2-butene. No presently-known theory of bond polarization or polarizability seems adequate to explain these several modes of orientation, especially since mixtures of structural isomers have not been observed during addition to the phenylalkenes.

The characterization of 2-methyl-1-phenyl-2-chloropropane was accomplished in two ways. Firstly, it was hydrolyzed to 2-methyl-1-phenylpropanol-2 which was identified as its phenylurethane by comparison with an authentic sample. Secondly, the halide was converted to its Grignard reagent which, upon treatment with phenylisocyanate, was converted to the known anilide of 2,2-dimethyl-3-phenylpropanoic acid.[2]

Experimental[3]

2-Methyl-1-phenyl-2-chloropropane.—Ten grams (0.076 mole) of freshly-distilled 2-methyl-1-phenyl-1-propene (prepared by dehydration of 2-methyl-1-phenylpropanol-2,[4] $n^{20}{}_D$ 1.5376, $d^{20}{}_4$ 0.903, washed with dilute ferrous sulfate) was cooled in an ice-water-bath while dry hydrogen chloride was bubbled through it slowly during six hours. Water and ether were then added. The non-aqueous layer was washed with dilute aqueous sodium carbonate, then dried and distilled, yielding 12.0 g. (94%), b.p. 95–97° (10 mm.), $n^{20}{}_D$ 1.5155.

2-Methyl-1-phenylpropanol-2.—A mixture of 5.0 g. (0.029 mole) of the halide just described with 16 g. (0.137 mole) of potassium carbonate in 100 ml. of water was stirred on the steam-bath for 11 hours. The cooled mixture was twice extracted with ether. This etherous solution was dried with magnesium sulfate and distilled, yield 3.5 g. (78%), b.p. 97–102° (10 mm.), $n^{20}{}_D$ 1.5170. A 0.6-g. portion (0.004 mole) was treated with 0.35 ml. (0.003 mole) of phenyl isocyanate and 0.2 ml. of dry pyridine. This mixture yielded 0.5 g. (64%) of the phenylurethan melting at 86–88°, and contaminated with carbanilide. Six crystallizations from 95% ethanol (1 ml. per g.) raised this melting point to 93.0–93.7°. A mixed melting point with an authentic sample prepared from dimethylbenzylcarbinol (Eastman Kodak Co.) was not lowered.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.8; H, 7.12; N, 5.20. Found: C, 75.6; H, 7.23; N, 5.28.

2,2-Dimethyl-3-phenylpropanoyl Anilide.—The preparation was identical with that reported by Whitmore.[2] The product melted at 106.5–107.5° whereas Whitmore reported 107–108°.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.6; H, 7.55. Found: C, 79.8; H, 7.45.

TORONTO, ONTARIO
RECEIVED OCTOBER 8, 1951

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[1] A. A. Shamshurin, *Trudy Uzbekskogo Gosudarst Univ. Sbornik Rabot Khim.* **15**, 75 (1939); *C. A.*, **35**, 3984 (1941).

[2] F. C. Whitmore, *et al.*, THIS JOURNAL, **65**, 1469 (1943).

[3] All melting points have been corrected against reliable standards.

[4] M. Tiffeneau and A. Orekoff, *Bull. soc. chim.*, **29**, 816 (1921).

Absence of Exchange of Sulfur between Sulfide and Thiocyanate Ions in Aqueous Solution

BY G. B. HEISIG AND R. HOLT

We have found that little or no exchange of sulfur occurs between 0.1 *M* sulfide and 0.1 *M* thiocyanate ions in slightly alkaline aqueous solutions after 23 hours at 25 or 50° or in 47 hours at 100°.

The experiments were made by using S^{35} as a tracer. In some runs $S^{*=}$ prepared by bubbling H_2S^* into the calculated volume of sodium hydroxide was used, while in others S^*CN^- from KSCN[1] contained the tracer. The KCNS was prepared by digesting a mixture of K_2S^*, KCN and S. The H_2S^* was obtained from BaS^* prepared by reducing $BaSO_4$ with carbon.[2] The S^* was obtained from the A.E.C. as the $S^{*=}$ but was actually present as $S^*O_4^=$.

The reaction mixtures were heated for the desired time in glass-stoppered bottles or sealed tubes from which the air had been displaced by nitrogen. Following the reaction period the $S^=$ ions were removed from the reaction mixtures by treating with freshly precipitated cadmium carbonate. The precipitated cadmium salts were separated from the solution by centrifugation and the sulfide was oxidized to $SO_4^=$ by bromine. The activity of the $BaSO_4$ was determined.[3]

The centrifugate was freed of any traces of $SO_4^=$ by adding more of these ions as a carrier and precipitating with Ba^{++}. The SCN^- were then oxidized with bromine, the $SO_4^=$ precipitated with Ba^{++} and the activity of the precipitate determined.[3]

In two runs made at 100°, one at 50° and four at 25°, the greatest transfer of activity from the active to the inactive form was 5% and this was accounted for by the small amount of thiosulfate ions or possibly the polythionate ions present in the active thiocyanate reagent. The per cent. of exchange at 100° was essentially the same for 23 hours as for 47 hours.

We wish to acknowledge the aid of Dr. Armstrong in determining the activity of the samples.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINNESOTA
RECEIVED MAY 7, 1951

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[1] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

[2] A. E. Wells, *J. Ind. Eng. Chem.*, **8**, 770 (1916).

[3] W. D. Armstrong and J. Schubert, *Anal. Chem.*, **20**, 270 (1948).

Thermodynamic Functions of Adsorbed Molecules from Heats of Immersion[1]

BY GEORGE JURA AND TERRELL L. HILL

If N_s molecules are adsorbed on a solid of area $\mathcal{A}$, it is of interest[2] to know the entropy and energy per molecule, $\mathrm{s_s} = S_\mathrm{s}/N_\mathrm{s}$ and $\mathrm{E_s} = E_\mathrm{s}/N_\mathrm{s}$, respectively. These functions can be calculated from two adsorption isotherms, measured at neighboring temperatures down to very low pressures, as illustrated in a paper by Hill, Emmett and Joyner.[3] In favorable cases, with careful measurements, this can be an accurate method. On the other hand, in other cases very serious errors in the surface pressure, φ, and hence in $\mathrm{s_s}$ and $\mathrm{E_s}$, may arise owing to uncertain extrapolation of the adsorption isotherm to $p = 0$. These errors can be especially serious in systems in which there are first order phase changes in the adsorbed phase: the phase change might be missed or the actual pressure at which it occurs may be uncertain.

An alternative and in general more precise method of obtaining $\mathrm{s_s}$ and $\mathrm{E_s}$ is to combine a computation of φ from a single adsorption isotherm with heats of immersion or ordinary integral calorimetric heats of adsorption, measured at the same temperature. Harkins and Jura[4] used this method to obtain thermodynamic functions referred to the *solid surface*. We shall point out below the relations between the Harkins–Jura functions and the thermodynamic functions of the adsorbed molecules (*e.g.*, $\mathrm{s_s}$ and $\mathrm{E_s}$). Incidentally, if the solid is perturbed by the adsorbed phase, the equations given below are still valid (see IX).

Let U_0 be the heat of immersion (in the liquid adsorbate) of the clean solid adsorbent, carried out in a container of fixed volume, and let U be the heat of immersion of the solid with N_s molecules adsorbed on it. Then it is easy to see that

$$\mathrm{E}'_\mathrm{L} - \mathrm{E_s} = (U_0 - U)/N_\mathrm{s} \tag{1}$$

where E'_L is the internal energy of the liquid adsorbate per molecule (in equilibrium with vapor). Also,[2] using Eq. (1)

$$T(\mathrm{s_s} - \mathrm{s}'_\mathrm{L}) = [(U - U_0)/N_\mathrm{s}] + (\varphi/\Gamma) - kT \ln x \tag{2}$$
$$x = p/p_0,\ \Gamma = N_\mathrm{s}/\mathcal{A}$$

assuming the vapor is a perfect gas and omitting a negligible volume term.

A comparison of the quantities calculated by Harkins and Jura[4] in their Fig. 9 with the present notation gives the following relations between the two sets of functions

$$(\gamma_\mathrm{s} - \gamma_\mathrm{sf})_\mathrm{HJ} = \varphi \tag{3}$$
$$(\epsilon_\mathrm{s} - \epsilon_\mathrm{sf})_\mathrm{HJ} = (U_0 - U)/\mathcal{A} = \Gamma(\mathrm{E}'_\mathrm{L} - \mathrm{E_s}) \tag{4}$$

$$-T(\mathrm{s_s} - \mathrm{s_{sf}})_\mathrm{HJ} = \Gamma(\mathrm{E}'_\mathrm{L} - \mathrm{E_s}) - \varphi = \Gamma[T(\mathrm{s}'_\mathrm{L} - \mathrm{s_s}) - kT \ln x] \tag{5}$$

Whenever there is *strong* binding of the first layer to the surface, regardless of the details (solid adsorbents with small pores are excepted) and independent of any particular theory, one would expect a minimum in $\mathrm{s_s} - \mathrm{s}'_\mathrm{L}$ at about the completion of a monolayer.[5] This is because a virtually filled monolayer has fewer possible statistical configurations than either an incomplete monolayer or a complete monolayer plus an incomplete second layer. When combined with an estimate of the surface area per molecule in a filled monolayer, the above entropy minimum[6] can be used as a method for surface area determination not dependent on a detailed theory. In the two cases worked out so far[3,7] excellent agreement with the B.E.T. surface area is obtained. Minima in the function $(\mathrm{s_s} - \mathrm{s_{sf}})_\mathrm{HJ}$ do not have this simple theoretical relation to surface area, because of Γ and x in Eq. (5).

Alternatively, instead of using heats of immersion, $\mathrm{E_s}$ in Eq. (1) (relative to gas or liquid), for use in Eq. (2), may be found from integral calorimetric heats of adsorption,[2] as done by Drain and Morrison.[7]

Finally, we wish to examine the effects of errors in φ of the type mentioned above. For this purpose, we assume that errors in the heat measurements are negligible and that errors in φ arise only from pressures below the pressure region under discussion. Following V, let φ be the true spreading pressure, Φ the incorrect spreading pressure and a the error in Φ

$$\Phi(p,T) = \varphi(p,T) + a(T) \tag{6}$$

Let $\mathrm{s_s}$ be the correct entropy obtained from Eqs. (V-86, 93) and s'_s the incorrect entropy found by using Φ instead of φ in these equations. In this latter case, let a_1 be the value of a at T_1 and a_2 at T_2. Then the error in the entropy is (V)

$$\mathrm{s}'_\mathrm{s} - \mathrm{s_s} = \frac{1}{\Gamma}\frac{\Delta a}{\Delta T} \tag{7}$$
$$\Delta a = a_2 - a_1,\ \Delta T = T_2 - T_1$$

On the other hand, using Eq. (2) and an intermediate a and T, the corresponding error is $a/\Gamma T$. If a is of the same order of magnitude as Δa, the error in the heat calculation will thus be smaller in the ratio $\Delta T/T$. However, if the error is systematic (*i.e.*, $\Delta a \cong 0$), the opposite result is possible ($\Delta a/\Delta T < a/T$).

We have also

$$\mathrm{E}'_\mathrm{s} - \mathrm{E_s} = \frac{T}{\Gamma}\left(\frac{\Delta a}{\Delta T} - \frac{a}{T}\right) \tag{8}$$

which corresponds to Equation (7).

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA AND THE
NAVAL MEDICAL RESEARCH INSTITUTE
BETHESDA, MARYLAND
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(1) Presented at an American Chemical Society Meeting, New York, September, 1951.

(2) T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949), hereafter referred to as V; *ibid.*, **18**, 246 (1950), hereafter referred to as IX; *Trans. Faraday Soc.*, **47**, 376 (1951) (in this paper H^σ should be replaced by $\mathcal{H}^\sigma$ in lines 29, 31, 33 and 34, p. 378).

(3) T. L. Hill, P. H. Emmett and L. G. Joyner, THIS JOURNAL, **73**, 5102 (1951). Errata: Change $\mathrm{s_s}$ to $\bar{\mathrm{s}}_\mathrm{s}$ in Eq. (1), in third line below Eq. (2), third equation, in third line below Eq. (17), and in line 17 of "Results and Discussion." Change $\mathrm{H_s}$ to $\bar{\bar{\mathrm{H}}}_\mathrm{s}$ in line below Eq. (6), and in Eq. (7). See THIS JOURNAL **73**, 5933 (1951).

(4) W. D. Harkins and G. Jura, *ibid.*, **66**, 919 (1944).

(5) See, for example, T. L. Hill, *J. Chem. Phys.*, **17**, 772 (1949).

(6) In many cases the differential entropy curve will be available but not the molar integral entropy curve. In this case, if there is a "loop" in the differential entropy,[2,3,7] the surface area can be estimated by assuming that a monolayer is completed at the inflection point in the loop.

(7) L. E. Drain and J. A. Morrison, American Chemical Society Meeting, New York, September, 1951.

The Ultraviolet Absorption Spectra of Some Monofluoroisoquinolines

BY SAMUEL B. KNIGHT, WILLIAM K. MILLER AND ARTHUR ROE

In previous papers the ultraviolet absorption spectra of the monofluoroquinolines were reported,[1] and the data were utilized to determine basic dissociation constants of the compounds[2] and to study the hydrolysis of 2-fluoroquinoline in acid solution.[3] The applicability of these results suggested that a similar study of the monofluoroisoquinolines would be desirable. This paper will be confined to the three isomers in which the fluorine atom is in the pyridinoid ring. The absorption spectra of these compounds as well as that of isoquinoline were measured in the same solvents in which those of the fluoroquinolines were measured,[1] and the maxima obtained in the various solvents are reported in Table I.

TABLE I

SPECTRAL DATA OF SOME FLUOROISOQUINOLINES[a]

Compound	Maxima: λ in mμ, $\epsilon \times 10^{-3}$		
	In 95% ethanol	In 10% ethanol	In 0.01 M HCl[b]
Isoquinoline	268 (3.56), 319 (2.79)	268 (3.29), 319 (2.67)	275 (1.94), 329 (3.86)
1-Fluoroisoquinoline	265 (4.14), 317 (2.96)	265 (3.92), 318 (3.00)	272 (6.78), 324 (4.63)
1-Hydroxyisoquinoline			272 (6.77), 324 (4.61)
3-Fluoroisoquinoline	270 (2.83), 326 (3.20)	270 (2.61), 325 (3.12)	[c]
4-Fluoroisoquinoline	270 (4.10), 320 (3.09)	270 (3.90), 321 (3.09)	274 (2.39), 333 (4.80)

[a] The spectra in 10% ethanol which is 0.01 M with sodium hydroxide is almost identical with that in 10% ethanol. [b] The HCl solution contains 10% ethanol by weight. [c] Identical with that in 10% ethanol.

Spiers and Wibaut[4] found that a halogen atom, when substituted in the pyridine nucleus, tended to produce both a bathochromic shift and an increase in intensity of the maximum absorption band, the displacement appearing greater when the halogen was closer to the nitrogen atom. No such systematic shifts of absorption were evident when a halogen was introduced into the quinoline nucleus.[1] Similarly, no definite pattern of absorption was found with the three fluoroisoquinolines as is evidenced in Fig. 1.

The ultraviolet spectrum of isoquinoline in 95% ethanol exhibits two distinct maxima (Fig. 1) beyond 230, at 268 and 319 mμ. The extinction coefficients at these wave lengths are 3.56 and 2.79 $\times 10^3$, respectively. Of the three fluoroisoquinolines whose spectra were measured, the 3- and 4-isomers exhibited bathochromic shifts of the first (268 mμ) maximum, while a hypsochromic shift was found in the spectrum of the 1-isomer. Increases in extinction at the first maximum were evident in the spectra of the 1- and 4-fluoroisoquinolines, but a marked decrease in intensity of absorption was found in the spectrum of the 3-isomer. Shifts of the second maximum were similar to those of the first, with the single exception that all of the isomers exhibited increases in extinction coefficient at the band of longer wave length. On the basis of these and previous results[1] it would not be feasible to predict the effect of the introduction of the fluorine atom into the four benzenoid ring positions of the isoquinoline nucleus. The latter study will have to await preparation of the remaining isomers.

The ultraviolet absorption spectra of isoquinoline, 3-fluoroisoquinoline, 4-fluoroisoquinoline and 1-fluoroisoquinoline in 95% ethanol, 10% ethanol, and 10% ethanol which is 0.01 M with HCl are shown in Figs. 2A, 2B, 2C and 3, respectively. The differences between the spectra in 95% ethanol and in 10% ethanol are slight but are quite similar for each compound and could be explained by possible solvate formation[1] or by the difference in polarity of the two solvents.

The differences between the spectra of the compounds in neutral and in 0.01 M HCl solutions are significant. The spectrum of isoquinoline in neutral or basic solution represents the absorption of the molecule, while that in 0.01 M HCl solution represents the absorption of the isoquinolonium ion, since the hydrochloride is formed in acid solution. A similar effect on the spectrum of 4-fluoroisoquinoline is observed in passing from neutral to acid solution. Hence, as would be ex-

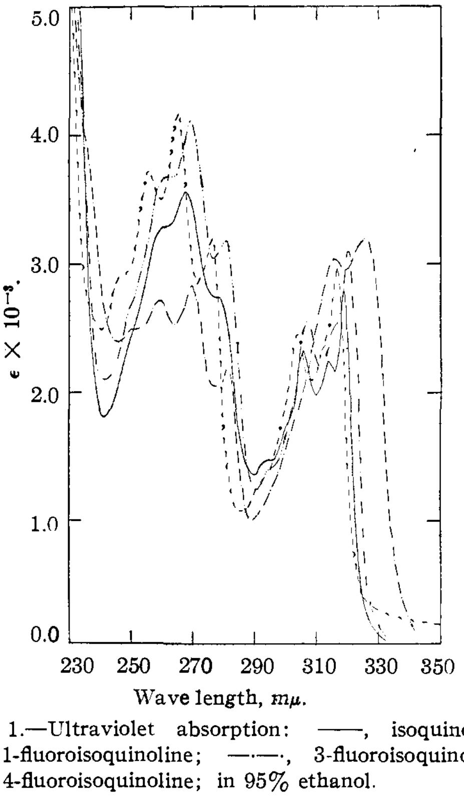

Fig. 1.—Ultraviolet absorption: ——, isoquinoline; - - -, 1-fluoroisoquinoline; —·—·, 3-fluoroisoquinoline; —··—, 4-fluoroisoquinoline; in 95% ethanol.

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[1] W. K. Miller, S. B. Knight and A. Roe, THIS JOURNAL, **72**, 1629 (1950).

[2] W. K. Miller, S. B. Knight and A. Roe, *ibid.*, **72**, 4763 (1950).

[3] W. K. Miller, S. B. Knight and A. Roe, *ibid.*, **72**, 4765 (1950).

[4] C. W. F. Spiers and J. P. Wibaut, *Rec. trav. chim.*, **56**, 573 (1937).

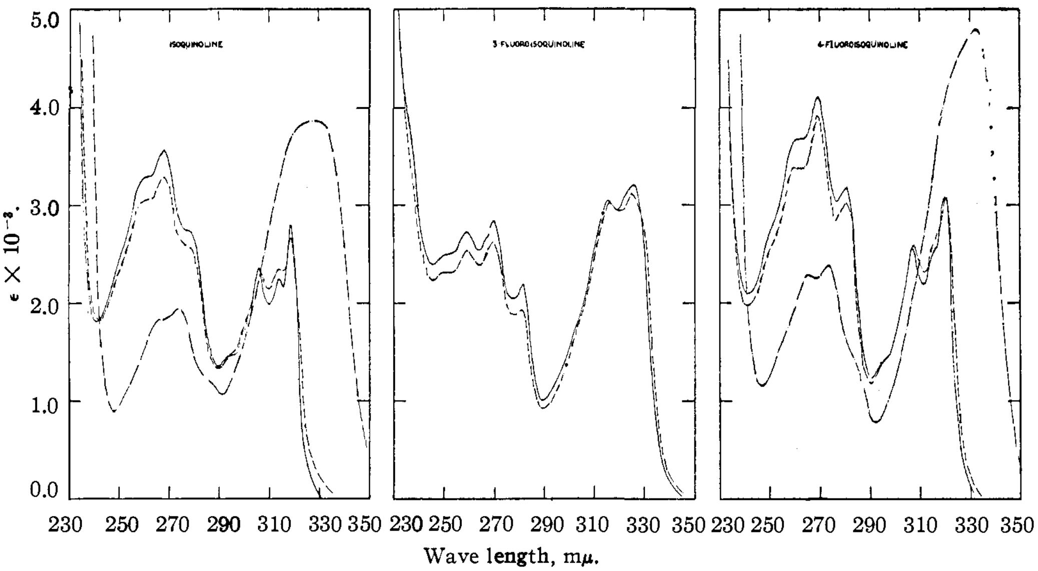

Fig. 2.—Ultraviolet absorption: ———, 95% ethanol; – – – – – –, 10% ethanol; —·—·—·—, 10% ethanol 0.01 *M* with HCl.

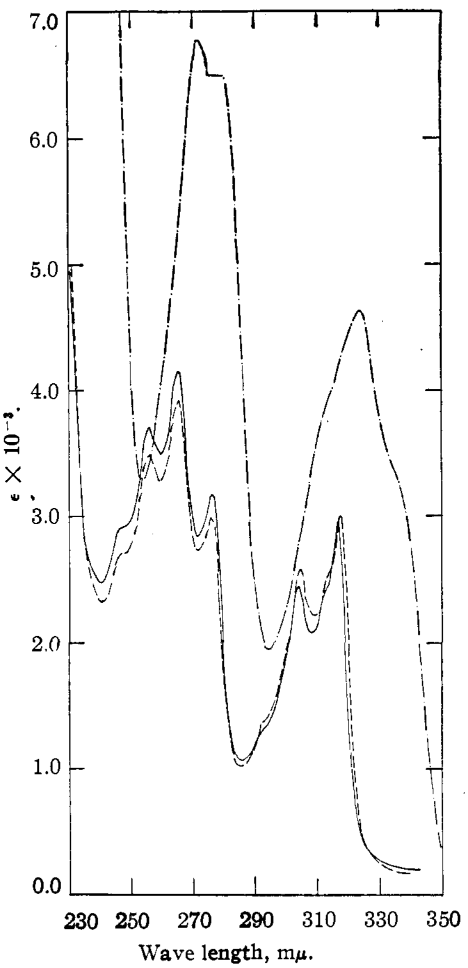

Fig. 3.—Ultraviolet absorption: 1-fluoroisoquinoline: ———, 95% ethanol; – – –, 10% ethanol; —·—, 10% ethanol which is 0.01 *M* with HCl.

pected, it is apparent that the latter compound is basic enough to form a hydrochloride.

Roe and Hawkins[5] reported that the 2-fluoro derivatives of both pyridine and quinoline were insoluble in dilute HCl, indicating that they were too weakly basic to form hydrochlorides. It would be reasonable to predict that the 1- and 3-fluoroisoquinolines would react similarly, since, in these isomers, the fluorine atom is attached to the carbon atom adjacent to the nitrogen as in 2-fluoroquinoline. No shift of the spectrum of 3-fluoroquinoline was evident in passing from neutral to 0.01 *M* HCl as solvent, indicating that no hydrochloride was formed. A marked shift of the absorption center of the 1-isomer occurred, but this was caused by hydrolysis of the compound in acid solution instead of hydrochloride formation.

In a previous paper[3] it was shown that 2-fluoroquinoline hydrolyzed in acid solution to 2-hydroxyquinoline. This suggested that both the 1- and 3-fluoroisoquinolines might react similarly since the fluorine atoms in these two compounds are situated the same as that in 2-fluoroquinoline with respect to the nitrogen atom. The spectrum of 1-fluoroisoquinoline in 0.01 *M* HCl solution was found to be identical with that of 1-hydroxyisoquinoline in the same solvent as measured by Ewing and Steck[6] and repeated by the authors. However, there was no shift of absorption of 3-fluoroisoquinoline in passing from neutral to acid solution as the solvent, revealing that the latter compound is not hydrolyzed in acid solution.

No attempt is made here to give an interpretive discussion of the data. Such a discussion should await the gathering of more data on many other heterocyclic halogen compounds, when perhaps worthwhile correlations can be made.

Experimental

Absorption Spectra.—The spectra were measured and plotted using the same technique as previously described;[1] the solvents were also the same.

Isoquinoline.—A synthetic Eastman Kodak Co. product

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[5] A. Roe and G. F. Hawkins, This Journal, **69**, 2443 (1947); **71**, 1785 (1949).

[6] G. W. Ewing and E. A. Steck, *ibid.*, **68**, 2181 (1946).

was dried over sodium hydroxide and distilled under reduced pressure.

All of the fluoroisoquinolines and 1-hydroxyisoquinoline were prepared in this Laboratory[7] and were redistilled until the absorption spectra of successive distillates were identical.

Acknowledgment.—This work is part of a study of the preparation and properties of heterocyclic fluorine compounds being carried out in this laboratory, and was supported in part by the Office of Naval Research, Contract No. N8onr-69900.

(7) A. Roe and C. E. Teague, THIS JOURNAL, **73**, 687 (1951).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.

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Sterols of Algae. III.[1] The Occurrence of Ergosterol in *Chlorella pyranoidosa*[2]

BY MARYLIN KLOSTY AND WERNER BERGMANN

It was reported in the first communication of this series,[3] that chondrillasterol is the principal sterol of the green alga, *Scenedesmus obliquus.* This sterol is of special interest because it is a $\Delta^{7,22}$-diene-3-ol and therefore potentially suitable for conversion into cortisone by methods now being investigated in several laboratories. The amount of chondrillasterol obtainable from *Scenedesmus,* however, appears too small to be of practical significance at this time. The studies on algae sterols have now been extended to other primitive algae of the class of *Chlorophyceae,* and in particular to those, whose commercial cultivation is contemplated by several organizations.

Through the courtesy of the Lederle Laboratories Division[4] the authors obtained several pounds of freeze-dried cells of a pure culture of the green alga, *Chlorella pyranoidosa.* Upon acetone extraction, the algae yielded 12.5% of lipoid material, of which 10% was unsaponifiable. The sterol content of the unsaponifiable fraction was approximately 20%, corresponding to 0.15–0.2% of the dry alga. A more efficient extraction was achieved when the cells were first triturated with warm glacial acetic acid and then exhaustively extracted with acetone. Cells so treated yielded a lipoid and sterol fraction corresponding, respectively, to 20 and 0.4%. The sterols were isolated from the unsaponifiable fraction either by precipitation with digitonine, by direct crystallization or better by way of their benzoates. The high negative rotation and the ultraviolet absorption spectra of the crude fractions indicated the presence of $\Delta^{5,7}$-sterols in excess of 75% of the mixture. Repeated recrystallizations of the benzoates eventually afforded ergosteryl benzoate, m.p. 169°; $[\alpha]^{25}\mathrm{D}$ −72°. It was converted to ergosterol, m. p. 164°; $[\alpha]^{25}\mathrm{D}$ −128°, and ergosteryl acetate, m.p. 176°; $[\alpha]^{25}\mathrm{D}$ −88°.

Chlorella pyranoidosa appears to be the first organism other than fungi and lichens in which ergosterol has been shown to be the principal sterol.[5] As a minor component, 0.1–5%, ergosterol has been found in the sterol mixtures from cocksfoot,[6] cottonseed oil,[7] scopolia root oil[7] and wheat germ oil.[8] More substantial amounts of ergosterol have been found in the sterol mixtures from certain animals,[9] in particular invertebrates.[10]

Experimental

The following extraction procedure was found to be the most efficient. Fifty grams of freeze-dried cells of *Chlorella pyranoidosa,* which contained about 10% of moisture, was heated for one hour at 70° with 100 ml. of glacial acetic acid. The acid was then removed by freeze-drying, and the residue ground, and extracted in a Soxhlet apparatus with acetone for 24 hours. The extract was filtered to remove some amorphous, gray solid (1.5 g.), and the solvent was removed first by distillation and finally by freeze-drying. The extract thus obtained, 10 g., was saponified under nitrogen with 45 g. of a 20% solution of potassium hydroxide in 80% ethanol. After 24 hours 150 ml. of water was added, and the solution extracted seven times with 100-ml. portions of peroxide-free ether. The combined ether layers were washed with water and concentrated under nitrogen. After freeze-drying, the residue weighed 1.5 g. The sterol content of the residue, as determined by the digitonide method, was 13.4%, corresponding to 0.4% of the algae.

The unsaponifiable fraction obtained from several hundred grams of algae was dissolved in a minimum amount of boiling methanol. Upon cooling a waxy, crystalline material was obtained in a yield of 23%. It was dissolved in anhydrous pyridine and treated with an excess of benzoyl chloride for 24 hours at room temperature. The mixture was then poured into methanol, and the precipitate, m.p. 144–156°, recrystallized from ether–methanol; yield 11% of unsaponifiable fraction; m.p. 156–162°; $[\alpha]^{25}\mathrm{D}$ −58. Several recrystallizations from dioxane–methanol and ethyl acetate afforded ergosteryl benzoate, m.p. 169°; $[\alpha]^{25}\mathrm{D}$ −72° in chloroform. The ultraviolet absorption spectra indicated a purity in excess of 95%.

Anal. Calcd. for $C_{35}H_{44}O_2$: C, 84.00; H, 9.60. Found: C, 83.75; H, 9.93.

The benzoate was refluxed for one hour with a 3% solution of potassium hydroxide in ethanol in an atmosphere of nitrogen. The solution was then diluted with water, and the precipitated ergosterol was recrystallized several times from acetone and ethyl acetate, m.p. 162°; $[\alpha]^{25}\mathrm{D}$ −128° (chloroform). Acetylation by reflux with acetic anhydride afforded ergosteryl acetate, m.p. 176°; $[\alpha]^{25}\mathrm{D}$ −92° (chloroform). None of the products gave depressions of melting points when mixed with authentic material.

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(1) Paper II, THIS JOURNAL, **73**, 2395 (1951).

(2) This investigation was supported by a research grant from the National Institute of Health, Public Health Service.

(3) W. Bergmann and R. J. Feeney, *J. Org. Chem.*, **15**, 812 (1950).

(4) American Cyanamid Co., Pearl River, New York.

(5) The statement made in Elsevier's "Encyclopaedia of Organic Chemistry," Vol. **14**, 69 (1940), that ergosterol is present in the brown alga, *Fucus crispus,* is in error. It is based on a brief note by Gérard (*Compt. rend.*, **126**, 909 (1898)) which states that the sterol of *Fucus* gives color reactions reminiscent of those shown by sterols from cryptogams. Since then it has been shown that fucosterol is the principal sterol of this alga.

(6) A. Pollard, *Biochem. J.*, **30**, 382 (1936).

(7) A. Windaus and F. Bock, *Z. physiol. Chem.*, **250**, 258 (1937).

(8) A. Windaus and F. Bock, *ibid.*, **256**, 47 (1938).

(9) A. Windaus and O. Stange, *ibid.*, **244**, 218 (1936)

(10) F. Bock and F. Wetter, *ibid.*, **256**, 33 (1938).

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

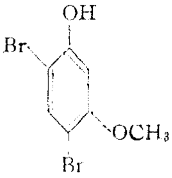
RECEIVED NOVEMBER 29, 1951

[FROM THE CHEMICAL LABORATORY OF THE ACADEMY OF COMMERCE IN VIENNA]

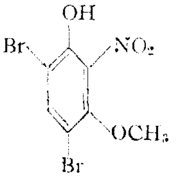
Bromination of Resorcinol Monomethyl Ether and Debromination of Tribromoresorcinol Monomethyl Ether

BY MORITZ KOHN

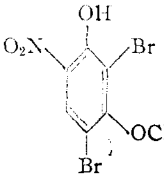
The bromination of resorcinol monomethyl ether with two molecules of bromine yields a crystalline dibromo product which must be 1-hydroxy-3-methoxy-4,6-dibromobenzene (I), since its methylation yields 4,6-dibromoresorcinol dimethyl ether.[1] The nitration of I yields a nitrodibromoresorcinol monomethyl ether, which according to the method of preparation should be 1-hydroxy-2-nitro-3-methoxy-4,6-dibromobenzene (II). The m.p. of this substance is, however, very close to the melting point of the isomeric 1-hydroxy-3-methoxy-2,4-dibromo-6-nitrobenzene (III) reported by Kohn and Loeff.[2,3] The nitration of purest 2,4,6-tribromoresorcinol monomethyl ether (IV) produces an identical substance. Therefore in the nitration of I a migration of the bromine atom from position 6 into position 2 takes place. A similar rearrangement was observed by Hodgson and Dyson[4] who found that the nitration of the 3-monobenzoate of 4,6-dibromoresorcinol leads to the 2,4-dibromo-6-nitroresorcinolmonobenzoate.



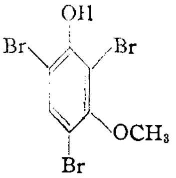
I



II



III



IV

Reduction of tribromoresorcinol monomethyl ether (IV) with zinc dust and acetic acid removes the bromine atom between the OH– and the OCH$_3$–group forming I. Thus the reduction of IV proceeds in the same way as the reduction of 2,4,6-tribromoresorcinol, whereby 4,6-dibromoresorcinol[5] is formed.

Experimental

4,6-Dibromoresorcinol Monomethyl Ether (I).—Resorcinol monomethyl ether (19.5 g.) is dissolved in 60 cc. of chloroform, the mixture cooled in an ice-bath and a cooled solution of 16 cc. of bromine in 60 cc. of chloroform is slowly added through a dropping funnel with continuous stirring. After 6 hours the chloroform is evaporated on a steam-bath. The residue is triturated with low boiling petroleum ether and the solid is collected (31 g.). After removal of the petroleum ether by evaporation an oily residue is obtained (about 10 g.). This oil yields by bromination in glacial acetic acid tribromoresorcinol monomethyl ether (IV) (10 g., m.p. 105° after recrystallization).

By recrystallization of 10 g. of the crude dibromoether from petroleum ether 6 g. of the pure substance is obtained; colorless prisms, m.p. 73–75°.

Anal. Calcd. for $C_7H_6O_2Br_2$: Br, 56.73. Found: Br, 56.65.

The substance is very difficultly soluble in boiling water, more easily when diluted with alcohol or methanol. Its methylation yields 4,6-dibromoresorcinol dimethyl ether,[1] m.p. 141–143°.

1-Hydroxy-3-methoxy-2,4-dibromo-6-nitrobenzene (III).—One and nine-tenths grams of I is dissolved in 15 cc. of glacial acetic acid and to this cooled solution a cooled mixture of 1.5 cc. of nitric acid in 10 cc. of glacial acetic acid is added. The liquid is kept in an ice-bath until the color turns light brown-yellow and is afterwards poured on 500 g. of ice. The solution is stirred until the oily precipitation solidifies. The crude product is collected, converted with potassium hydroxide into its red potassium salt, which is collected (1.4 g.) and then decomposed by diluted sulfuric acid. The yellow nitro product is recrystallized from alcohol; prisms, m.p. 123–126°.

Anal. Calcd. for $C_7H_5O_4NBr_2$: N, 4.29. Found: N, 4.03.

The m.p. of a sample prepared according to Kohn and Loeff[2] was 125–127°, its mixed m.p. with III prepared from I gives no depression.

Debromination of the tribromoresorcinol monomethyl ether (IV) is accomplished by dissolving 5 g. of IV in 10 cc. of glacial acetic acid and 10 cc. of water and boiling with 5 g. of zinc dust for 12 minutes. The mixture is cooled, filtered and the filtrate precipitated by the addition of ice-water (3 g.). The crude product is recrystallized from petroleum ether and washed with benzine, m.p. 72–74°. The m.p. of a mixture of this substance and the product of the bromination of resorcinol monomethyl ether is not depressed. The methylation of this substance yields 4,6-dibromoresorcinol dimethyl ether, m.p. 141–143°.[1]

536 West 113 St.
New York 25, N. Y.

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[1] M. Kohn and G. Loeff, *Monatsh.*, **45**, 590 (1924).

[2] M. Kohn and G. Loeff, *ibid.*, **45**, 594 (1924).

[3] L. Raiford and J. H. Scott, *J. Org. Chem.*, **2**, 213 (1937).

[4] H. Hodgson and R. C. Dyson *J. Chem. Soc.*, 946 (1935).

[5] M. Kohn and L. Striner, *J. Org. Chem.*, **12**, 30 (1947).

Ultrasonic Velocity in Some Alkyl Aryl Ketones

By R. T. Lagemann,[1] B. F. Landrum,[2] C. T. Lester, O. Milner and E. G. McLeroy

The results to be described represent further efforts to find what relationships exist between molecular structure and the velocity of ultrasonic waves in liquids. Previous work has been reviewed by several writers,[3–5] including a recent paper by two of the present authors.[6]

The fifteen alkyl aryl ketones investigated are listed in Table I. An examination of Table I shows that increase in molecular weight is accompanied by a decrease in ultrasonic velocity within the limits of this series. When increase in molecular weight is accompanied by chain branching a considerably greater drop in velocity is noted. A similar effect of chain branching has been noted in isomeric alcohols.[7] When the molecular sound velocity[8] of these ketones are computed, the most highly branched ketones also show the lowest values within any group of isomers.

Experimental[9]

Preparation of Ketones.—The acetophenones, propiophenones and isobutyrophenones were prepared by a standard procedure.[10] The pivalophenones were prepared by the procedure of Marvel and co-workers.[11] All the ketones were twice distilled through an efficient column. Constant boil-

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[1] Physics Dept., Vanderbilt University, Nashville, Tennessee.

[2] Taken in part from the Ph.D. Thesis of B. F. Landrum, Emory University, 1951.

[3] S. Parthasarathy, *Current Science*, **6**, 322 (1938).

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[7] A. Weissler, *ibid.*, **70**, 1634 (1948).

[8] M. R. Rao, *J. Chem. Phys.*, **9**, 692 (1941).

[9] All m.ps. and b.ps. reported are uncorrected.

[10] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[11] J. H. Ford, C. D. Thompson and C. S. Marvel, This Journal, **57**, 2619 (1935).

TABLE I

ALKYL ARYL KETONES

4-R	B.p. °C.	B.p. Mm.	$n^{30}D$	d_{30}	Veloc., m./sec. V_{10}	Veloc., m./sec. V_{20}	Veloc., m./sec. V_{30}	Mol. sound veloc. at 30°	Ad. comp., dynes cm.² at 30° × 10¹²
A. 4-R-Acetophenones									
H	100	12	1.5280	1.0193	1537[p]	1502[p]	1463[p]	1338	45.9[p]
Me[a,b]	70	3	1.5303	0.9966	1532	1495	1457	1526	47.2
Et[a,c]	89	3	1.5252	.9849	1526	1487	1453	1704	48.1
Isoprop[d]	109	3	1.5187	.9705	1503	1467	1429	1883	50.5
t-Bu[e]	112	2	1.5168	.9574	1499	1464	1427	2073	51.3
B. 4-R-Propiophenones									
H	90	3	1.5212	1.0014	..	1493[p]	1456[p]	1519	47.1[p]
Me[f]	100	3	1.5238	0.9831	1525	1486	1450	1706	48.4
Et[a,g]	108	3	1.5199	.9704	1517	1481	1444	1889	49.4
Isoprop[h]	125	3	1.5141	.9560	1498	1460	1424	2074	51.6
t-Bu[i]	162	5	1.5138	.9495	1493	1457	1420	2252	52.2
C. 4-R-Isobutyrophenones									
H[j]	107	3	1.5134	0.9747	1486	1448	1408	1704	51.8
Me[k]	119	4	1.5147	.9605	1484	1448	1410	1894	52.4
Et[l]	122	3	1.5126	.9510	1484	1445	1411	2079	52.8
Isoprop[m]	126	2	1.5079	.9383	1474	1433	1399	2268	54.4
t-Bu[n]	132	2	1.5072	.9361	1470	1432	1395	2439	54.9
D. 4-R-Pivalophenones									
H[o]	71	2	1.5057	.9612	1461	1423	1383	1880	54.4
Me[o]	77	2	1.5066	.9486	1461	1425	1387	2072	54.8

[a] A. Klages and G. Lickroth, *Ber.*, **32**, 1558 (1899). [b] M.p., semicarbazone, 205°. [c] M.p., semicarbazone, 196°. [d] O. Widman, *Ber.*, **21**, 2225 (1888); m.p., semicarbazone, 203°. [e] G. F. Hennion and S. F. deC. McLeese, THIS JOURNAL, **64**, 2421 (1942); m.p., semicarbazone, 230°. [f] A. Klages, *Ber.*, **35**, 2252 (1902); m.p., semicarbazone, 188°. [g] M.p., semicarbazone, 151°. [h] *Anal.* Calcd.: C, 81.77; H, 9.15. Found: C, 82.07; H, 9.24; m.p., semicarbazone, 158°. [i] H. A. Bruson and O. Stein, *C. A.*, **29**, 4773 (1935); m.p. semicarbazone, 200°. [j] A. Lapworth and V. Steele, *J. Chem. Soc.*, **99**, 1883 (1911); m.p. semicarbazone, 181°. [k] K. V. Auwers, *Ann.*, **408**, 244 (1915); m.p., semicarbazone, 102°. [l] *Anal.* Calcd.: C, 81.77; H, 9.15. Found: C, 81.89; H, 9.40; m.p., semicarbazone, 105°. [m] *Anal.* Calcd.: C, 82.10; H, 9.47. Found: C, 81.84; H, 9.58; m.p., semicarbazone, 107°. [n] G. F. Hennion and L. A. Auspos, THIS JOURNAL, **65**, 1603 (1943); m.p., semicarbazone, 116°. [o] D. E. Pearson, *ibid.*, **72**, 4169 (1950). [p] Previously determined, *cf.* ref. 6.

ing, constant index center cuts were used in the determinations of physical properties listed in Table I.[12] Acetophenone and propiophenone were purchased from Matheson Co. and are included for comparison.

Measurement of Velocity.—The ultrasonic velocity of the liquids was measured by use of a variable-path ultrasonic interferometer[13] which employs a piezo-electric quartz crystal driven at 500 kc. per second by a crystal-controlled oscillator. All measurements were made with the interferometer submerged in a constant temperature water-bath.

Acknowledgment.—We wish to thank R. E. Donaldson, Dr. D. R. McMillan and A. E. Robinson for their help on this problem. One of us (R. T. L.) wishes to acknowledge a grant from the Research Corporation.

(12) The expense of ketone synthesis was borne by a contract from the Office of Naval Research. The rates of oximation of all but the last two have been reported, *cf.* M. J. Craft, B. F. Landrum, E. C. Suratt and C. T. Lester, THIS JOURNAL, **73**, 4462 (1951).

(13) D. R. McMillan, Jr., and R. T. Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).

DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA
RECEIVED AUGUST 16, 1951

The Behavior of Anthrone on Some Alumina Columns

BY J. H. PINCKARD, A. CHATTERJEE AND L. ZECHMEISTER

When a benzene solution of pure, pale-yellow anthrone is adsorbed from benzene on a suitable alumina–celite column, a colored heterogeneous zone appears within a few minutes. When, subsequently, this adsorbate is washed with large volumes of benzene, the colored zone is resolved and some of its components migrate slowly downwards while much larger quantities of a colorless and non-fluorescent substance runs through the column. The latter substance is, however, not anthrone but anthraquinone. Under the conditions applied the yield varies between 80–90%. In contrast, a mixture of roughly equal parts of anthrone and anthraquinone is obtained in the washings if an "acid" brand of alumina is applied. A celite column has no effect on anthrone.

Experimental

One gram of vacuum-sublimed analytically pure anthrone (Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.71; H, 5.12; m.p. 154–158°, cor.) which according to spectroscopic tests did not contain any anthraquinone, was dissolved in 100 ml. of benzene and poured, with suction, onto a 24 × 4.2 cm. alumina celite column (4:1). (Activated alumina "Alorco." Grade F, −80 mesh, reground to −200 mesh; Celite No. 545, Johns-Manville.) About a 2 cm. broad, brownish-yellow zone appeared near the top which during the subsequent development by means of 8 liters of benzene was resolved into a narrower, very strongly adsorbed brownish-red zone and a pale yellow substance with greenish fluorescence in ultraviolet light. This substance was present in small amounts only and spread over the rest of the adsorbent; only traces of it reached the chromatographic filtrate.

The main product of the conversion, *i.e.*, anthraquinone, ran through much more easily and could be collected from the filtrate. While passing through the column, it quenched the moderate fluorescence of the commercial alumina. (An authentic sample of anthraquinone behaved very similarly.) The filtrate was evaporated and the anthraquinone isolated in crystals. Its molecular extinction curve, taken in hexane solution, was identical with that of an authentic sample; m.p. 280–284° (cor.).

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.87. Found: C, 80.96; H, 3.97.

The yield was about 83% which could be somewhat increased by a subsequent washing with 1 liter of acetone, which, however, also carried some fluorescent and slightly colored material into the filtrate. In every instance ³/₄ of the product was present in the first 2-liter benzene fraction.

In another experiment 0.1 g. of anthrone was chromatographed on a 16.5 × 1.9 cm. column made up using an acid brand of alumina, *viz.*, "Aluminiumoxyd sauer," manufactured by M. Woelm in Eschwege, Germany. After the adsorbate was washed with benzene which was followed by acetone and ethanol, a photometric estimate showed the ratio, anthrone:anthraquinone = 1:0.8. Presumably, this incomplete reaction was due to lower conversion rates on the acid column. The recovery was practically complete.

GATES AND CRELLIN LABORATORIES
OF CHEMISTRY (NO. 1639), CALIFORNIA
INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA RECEIVED NOVEMBER 16, 1951

The Preparation and Properties of Stannous Fluoride[1]

BY WM. H. NEBERGALL, JOSEPH C. MUHLER AND HARRY G. DAY

In connection with investigations of the effectiveness of various fluorine-containing compounds in reducing the acid solubility of dental enamel and the incidence of dental caries in rats, stannous fluoride was found to be most effective.[2] Samples of materials labeled "Stannous Fluoride" obtained from several different chemical supply houses and different samples from the same supply house were found to vary widely in appearance, water solubility, melting point and composition. In addition, the effect in reducing the acid solubility of powdered enamel and the incidence of experimental caries in rats has been found to vary when different samples of such "stannous fluorides" were employed. The work reported herewith was done in order to make available stannous fluoride of known and dependable composition, purity and solubility for further studies of the type mentioned, and for extensive clinical programs involving the topical application of stannous fluoride preparations which are now in progress.

The interaction of stannous oxide and hydrofluoric acid has been investigated as a basis for the preparation of stannous fluoride. Although this reaction was studied almost 100 years ago,[3] significant details and properties have never been reported.

Experimental

Stannous Fluoride from Stannous Oxide and Hydrofluoric Acid.—Stannous oxide,[4] 67.4 g. (0.5 mole), was weighed into a 200-ml. polyethylene beaker and sufficient oxygen-free water (15–20 ml.) was added to thoroughly wet the stannous oxide. With an atmosphere of oxygen-free nitrogen maintained above the stannous oxide, it was heated to 60° on a steam-bath, and 46.0 g. (1.1 moles, a 10% excess) of 48% hydrofluoric acid was slowly added while the reaction mixture was being gently swirled. After about one-half of the stannous oxide had dissolved, the reaction became quite vigorous due to the evolution of heat. The reaction mixture was stirred until all of the stannous oxide had dissolved and then placed in a desiccator to cool under an atmosphere of nitrogen. After two hours, the mother liquor was decanted from the first crop of crystals into another polyethylene beaker. Both the crystals and the mother liquor were placed in desiccators over a 1:1 mixture of calcium chloride and potassium hydroxide for the purpose of drying and obtaining a second crop of crystals, respectively. After two days, further drying of the stannous fluoride was carried out over magnesium perchlorate. After 4 days, the second crop of crystals from the mother liquor was collected and dried in the same manner as the first crop; yield first crop, 69%; second crop, 17%; total, 86%. Both crops were identical in purity and properties.

Anal. Calcd. for SnF_2: Sn, 75.75; F, 24.25. Found: Sn, 75.7, 75.8, 75.8; F, 24.0, 24.5, 24.6.

The above procedure for the preparation of stannous fluoride represents the combination of the optimum conditions as ascertained by a study of the following: the effect of suspending the stannous oxide in varying quantities of water; the effect of the initial temperature upon the reaction; the effect of the extent of excess of hydrofluoric acid upon the reaction and nature of the product; the effect of protecting the reaction mixture from oxygen of the air; and the effect of various drying procedures on the nature of the product. Fremy[3] reported that an excess of hydrofluoric acid acting upon stannous oxide gave rise to the acid fluoride. In the present investigation, no indications of any product other than the normal salt were found when an excess of acid up to and including 200% was employed.

Properties of Stannous Fluoride.—Stannous fluoride crystallizes as colorless prisms and melts at 210–215°. The compound dissolves in water (29.6% at 18°) to form essentially clear solutions initially. After about an hour, aqueous solutions of stannous fluoride become cloudy due to hydrolysis and finally a fine white precipitate, probably stannous hydroxide, begins to separate. The *p*H of a freshly prepared 2% solution was found to be 2.90, and after standing for 25 hours, the *p*H was 2.38. The precipitate which forms from hydrolysis was found to contain less than 0.01% fluorine. Clear solutions of stannous fluoride may be maintained by adding a dilute mineral acid to repress the hydrolysis.

X-Ray Powder Diffraction Data[5] for Stannous Fluoride.—In the following table are listed the interplanar spacings ("*d*") and the relative line intensities found to be characteristic SnF_2:

5.460 VW	4.454 W	3.878 W	3.511 VS	3.444 S	3.343 S
3.179 VS	3.114 S	2.741 M	2.587 M	2.517 M	2.438 M
2.346 S	2.299 W	2.213 VW	2.105 M	2.080 S	2.049 S
1.977 S	1.945 S	1.929 S	1.884 M	1.848 S	1.787 VW
1.768 S	1.742 VW	1.700 W	1.686 W	1.622 W	1.612 W
1.594 W	1.572 VW	1.555 W	1.525 M(diffuse)	1.500 M	
1.450 M	1.424 W	1.391 W	1.379 W	1.353 W(diffuse)	
1.325 M	1.310 W	1.296 W	1.282 W	1.267 W	1.242 W

DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA RECEIVED NOVEMBER 2, 1951

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[1] Contribution No. 536 from the Department of Chemistry, Indiana University.

[2] J. C. Muhler and G. Van Huysen, *J. Dent. Res.*, **26**, 119 (1947); J. C. Muhler, T. M. Boyd and G. Van Huysen, *ibid.*, **29**, 182 (1950); J. C. Muhler and H. G. Day, *J. Am. Dent. Assoc.*, **41**, 528 (1950); J. C Muhler and H. G. Day, *J. Nutr.*, **44**, 413 (1951).

[3] E. Fremy, *Ann. Chim. Phys.*, [3] **47**, 37 (1856).

[4] Obtained from Metal and Thermit Corporation, Carteret, N. J.

[5] X-Ray diffraction data by A. Lessor, Department of Chemistry, Indiana University.

Equilibria between Aliphatic Acids and a Strong Base Anion Exchanger[1]

BY SIGFRED PETERSON AND ROBERT W. JEFFERS

As part of an investigation of ion exchange behavior of carboxylic acids, we measured equilibria between a series of aliphatic acids and the hydroxide of a strong base type anion exchange resin. The resin chosen, Nalcite SAR (Dowex-2), has been described in recent papers.[2,3] Exchange equilibria between the chloride of this resin and several anions have been recently reported.[2]

Experimental

Eastman Kodak white label chloropropionic acids, Tennessee Eastman crotonic acid, C.P. Baker Analyzed formic and acetic acid, Coleman and Bell C.P. butyric acid, and Dow specially purified chloroacetic acid were used. Eimer and Amend C.P. propionic acid and Sapon Laboratories isobutyric acid were distilled, the fractions used boiling, respectively, at 141.0° (750 mm.) and 158.4° (760 mm.).

The resin, obtained as the chloride, was left in 500-g. batches in contact with distilled water for a week, with water changed once or twice daily. The resin was then placed in a large buchner funnel, washed with one liter of distilled water using gentle suction, treated with three one-liter portions of 5% sodium hydroxide and washed again with water. It was then treated with a 5% solution of hydrochloric acid without suction until sufficient acid had been run through to convert the resin to the chloride form, washed and treated as before with sodium hydroxide. This washing with sodium hydroxide was followed by washing with water and continued until the *p*H of the washings was the same as that of the water used. Full suction was then applied for one hour. The resin was then removed from the funnel and dried *in vacuo* over calcium chloride for three days. Resin was used soon after processing to avoid decomposition.

Laboratory distilled water was further demineralized by a mixed-bed ion exchange column.

To weighed samples of resin (usually about 2 g.) in Pyrex glass-stoppered bottles were added 100-ml. portions of acid of known concentration. The bottle was then agitated gently, sealed with paraffin wax and placed in a constant temperature bath at 30.3° for 72 hours, a time found to be quite sufficient for the system to reach equilibrium. The bottles were then removed and the concentration of the acid in the solution measured.

Acid concentrations were measured by titration with standardized sodium hydroxide. For acid concentrations below 0.02 *M* conductometric titrations[4] were used. From the decrease in acid concentration in the solution the concentration of acid in the resin phase is calculated in millimoles per gram of dry resin. This neglects the possibility of water transferred between the solution and the resin, a phenomenon which is known to affect cation exchange equilibria.[5] This source of error is in our work significant only at the higher concentrations, and there not sufficient to alter the qualitative significance of our results.

Results and Discussion

The equilibrium measured is presumably

$$R^+OH^- + HA \rightleftharpoons R^+A^- + H_2O$$

where *R* represents one equivalent of resin cation. The anion of the acid neutralized replaces the hydroxide ion in the resin to maintain electrical neutrality of the phases. Equilibrium isotherms determined simultaneously at 30.3° are shown for six acids in Fig. 1 with the acid neutralized per gram of resin plotted against the equilibrium concentration in the solution.

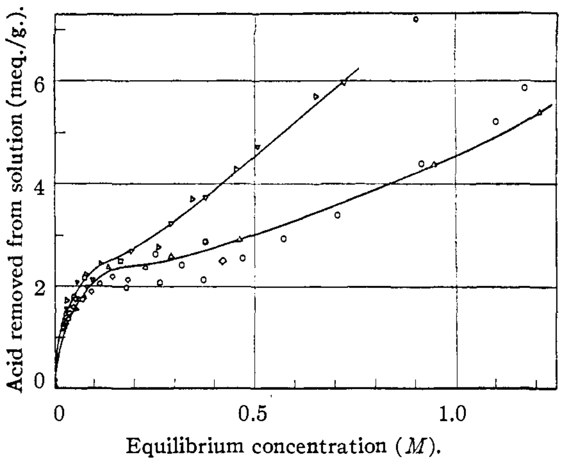

Fig. 1.—Equilibrium isotherms at 30.3° for Nalcite SAR and the acids: ○, acetic; ▷, butyric; □, chloroacetic; ◇, formic; ▽, isobutyric; △, propionic. Curves are drawn in to fit the data for propionic and isobutyric.

It can be seen from the graph that in the dilute range, in which the isotherms should be expected to be most closely related to the acid strengths the differences between the different acids are not much greater than the experimental error. For this reason, no attempt will be made at this time to give an interpretation to these data. The form of the isotherms and their high concentration behavior call for comment, however. The capacity of the resin is 2.69 milliequivalents of quaternary ammonium groups per gram of dry resin and essentially no weakly basic groups.[6] This figure should limit the acid removed from solution by the resin if no processes are occurring other than the neutralization. The isotherms appear to level off at a value somewhat lower than this capacity, probably because either our resin was not completely dry when weighed and possibly not completely in the hydroxide form. But increase of the acid concentration leads to a more or less sharp increase in the acid removed from solution to values considerably beyond the capacity of the resin. We have observed the same behavior with a weak base resin, only less prominently, probably because of the much greater capacity of that resin. That with both resins the phenomenon is greater with butyric and isobutyric acids suggests it is probably true adsorption of acid on the resin. It even appears that this must account for part of the removal of these two acids from dilute solutions by the strong base resin.

A second series of measurements, divided between two temperatures, with seven acids, including three not previously studied, is shown in Fig. 2 for the range of concentrations covered with the added acids. The form and proportions of the curves for the acids common to both series are the same in both series, including data we have beyond the range of concentrations shown in Fig. 2. The

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(1) Presented before the Southwide Chemical Conference, Wilson Dam, Alabama, Oct. 18–20, 1951.

(2) R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1088 (1951).

(3) F. K. Lindsay and J. S. D'Amico, *ibid.*, **43**, 1085 (1951).

(4) H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1951, p. 235.

(5) W. K. Lowen, R. W. Stoenner, W. J. Argersinger, Jr., A. W. Davidson and D. N. Hume, THIS JOURNAL, **73**, 2666 (1951).

(6) F. K. Lindsay, private communication.

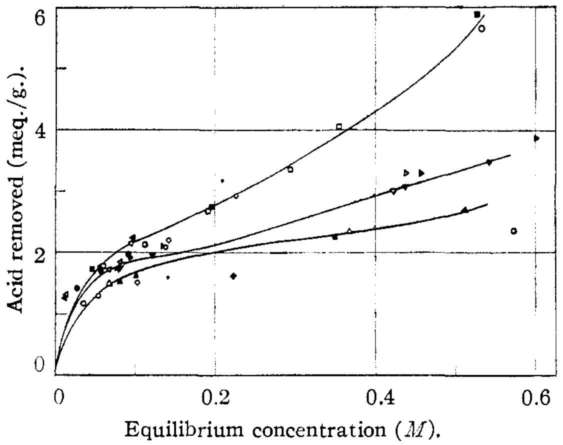

Fig. 2.—Equilibria at two temperatures for Nalcite SAR and the acids: ▷, butyric; □, α-chloropropionic; ○, β-chloropropionic; △, crotonic; ◇, formic; ▽, isobutyric; △, propionic at 30.3°; corresponding symbols filled in represent the same acids at 18.0°. Curves are drawn in to fit the data for α-chloropropionic, isobutyric and propionic.

curves for the second series, obtained with resin processed in a different batch, show lower concentrations in the resin for corresponding solution concentrations, no doubt due to a less complete conversion of resin to hydroxide during the processing. That the acid removal beyond resin capacity is greater for crotonic acid and the chloropropionic acids than for butyric and isobutyric shows that acid removal beyond capacity by this resin is favored by unsaturation and substitution of chlorine for methyl groups. That the measurements at 18.0 and 30.3° for any one acid fit the same curve within the reproducibility of the measurements shows a negligible temperature coefficient for the process. The heat of neutralization of a carboxylic acid by a strong base is not small, although different energies of hydration of the ions in the resin phase than in water may make the heat of neutralization by the resin considerably different than that by aqueous hydroxide ion. It appears that the added process which contributes a large part of the equilibrium has little heat effect.

While adsorption is suggested as this added process, a perhaps more plausible process is the distribution of un-ionized acid between the water within the resin granules and the water outside the resin. This picture is consistent with the approximate linearity of the high concentration parts of the isotherms and the small temperature coefficient of the equilibrium. Adsorption, probably of this same nature, has recently been found[5] to be an important factor in some cation exchange equilibria.

It appears that our original purpose, the correlation of the equilibria of formation of resin carboxylates with anion structure, could have been served better by equilibration of the resin chloride with solutions of salts as has been done for a variety of other anions by Wheaton and Bauman.[2] The lack of sensitivity of our method at low concentrations, the instability of the resin hydroxide as indicated by darkening on standing and the removal of acid without complete neutralization by the resin prevent such a correlation. The last of these three is a new phase of the behavior of resins of this type in contact with acid solutions.

Acknowledgment.—This work was performed under a contract with the Atomic Energy Commission. We are indebted to the College of Arts and Sciences Research Fund for some support, to the National Aluminate Corporation for a generous sample of the resin, to the Tennessee Eastman Corporation for a sample of crotonic acid and to Mr. John Mason and Mr. Merle Likens for preliminary experiments.

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COLLEGE OF ARTS AND SCIENCES
UNIVERSITY OF LOUISVILLE
LOUISVILLE 8, KENTUCKY
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Formation of Ether by Association of Alkyl and Alkoxy Free Radicals

BY JOHN H. RALEY AND DAVID O. COLLAMER, JR.

Coexisting alkoxy and alkyl free radicals undergo various reactions including alkyl–alkyl association, hydrogen atom transfer, and decomposition of the alkoxy radicals.[1-3]

A priori it might be expected that, under proper conditions, these two types of radicals would also associate to form an ether. Previous attempts in this Laboratory to isolate an ether from the decomposition products of di-*t*-alkyl peroxides have been unsuccessful. This note, however, reports the identification of methyl ethyl ether as a product of the pyrolysis of methyl *t*-amyl peroxide, a source of methoxy and ethyl radicals. The ether is believed to arise from an association process rather than from attack of either radical on the peroxide, since the latter reaction is known to result in hydrogen atom transfer.[4] It is clear from the ether yield, however, that under the stated conditions reactions of the radicals other than ether formation predominate. It is not surprising, hence, that experiments with the less thermally stable *t*-alkoxy radicals failed to produce detectable amounts of ethers.

Experimental

Methyl *t*-amyl peroxide was prepared by adding dimethyl sulfate to an aqueous solution of the potassium salt of *t*-amyl hydroperoxide. The distilled product (b.p. 32° (60 mm.), n^{20}D 1.3924; C, 61.5; H, 12.3; equivalent weight by reaction with HI, 65.8; theoretical values, respectively, 60.98, 11.94 and 59.09) contained no hydroxyl, carbonyl, ethylenic or aromatic groups detectable by an infrared examination.

The peroxide and nitrogen, in a molar ratio of 2:3, were passed through an unpacked Pyrex tube at 195°. Complete decomposition occurred during the two-minute residence time. The effluent was conducted through a water scrubber and traps held at about 0 and −70°. The remaining vapor, together with that evolved from the receivers upon subsequent warming to room temperature, was collected and analyzed by Orsat and mass spectrometric procedures. The combined liquid from the receivers was then distilled and the various fractions analyzed by standard procedures.

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[2] G. K. Adams and C. E. H. Bawn, *Trans. Faraday Soc.*, **45**, 494 (1949).

[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, pp. 141-143.

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Methyl ethyl ether was obtained as a fraction distilling at 7-14° (75% at 7-9°). Identification was made by a molecular weight determination and a comparison of the infrared absorption spectrum in the 2-15 μ region with that of an authentic sample. An additional amount was identified in the vaporous product by mass spectrometric comparison with the authentic sample (for example, the ratio of the intensity for ions of $m/q = 31$ to that for ions of $m/q = 60$ was 0.68 for both the reaction product and the known).

The amounts of the various products obtained, in moles per mole of peroxide decomposed, were: $(CH_3)_2CO$ (0.78), CH_3OH (0.29), H_2CO (0.25), C_2H_6 (0.21), CO (0.12), n-C_4H_{10} (0.11), $CH_3COC_2H_5$ (0.093), $C_2H_5C(CH_3)_2OH$ (0.086), *$CH_3OC_2H_5$ (0.078)*, C_2H_4 (0.077), C_3H_8 (0.061), H_2 (0.039), CH_4 (0.036) and C_4H_8 (0.007).

Acknowledgment.—We wish to thank Mr. W. R. Harp, Jr., and Dr. D. P. Stevenson of this Company for supplying the necessary infrared and mass spectral data.

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The Ternary System Thallous Sulfate–Sodium Sulfate–Water at 25 and 45°

BY JOHN E. RICCI AND JACK FISCHER

The solubility isotherms at 25 and 45° for the system Tl_2SO_4–Na_2SO_4–H_2O were determined for comparison with the corresponding system Ag_2SO_4–Na_2SO_4–H_2O.[1] In contrast with the continuous solid solution of silver sulfate and anhydrous sodium sulfate, the thallous salt forms no solid solution with the sodium salt at these temperatures.

The materials and the procedure used were those already described in a report on a number of other systems involving thallous sulfate.[2] Complexes prepared from pure Tl_2SO_4 and C.P. Na_2SO_4 were brought to equilibrium and the saturated solution was then analyzed for total solid and for thallium. The mixtures at 25° were seeded with $Na_2SO_4 \cdot 10H_2O$ after the first 24 hours of stirring. In this connection it was noted that the solutions had to be saturated with the sodium sulfate, prior to the seeding with the decahydrate, in order to initiate the precipitation of the new phase, the seed otherwise dissolving without effect. The mixtures were stirred for 7 to 38 days before analysis of the solution, and attainment of equilibrium was proved by constancy of composition on reanalysis after further stirring.

The measurements, in terms of weight percentage, are listed in Table I for the two temperatures studied, and those for 45° are plotted in the usual fashion in Fig. 1. According to the tie-lines the only solid phases formed are the pure salts, Tl_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ at 25°, Tl_2SO_4 and Na_2SO_4 at 45°. The average absolute error from the compositions of the pure solids, calculated by algebraic extrapolation of the 14 tie-lines involved, is only 0.23% (with 0.77 maximum) on the phase diagram.

TABLE I

SYSTEM $Tl_2SO_4(A)$–$Na_2SO_4(B)$–$H_2O(W)$

Complex % A	Complex % B	Solution % A	Solution % B	Density	Solid phase
		Temperature: 25°			
...	0.00	5.222	0.00	1.046	A
19.49	4.89	6.24	5.69	1.112	A
14.97	9.98	7.32	10.87	1.178	A
12.45	15.21	8.06	15.95	1.245	A
14.99	16.98	8.27	18.34	1.275	A
13.99	21.97	8.48	21.23	1.313	A + B·10W
7.98	27.99	8.42	21.34	1.315	A + B·10W
5.47	25.37	6.59	21.50	1.290	B·10W
3.51	25.98	4.36	21.56	1.256	B·10W
1.41	26.11	1.77	21.58	1.219	B·10W
0.00	...	0.00	21.66	1.210	B·10W
		Temperature: 45°			
...	0.00	7.73	0.00	1.064	A
20.02	7.00	9.62	8.00	1.166	A
20.22	13.07	10.86	14.65	1.254	A
17.94	16.96	11.32	18.39	1.308	A
20.03	19.96	11.41	22.11	1.356	A
18.02	27.00	11.05	28.80	1.434	A + B
11.68	32.43	11.04	28.78	1.435	A + B
10.02	35.07	10.95	28.75	1.434	B
7.50	37.50	8.46	29.57	1.399	B
4.96	39.89	5.74	30.42	1.362	B
0.00	...	0.00	32.05	1.308	B

The solubility of $Na_2SO_4 \cdot 10H_2O$ at 25° is seen to be hardly affected by the Tl_2SO_4, although that of the anhydrous Na_2SO_4 at 45° does suffer the expected decrease. The solubility of Tl_2SO_4 at both temperatures, on the other hand, is distinctly increased by Na_2SO_4, suggesting the formation of some complex involving thallous sulfate and sulfate ion. Potassium oxalate similarly increases the solubility of thallous oxalate.[3]

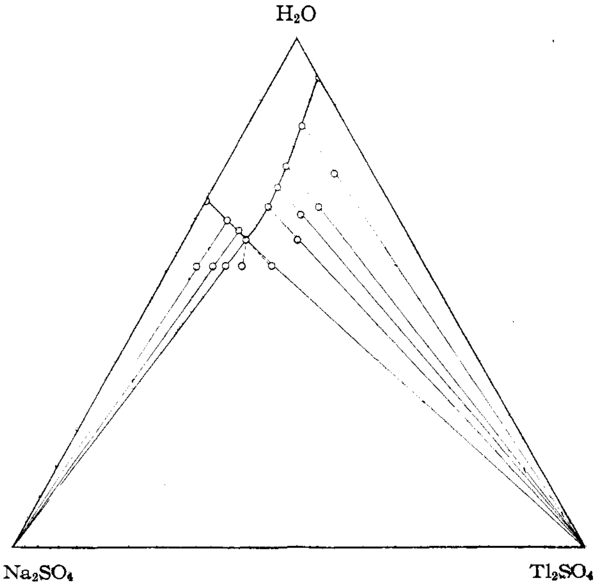

Fig. 1.—System Tl_2SO_4–Na_2SO_4–H_2O at 45°.

Silver and thallous sulfates form solid solutions, besides a 1:1 compound, in their binary system at the melting curve.[4] At room temperatures, however, the argentous salts form solid solutions with various corresponding sodium salts (sulfate,[1] bro-

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[1] E. L. Simons and J. E. Ricci, THIS JOURNAL, **68**, 2194 (1946).

[2] J. E. Ricci and J. Fischer, *ibid.*, **73**, 1443 (1951).

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[4] S. I. Sokolov, *J. Russ. Phys. Chem. Soc.*, **62**, 2319 (1930); from *C. A.*, **25**, 4772 (1931).

mate,[5] chlorate,[6] nitrate,[7] for example) but not with potassium and ammonium salts,[1,6,8] while the thallous salts form solid solution with corresponding potassium and ammonium salts (sulfate,[2] chlorate,[9] primary orthophosphate,[10] for example) but not, at least in the present case, with the sodium salt.[11] According to the ionic radii usually listed[12] (Na^+, 0.95, K^+, 1.33; NH_4^+, 1.48; Ag^+, 1.26; Tl^+, 1.44), one would not quite expect this difference between argentous and thallous salts. The values listed by Sidgwick[13] (Na^+, 0.98; K^+, 1.33; Ag^+, 1.13; Tl^+, 1.49), on the other hand, would be in better agreement. While the sulfates of all of these five cations are orthorhombic, moreover, the axial ratios (a:b:c) fall into two groups.[14] For Na_2SO_4 and Ag_2SO_4 they are 0.598:1:1.252 and 0.570:1:1.235, respectively. In the other group we have 0.573:1:0.742 for K_2SO_4, 0.563:1:0.732 for $(NH_4)_2SO_4$, and 0.555:1:0.733 for Tl_2SO_4.

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(5) J. E. Ricci and J. J. Aleshnick, THIS JOURNAL, **66**, 980 (1944).

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(7) D. J. Hissink, *Z. physik. Chem.*, **32**, 537 (1900).

(8) F. A. H. Schreinemakers, *ibid.*, **65**, 555 (1908).

(9) H. W. B. Roozeboom, *ibid.*, **8**, 531 (1891).

(10) Mme. Bruzau, *Bull. soc. chim. France*, 1177 (1948).

(11) According to V. A. Palkin, $TlNO_3$ forms no solid solution with $AgNO_3$, $NaNO_3$ or KNO_3, *Doklady Akad. Nauk. S. S. S. R.*, **66**, 651 (1949), from *C. A.*, **44**, 9232 (1950); *J. Gen. Chem., U. S. S. R.*, **19**, 367 (1949), from *C. A.*, **44**, 9237 (1950).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1948, pp. 346, 350.

(13) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford Univ. Press, 1950, p. xxix.

(14) A. N. Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, Inc., New York, N. Y., 1931, pp. 216–217; R. W. G. Wyckoff, "The Structure of Crystals," Supplement to 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1935, p. 64.

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Formylation during Nitrolysis in Chloroform

BY JOHN H. ROBSON[1] AND GEORGE F WRIGHT

It has been shown[2] that the nitrolysis of N,N′-dicyclohexylimidazolidine in acetic anhydride–nitric acid yields mainly N-nitro-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (I), although some N-nitro-N′-aceto-N,N′-dicyclohexyl-1,2-diaminoethane is also formed, presumably by acetylation of I. When chloroform is included in the nitrolysis medium neither of these products can be isolated. Instead a mixture is obtained which, when partially purified, shows by its X-ray diffraction powder pattern that it contains N-nitro-N′-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane (II). Destruction of this component by potassium persulfate–absolute nitric acid mixture leaves a compound for which analysis indicates the formula $C_{15}H_{27}N_3O_3$. This substance gives a positive Franchimont nitramine test and a negative lanthanum nitrate test for an aceto group. It has been proven to be N-nitro-N′-formyl-N,N′-dicyclohexyl-1,2-diaminoethane (III) by its synthesis *via* formylation of I.

The presence of a formyl group in III may be ascribed either to oxidation of the methylene linkage of the imidazolidine or to formylation of I by mixed formic–acetic anhydride. Such an anhydride might arise from formic acid produced by decomposition of chloroform in the nitrolysis medium. The latter interpretation is preferred because none of III was formed when chloroform was absent. Furthermore a small yield of III could be obtained when formic acid rather than chloroform was used in the reaction mixture. This meager yield was not unexpected in consideration of the instability of formic acid in the nitrolysis medium. Indeed the stability of the disubstituted formamide (III) in this medium was unexpected and is being investigated further.

Experimental[3]

N-Nitro-N′-formyl-N,N′-dicyclohexyl-1,2-diaminoethane (III).—To 21.0 ml. (0.5 mole) of absolute nitric acid at −2 to 0° was added dropwise with stirring, a solution of 5.9 g. (0.025 mole) of N,N′-dicyclohexylimidazolidine in 25 ml. of chloroform (ethanol-free and dry). Then 100 ml. of distilled acetic anhydride was added at 0–5° and the stirred suspension maintained at 35–45° for seven hours. All volatile solvents were removed under reduced pressure. The residual oily solid was thrice-crystallized from ethanol to yield 2.0 g., m.p. 147–148°. This material did not depress the melting point of authentic N-nitro-N′-nitroso-N,-N′-dicyclohexyl-1,2-diaminoethane (m.p. 147–148°) and the X-ray (Cu,Kα; Ni filtered) diffraction powder pattern included spacings (Å.) characteristic of pure II. Thus intensities [I/I_0] and spacings for II are: [10] 4.62; [7] 3.12; [6] 5.67, 4.03, 3.70; [5] 8.34, 2.81, 2.38; [4] 2.71, 1.90; [3] 2.59, 2.19; [2] 6.70, 5.15, 2.00, 1.77; [1] 2.27, 2.06, 1.72, 1.65, 1.48, 1.26. The impure 2.0 g. portion gave a comparable pattern: [10] 4.66; [6] 5.67, 3.86, 2.84; [5] 3.12; [4] 4.07, 2.39; [3] 8.18, 3.70, 2.13; [2] 5.15, 3.45, 2.71; [1] 2.55, 2.21, 1.96, 1.92, 1.79, 1.76, 1.51. In order to demonstrate the non-identity with N-nitro-N′-aceto-N,N′-dicyclohexyl-1,2-diaminoethane the powder pattern for the latter substance was also determined: [10] 5.03, 4.57; [7] 5.71; [6] 4.23, 3.42; [5] 3.66, 3.10; [4] 8.42, 2.42; [3] 2.76; [2] 2.26, 2.08; [1] 2.59, 2.23.

Furthermore purification of the 2-g. portion was accomplished firstly by treatment with 7.2 g. of ammonium persulfate in 7.2 g. of absolute nitric acid at 0–5° for four hours to yield a semi-solid oil after drowning in ice. This oil was treated five minutes with 15 ml. of hot 70% nitric acid, the mixture drowned in ice, and the resulting solid crystallized from ethanol or diisopropyl ether to yield 0.94 g. (13%) of III, m.p. 163–164°.

Anal. Calcd. for $C_{15}H_{27}N_3O_3$: C, 60.6; H, 9.17; N, 14.2. Found: C, 60.5; H, 9.05; N, 14.3.

The X-ray diffraction pattern with CuKα (Ni filtered) radiation included spacings in Å. with intensities [I/I_0] as follows: [10] 4.97; [7] 4.15; [6] 3.86; [5] 5.60, 2.83; [3] 3.45, 2.99; [2] 3.23, 2.32, 2.14, 1.79; [1] 2.62, 2.49, 1.76.

If the chloroform was eliminated from the preparative procedure and 10 ml. of formic acid was, instead, added at 0° subsequent to addition of the acetic anhydride, the otherwise identical method gave a 13% yield of I and a 2% yield of III.

When 1.50 g. (0.0047 mole) of I was dissolved in 7 ml. of 99% formic acid, the solution warmed to 50°, and 2.2 ml. (0.0225 mole) of acetic anhydride added dropwise with stirring at 50–55° over a 45-minute interval, subsequent dilution into ice–water mixture gave 0.67 g., m.p. 130–155°. Crystallization from 70% nitric acid and then from ethanol yielded 0.14 g., (48% crude yield, 10% pure), m.p. 162–164°. A mixed melting point with III obtained by nitrolysis was not depressed.

DEPT. OF CHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, ONTARIO

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(1) Defence Research Board Fellow, 1950–1951. Present address: Michelson Laboratory, Naval Ordnance Test Station, China Lake, Calif.

(2) J. L. Boivin and G. F Wright, *Can. J. Res.*, **B28**, 213 (1950).

(3) All melting points are corrected against reliable standards.

Esters of Lactyllactic Acid[1]

BY C. E. REHBERG AND MARION B. DIXON

The process of making esters of lactyllactic acid from lactide was discovered by Claborn,[2] who described the methyl, ethyl and butyl esters. Lactyllactates can also be made by the self-alcoholysis of esters of monomeric lactic acid.[3]

Because the acylation of lactyllactates with monocarboxylic[3] and dicarboxylic[4–6] acids yields esters useful as plasticizers, it was of interest to characterize more fully those lactyllactates which were available to us. These esters were obtained as byproducts in the preparation of simple lactates on a large laboratory scale, the conversion to lactyllactate usually being 5 to 20%, depending on the ratio of alcohol to lactic acid used in the esterification.

Table I shows the esters studied and the physical properties determined

The boiling points shown were read from lines on a Cox chart. This chart was notable for the unusally low value of the Antoine constant *C*, its value being 183 instead of the usual 220–240. Paper graduated for $C = 273$ was converted to $C = 183$ by adding 90° to each temperature on the scale.[7]

TABLE I

PHYSICAL PROPERTIES OF LACTYLLACTATES

Lactyllactate	n^{20}_{D}	n^{40}_{D}	d^{20}_{4}	d^{40}_{4}	Viscosity, cps. 20°	Viscosity, cps. 40°	Boiling points at various pressures[c] 0.1 mm.	1.0 mm.	10 mm.	Solubility in water, g./100 g. (25°)
Methyl[a]	1.4314	1.4240	1.1609	1.1396	28.14	9.36	44	73	111	∞
Ethyl[a]	1.4292	1.4212	1.1136	1.0929	17.09	6.77	48	77	116	∞
n-Propyl	1.4304	1.4222	1.0764	1.0567	14.20	6.09	54	85	124	2.2
n-Butyl[a]	1.4329	1.4247	1.0622	1.0425	17.06	7.04	63	94	134	0.92
n-Hexyl	1.4362	1.4282	1.0280	1.0094	21.64	8.55	79	111	153	.08
n-Octyl	1.4396	1.4317	1.0042	0.9866	26.57	10.45	97	131	176	< .01
s-Butyl	1.4295	1.4216	1.0528	1.0332	20.10	7.58	56	86	126	1.16
2-Octyl	1.4358	....	0.9894	....	...	...	89	122	164	< .01
Allyl[b]	1.4448	1.4366	1.1172	1.0971	18.60	7.45	58	88	128	4.2
2-Butoxyethyl	1.4390	1.4312	1.0760	1.0570	30.89	11.46	91	125	169	.38
2-(2-Butoxyethoxy)-ethyl	1.4433	1.4352	1.0726	1.0531	32.09	12.81	115	150	196	.31
Tetrahydrofurfuryl	1.4578	....	1.1691	....	...	...	120 (0.3 mm.)	...		....
2-Chloroethyl	1.4540	1.4458	1.2351	1.2152	60.20	18.31	94 (0.3 mm.)	...		....

[a] Previously reported by Claborn (ref. 2). The properties he reported are in substantial agreement with ours. [b] Previously reported [Rehberg, Dixon and Fisher, *J. Org. Chem.*, **15**, 560 (1950)]. [c] Values read from a Cox chart.

TABLE II

ANALYSES OF LACTYLLACTATES[a]

Lactyllactate	Saponification equivalent Calcd.	Saponification equivalent Found	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Mol. refraction Calcd.	Mol. refraction Found 20°
n-Propyl	102.1	100.7	52.9	52.7	7.9	7.9	48.60	49.04
n-Hexyl	123.2	126.2	58.5	58.6	9.0	9.1	62.45	62.68
n-Octyl	137.2	138.4	61.3	61.2	9.6	9.7	71.69	71.94
s-Butyl	109.1	109.0	55.0	55.0	8.3	8.3	53.21	53.50
2-Octyl	137.2	142.4	61.3	61.9	9.6	9.8	71.69	72.47
2-Butoxyethyl	131.2	130.4	54.9	54.8	8.5	8.6	64.09	64.11
2-(2-Butoxyethoxy)-ethyl	153.2	159.5	54.9	54.7	8.6	8.5	74.97	75.77
Tetrahydrofurfuryl	123.1	125.3	53.6	53.8	7.4	7.5	57.27	57.45
2-Chloroethyl	15.8[b]	15.8[b]	42.8	42.9	5.8	5.9	48.84	29.25

[a] The authors are indebted to C. O. Willits, C. L. Ogg, and their associates, of this Laboratory, for the analyses shown [b] Chlorine, %.

Most of the esters in Table I are new compounds, and analytical data on those not previously described are shown in Table II.

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[1] Contribution from the Eastern Regional Research Laboratory, Philadelphia 18, Pennsylvania. One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] H. V. Claborn, U. S. Patent 2,371,281, March 13, 1945.

[3] E. M. Filachione, E. J. Costello, T. J. Dietz and C. H. Fisher, Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, AIC-295, Feb. 1951 (Processed).

[4] C. E. Rehberg, M. B. Dixon, T. J. Dietz and C. H. Fisher, *Ind. Eng. Chem.*, **42**, 1409 (1950).

[5] C. E. Rehberg and M. B. Dixon, THIS JOURNAL, **72**, 5757 (1950).

[6] C. E. Rehberg, T. J. Dietz, P. E. Meiss and M. B. Dixon, "Plasticizers from Lactic Acid. Lactate Esters Esterified with Dibasic Acids," submitted for publication in *Ind. Eng. Chem.*

[7] C. E. Rehberg, *Ind. Eng. Chem.*, **42**, 829 (1950).

EASTERN REGIONAL RESEARCH LABORATORY
PHILADELPHIA, PENNA.
RECEIVED OCTOBER 13, 1951

Synthesis of Δ^1-Allopregnene-17α,21-diol-3,11,20-trione-21-acetate

BY EVELYN WILSON AND MAX TISHLER

The recent publication by St. Kaufmann and Pataki[1] in which they describe the synthesis of Δ^1-allopregnene-17α,21-diol-3,11,20-trione-21-acetate ("Δ^1-allocortisone acetate") (II) has prompted us

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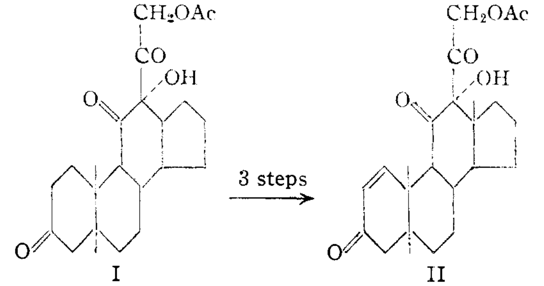
[1] St. Kaufmann and J. Pataki, *Experientia*, **7**, 260 (1951).

to report our experiences on the synthesis of this cortisone isomer.

Our work was undertaken for the purpose of comparing the biological activity of this cortisone isomer with that of cortisone itself.

Allopregnane-17α,21-diol-3,11,20-trione-21-acetate (I), required for this synthesis, was first prepared from cortisone acetate[2] by hydrogenation in methanol using palladium oxide and a small amount of alkali. In this reduction the desired saturated trione (I) and its C_5-epimer were formed. Separation of the two was achieved by fractional crystallization from acetone, the allo-epimer being the less soluble one.



I II

Bromination of the allo-ketone I and dehydrobromination of the resultant 2-bromo derivative by the 2,4-dinitrophenyl hydrazine–pyruvic acid method[3] gave Δ^1-allopregnene-17α,21-diol-3,11,20-trione-21-acetate (II).

Preliminary biological testing[4] of Δ^1-allopregnene-17α,21-diol-3,11,20-trione-21-acetate showed the compound was essentially inactive in inhibiting the edema produced by the injection of an irritant into the foot of a rat. In the liver glycogen deposition test in rats the compound may have been as much as 10–20% as active as cortisone acetate.

In a preliminary test[5] Δ^1-allopregnene-17α,21-diol-3,11,20-trione-21-acetate showed some ability to inhibit the development of the Patterson lymphosarcoma in AKm. mice. At a dosage of 375 mg./kg./day for one week this cortisone isomer markedly retarded the growth of the tumor; at one-half this dose level the inhibition effect was slight. Cortisone under similar conditions causes marked inhibition at 25–37.5/mg./kg./day.

Allopregnane-17α,21-diol-3,11,20-trione-21-acetate (I) was inactive in the liver glycogen deposition and edema-inhibition tests; it was in fact antagonistic to cortisone acetate in the latter test. In its tumor-inhibiting effect allopregnane-17α,21-diol-3,-11,20-trione-21-acetate had slight, if any, activity at a dose level of 375 mg./kg./day.[5]

Experimental

***Allo*pregnane-17α,21-diol-3,11,20-trione-21-acetate (I).**—A suspension of 7.25 g. (0.018 mole) of 3,11,20-triketo-17α-hydroxy-21-acetoxy-Δ^4-pregnene (cortisone acetate) in 600 cc. of methanol was treated with 600 mg. of palladium oxide catalyst and 12 cc. of 0.001 *N* potassium hydroxide solution. The mixture was then hydrogenated at room temperature at forty pounds pressure. In about one-half hour the uptake of hydrogen stopped; the amout of hydrogen absorbed corresponded to one mole. The reaction mixture was filtered from the catalyst, and the latter was washed thoroughly with chloroform. The combined filtrates were treated with the theoretical amount of ethanolic hydrogen chloride and concentrated to dryness *in vacuo* at 40°. The residue was dissolved in chloroform, and the solution was again concentrated to dryness at 40°. The residue was crystallized twice from acetone and dried at 50° *in vacuo*. The fine white needles melted at 229–233°; wt. 3.1 g. (43%); $[\alpha]^{24}\text{D}$ +100° (0.2% chloroform); +78.5° (0.2% acetone).

Anal. Calcd. for $C_{23}H_{32}O_6$ (404.49): C, 68.29; H, 7.97. Found: C, 68.46; H, 7.68.

From the acetone mother liquors of the allo compound the C_5-epimer, pregnane-17α,21-diol-3,11,20-trione-21-acetate, m.p. 225–230°, was obtained. The latter did not depress the melting point of an authentic specimen. A mixture of I and authentic 3,11,20-triketo-17α-hydroxy-21-acetoxypregnane melted at 214–220°.

2-Bromo-*allo*pregnane-17α,21-diol-3,11,20-trione-21-acetate.—Compound I (5.51 g., 0.0136 mole) was dissolved in 50 cc. of chloroform, and 500 cc. of reagent glacial acetic acid was added. A few drops of 1.3 *N* hydrogen bromide in acetic acid was added, and the solution was stirred while 0.0139 mole of bromine in 19 cc. of glacial acetic acid was added dropwise at room temperature. The solution was concentrated to dryness *in vacuo* at 25–35°. The residue was triturated with low-boiling petroleum ether, filtered and recrystallized from ethyl acetate, m.p. 179–185° (dec.); $[\alpha]^{24}\text{D}$ +102° (0.5% chloroform); wt. 4.5 g. (68.5%).

Δ^1-*Allo*pregnene-17α,21-diol-3,11,20-trione-21-acetate.—A mixture of 4.35 g. (0.009 mole) of bromoalloketone and 2.2 g. of 2,4-dinitrophenylhydrazine in 125 cc. of glacial acetic acid was stirred and heated at 50–55° in a nitrogen atmosphere for three hours. Then 375 cc. of distilled water was added and the mixture was chilled for two hours. The orange solid was filtered, washed well with water and air-dried. The crude hydrazone showed absorption at 3750 Å.: log *E* 4.45 (methanol). A Beilstein test was negative.

The combined filtrates from the hydrazone contained 95% of the theoretical amount of bromide ion. The crude hydrazone was mixed with 175 cc. of 90% pyruvic acid and 35 cc. of glacial acetic acid and stirred under nitrogen at 80–85° for 5.5 hours. (A clear solution is obtained in about 45 minutes.) The solution was concentrated to a small volume *in vacuo*, and the residue was diluted with a large quantity of chloroform. The solid that precipitates was filtered, and the chloroform filtrate was extracted twice with water, three times with dilute potassium bicarbonate, and finally again with water. The chloroform solution was then distilled to one-half its initial volume at atmospheric pressure. The dark solution was treated with 20 cc. of acetic anhydride and 5 cc. of pyridine. The solution was kept at room temperature overnight; it was then shaken with water. The chloroform layer was then washed successively with 2.5 *N* hydrochloric acid, water, dilute potassium bicarbonate, and then water. The solution was dried with Drierite and passed through a column of 100 g. of acid-washed alumina. The chloroform eluates were treated with Norit, filtered, and the filtrate was concentrated dry *in vacuo*. Recrystallization of the residue from ethyl acetate gave fine white needles, m.p. 253–256° (dec.), wt. 900 mg., $[\alpha]^{24}\text{D}$ +115° (0.2% chloroform); $\lambda^{\text{EtOH}}_{\text{max.}}$ 2280 Å.; log *E* 4.1; $[\alpha]^{24}\text{D}$ +123° (0.5% acetone). The material forms a solvate with one-half mole of methanol, m.p. 237–242° (dec.). An analytical sample crystallized from ethyl acetate was analyzed.

Anal. Calcd. for $C_{23}H_{30}O_6$ (402.47): C, 68.63; H, 7.51. Found: C, 68.53; H, 7.66.

The same compound was obtained when the bromoalloketone was dehydrohalogenated with γ-collidine. The yield of the Δ^1-compound, however, by this method was less.

RESEARCH AND DEVELOPMENT DIVISION
MERCK AND CO., INC.
RAHWAY, NEW JERSEY

RECEIVED NOVEMBER 7, 1951

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[2] For the partial synthesis of this compound see G. Rosenkranz, J. Pataki and C. Djerassi, THIS JOURNAL, **73**, 4055 (1951); J. M. Chemerda, E. M. Chamberlin, E. H. Wilson and M. Tishler, *ibid.*, **73**, 4053 (1951).

[3] V. R. Mattox and E. C. Kendall, *ibid.*, **70**, 882 (1950); *J. Biol. Chem.*, **185**, 601 (1950).

[4] We are indebted to Drs. C. C. Porter, R. H. Silber and C. A. Winter of the Merck Institute for Therapeutic Research for carrying out these tests for us.

[5] The tumorlytic-activity tests were kindly carried out for us by Drs. C. C. Stock and K. Sugiura at the Sloan-Kettering Institute for Cancer Research and details of this work will be reported later by them.

Tracer-diffusion in Liquids. II. The Self-diffusion as Sodium Ion in Aqueous Sodium Chloride Solutions[1]

By Jui Hsin Wang and Sara Miller

The self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions have been determined both by the diffusion tube method[2] and by the diaphragm cell method.[3] In the first method, in order to get enough intensity of γ-radiation to be measured, Jehle had to use a diffusion tube of 11 cm. inside diameter. With such a large diffusion tube it becomes extremely difficult to eliminate convection during the measurement. Later in a modification of Jehle's method,[4] Wang and Kennedy used a plastic cell which has tubes of 1.7 mm. inside diameter. They used a shearing mechanism to sample out the solution and measured the β-radiation after evaporating the sample solution to dryness. It is doubtful whether their method warrants complete elimination of convection. Furthermore, in their method a slight amount of grease used to lubricate the interfaces between plastic parts might be carried into the diffusion tube during the shearing process, causing the actual cross-sectional area of the tubes to be a little smaller than that estimated from geometric measurements. The diaphragm cell has the disadvantage that appreciable error in the measured value of diffusion coefficient may be introduced by the adsorption of ions on the large surface of the sintered glass disk.[3] Furthermore, Stokes showed[5] that the cell constant seemed to vary appreciably with the density gradient of liquid across the sintered glass disk unless internal stirring was used. Since no internal stirring has been used in diaphragm cell measurements of self-diffusion,[6] the reliability of the self-diffusion coefficients obtained by the diaphragm cell method becomes doubtful inasmuch as it is uncertain whether the cell-constant obtained by calibrating the cell with salt-diffusion measurement (where the density gradient is finite) can be regarded as equal to that for self-diffusion (where the density gradient is zero). However, the capillary method, which was first used by Anderson and Saddington[7] and later improved by Wang,[1,8] has no calibration difficulties because the dimensions of the uniform capillaries used are known. Moreover since the inside diameter of capillaries used (*ca.* 0.5 mm.) are still large as compared to that of the hydrated ions, it can easily be shown that the possible adsorption error in 0.005 formular-weight per liter solution is less than 0.2% even if we assume that the entire surfaces of the capillaries are covered by a monomolecular layer of ions. The diffusion potential should be negligible if solutions inside and outside of each capillary have been carefully prepared to be of equal chemical concentration. The convection error in these capillaries has been shown to be negligible in Paper I of this series. Thus it seems desirable to redetermine the self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions by the capillary method.

Results

In the present work the self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions of concentration between 0.005 to 5.000 formular-weight per liter at 25° have been determined by the capillary method. The principle and technique of the experimental method used have already been described in Paper I[1] of this series. The results are listed in Table I.

TABLE I

TRACER-DIFFUSION COEFFICIENTS OF Na^+ IN NaCl(AQ.) AT 25°

Concentration of NaCl solution (formular-weight per liter)	$D \times 10^5$ (cm.²/sec.)
0.005	1.32 ± 0.02
.010	1.31 ± .03
.050	1.30 ± .02
.100	1.31 ± .02
.1750	1.313 ± .021
.200	1.32 ± .03
.300	1.35 ± .038
.350	1.34 ± .035
.500	1.32 ± .02
.625	1.31 ± .03
1.000	1.25 ± .03
2.000	1.13 ± .02
3.000	1.02 ± .025
4.000	0.904 ± .016
5.000	0.796 ± .018

Discussion

The Onsager equation[9] for tracer diffusion is

$$D_j = \omega_j[kT - (\kappa e_j^2/3\mathfrak{D})(1 - \sqrt{d(\omega_j)})] \qquad (1)$$

with

$$\omega_j = \frac{RT\,\lambda_j^0}{|Z|\,\mathfrak{F}^2} \qquad (2)$$

$$d(\omega_j) = \frac{\bar{\lambda}}{\bar{\Gamma}} \sum_i \frac{t_1}{(\omega_i + \omega_j)} \qquad (3)$$

$$\bar{\lambda} = \sum_i n_i\, e_i^2\, \omega_i \qquad (4)$$

$$t_i = n_i\, e_i^2\, \omega_i/\bar{\lambda} \qquad (5)$$

$$\kappa^2 = (4\pi/\mathfrak{D}kT)\,\bar{\Gamma} \qquad (6)$$

$$\bar{\Gamma} = \sum_i n_i\, e_i^2 \qquad (7)$$

where D_j is the diffusion coefficient of tracer ions of the *j*th kind in a given salt solution, e_i is the absolute electric charge, Z_i the charge in electronic units of ion *i*, κ_i is the inverse mean radius of ion-atmospheres, n_i the concentration in number of ions per cc., λ_i^0 the limiting ionic conductance of ion *i*, $\mathfrak{D}$ the dielectric constant of solvent, *k* the Boltz-

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[1] Paper I, THIS JOURNAL, **74**, 1182 (1952).

[2] L. Jehle, Ph.D. Thesis, University of California, Berkeley, 1938.

[3] A. W. Adamson, J. W. Cobble and J. M. Nielson, *J. Chem. Phys.*, **17**, 740 (1949).

[4] J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950).

[5] R. H. Stokes, *ibid.*, **72**, 763, 2243 (1950).

[6] When the present note was in press an article by Nielsen, Adamson and Cobble appeared (*ibid.*, **74**, 446 (1952)). These authors measured self-diffusion by means of diaphragm cells with internal stirring. They also showed that both sintered-glass and stainless steel diaphragms may cause serious errors in diffusion measurements due to surface adsorption.

[7] J. S. Anderson and K. Saddington, *J. Chem. Soc.*, 5381 (1949).

[8] J. H. Wang, THIS JOURNAL, **73**, 510 (1951); *ibid.*, **73**, 4181 (1951).

[9] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

mann constant, R the gas constant, $\mathfrak{F}$ the Faraday constant, and T the absolute temperature.

If we express λ_j^0 in (coulomb/sec.) (cm.^{2}/volt), $\mathfrak{F}$ in coulombs, R in joules per ° C. per mole, and replacing n_l by c_i which denotes concentration in moles per liter, equation (1) can be written as

$$D_j = \frac{RT\,\lambda_j^0}{|Z|\,\mathfrak{F}^2} - \frac{\lambda_j^0\,|Z_j|\,\mathfrak{F}}{3N\mathfrak{D}} \times$$
$$2.694 \times 10^{16} \sqrt{\frac{4\pi}{\mathfrak{D}RT}}\,[1 - \sqrt{d(\omega_j)}]\,\sqrt{\sum_i c_i Z_i^2} \quad (8)$$

For the diffusion of tracer amounts of radioactive ions of chemical species No. 1 in salt solution containing non-radioactive ions of chemical species No. 1 and No. 2, we have

$$c_1|Z_1| = c_2|Z_2| \quad (9)$$

For uni-univalent electrolyte $|Z_1| = |Z_2| = 1$, and equation (3) can be written as

$$d(\omega_1) = \frac{1}{2}\left[\frac{1}{2} + \frac{\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right] \quad (10)$$

If we take $\lambda_1^0 = 50.11$ for the sodium ion and $\lambda_2^0 = 76.36$ for the chloride ion[10] at 25°, equations (8) and (10) can be combined to give

$$D \times 10^5 = 1.334 - 0.268\sqrt{c} \quad (11)$$

for the diffusion of tracer amount of radioactive sodium ion in aqueous sodium chloride solutions at 25°.

The self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions at 25° listed in Table I are plotted *vs.* the square root of concentration in Fig. 1. The straight line in the dilute concentration region represents equation (11) according to Onsager's theory. Figure 1 indicates that the measured self-diffusion coefficients agree with the values predicted by the Onsager equation within experimental uncertainty at concentrations below 0.04 formular-weight per liter. Above 0.05 formular-weight per liter the self-diffusion coefficient increases with increasing salt concentrations, reaches a maximum value near 0.4 formular-weight per liter and then starts again to decrease with increasing salt concentration. The general shape of the present D *vs.* $\sqrt{c}$ curve resembles that for the diffusion of tracer amount of sodium ion in aqueous potassium chloride solution, but the peak of the D *vs.* $\sqrt{c}$ curve obtained in the present work appears at $c = 0.4$ instead of at $c = 1.3$ for the diffusion of tracer amount of sodium ion in aqueous potassium chloride solution. A possible explanation is given below.

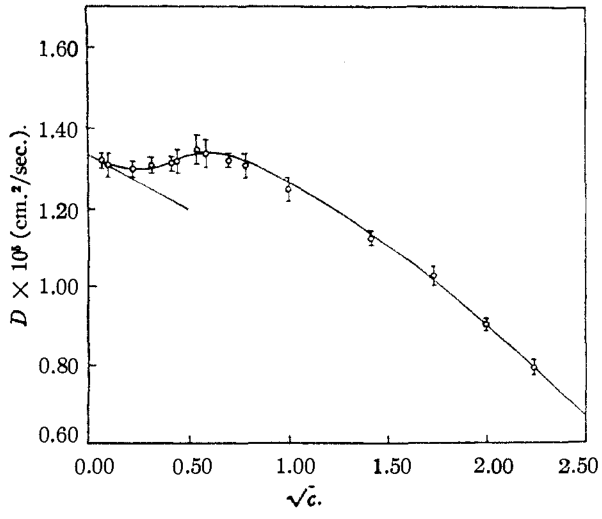

Fig. 1.—Self-diffusion coefficient of Na$^+$ in aqueous sodium chloride solutions at 25°.

In an aqueous potassium chloride solution containing tracer amount of sodium ion, the potassium ions, because of their smaller radii, tend to have closer association with chloride ions than the tracer amount of sodium ions. Consequently the nearest chloride ions surrounding each sodium ion are pulled away from the sodium ion by the potassium ions. Because of this effect the average center to center distance between each of the tracer amount of sodium ions and its nearest chloride ions in aqueous potassium chloride solution becomes larger than the corresponding distance in a pure sodium chloride solution of the same chemical concentration. Consequently, the forces that produce the maximum in the D *vs.* $\sqrt{c}$ curve for the tracer-diffusion of sodium ion in potassium chloride solution should come into play and produce a similar effect on the shape of D *vs.* $\sqrt{c}$ curve for the self-diffusion of sodium ion in sodium chloride solution at a more dilute concentration. The large difference between the two concentrations at the maxima of the two D *vs.* $\sqrt{c}$ curves is not too startling because for a given directional distribution of ions, the average distance between nearest neighbors varies inversely with $c^{1/3}$. However, in view of the complexity of the present problem, it appears unlikely that a quantitative correlation of these two concentrations can successfully be made before a satisfactory theory of liquid water has been formulated.

Acknowledgment.—In preparing the present work the authors have benefited by discussion with Professor H. S. Harned. A research fellowship granted by the du Pont de Nemours Co. to one of us (J. H. W.) is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT RECEIVED NOVEMBER 19, 1951

Tracer-diffusion in Liquids. III. The Self-diffusion of Chloride Ion in Aqueous Sodium Chloride Solutions

BY JUI HSIN WANG

The self-diffusion coefficients of chloride ion in aqueous sodium chloride solutions at 35° have been determined by Jehle.[1] However, extrapolation of Jehle's values yields a limiting tracer-diffusion coefficient at infinite dilution for chloride ion which is almost 20% higher than Nernst's limiting value as calculated from conductance and transference data. In view of the extensive work done by Harned and

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(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Appendix A.

(1) L. Jehle, Ph.D. Thesis, University of California, Berkeley, 1938.

co-workers[2] in the past few years, it is extremely unlikely that Nernst's limiting relationship can be wrong. Furthermore, the shape of the diffusion coefficient *vs.* concentration curve obtained by Jehle showed close resemblance to that for salt diffusion which exhibits rapid increase of diffusion coefficients with salt concentration at high concentrations. This increase in salt diffusion coefficient at high salt concentrations is primarily due to the variation of the activity coefficient of the diffusing salt along the path of diffusion. Since in tracer-diffusion the activity coefficient of the diffusing tracer ion is practically constant along the diffusion path, we can only infer that the mobility of chloride ion in aqueous sodium chloride solution continues to increase with increasing salt concentration even at 2 molal if Jehle's result is to be accepted. Such a conclusion, if accepted, would invalidate the picture adopted to explain the concentration dependence of the tracer-diffusion coefficients of sodium ion in aqueous potassium chloride[3] and sodium chloride[4] solutions. Since Jehle's work appears to be the only piece of experimental work that has been done on the tracer-diffusion of chloride ion, it seems desirable to redetermine the tracer-diffusion coefficients of chloride ion by the improved capillary technique. In the present work the self-diffusion of chloride ion in aqueous sodium chloride solutions has been measured with Cl^{36} as tracer.

Experimental

The Cl^{36} used was obtained from the Isotopes Division of U. S. Atomic Energy Commission at Oak Ridge, Tennessee. The Cl^{36} was originally shipped in the form of hydrochloric acid solution. This was converted to dry sodium chloride before being used to prepare radioactive sodium chloride solutions. The diffusion apparatus and manipulations have already been described in Paper I[3] of this series.

Results

The measured self-diffusion coefficients of chloride ion in aqueous sodium chloride solutions of various concentrations at 25.00° are listed in Table I.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF Cl^- IN NaCl(AQ.) AT 25°

Concn. of NaCl soln., formular-wt. per l.	$D \times 10^5$, cm.²/sec.	Concn. of NaCl soln., formular-wt. per l.	$D \times 10^5$, cm.²/sec.
0.030	1.975 ± 0.015	1.000	1.77 ± 0.016
.050	1.96 ± 0.04	2.000	1.61 ± 0.03
.100	1.94 ± 0.024	3.000	1.44 ± 0.035
.250	1.91 ± 0.025	4.000	1.24 ± 0.015
.500	1.85 ± 0.04	5.000	1.06 ± 0.03

Each value listed in Table I is the average result of three or four measurements. The standard deviation varies from 2.6% for 3.000 molal to 0.75% for 0.030 molal concentration. Measurement of the self-diffusion coefficient of chloride ion in sodium chloride solution below 0.03 molal concentration became tedious because of the low specific activity of Cl^{36} used, and was therefore not attempted.

Discussion

When appropriate units are used, the Onsager equation[5] can be written as[3,4]

$$D_j = \frac{RT\,\lambda_j^0}{|Z_j|\,\mathfrak{F}^2} - \frac{\lambda_j^0\,|Z_j|\,\mathfrak{F}}{3N\,\mathfrak{D}} \times$$

$$2.694 \times 10^{16}\sqrt{\frac{4\pi}{\mathfrak{D}\,RT}}\,[1 - \sqrt{d(\omega_j)}]\,\sqrt{\sum_i c_i Z_i^2} \quad (1)$$

where for the diffusion of tracer amount of radioactive ions of chemical species No. 1 in salt solution containing non-radioactive ions of chemical species No. 1 and No. 2

$$d(\omega_1) = \frac{1}{2}\left[\frac{1}{2} + \frac{\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right] \quad (2)$$

If we take $\lambda_1^0 = 76.36$ for the chloride ion and $\lambda_2^0 = 50.11$ for the sodium ion,[6] we obtain from equations (1) and (2)

$$D \times 10^5 = 2.033 - 0.526\sqrt{c} \quad (3)$$

for the self-diffusion coefficient of chloride ion in aqueous sodium chloride solutions at 25°. Values of self-diffusion coefficients of chloride ion in aqueous sodium chloride solutions at 25° listed in Table I are plotted *vs.* the square root of concentration in Fig. 1. The straight line in the dilute concentration range represents equation (3). Although in the present work it has not been possible to make measurements below 0.03 formular-weight per liter in concentration because of the limited specific activity of radioactive chlorine used, it appears from the diagram that as the concentration of the solution approaches zero measured diffusion coef-

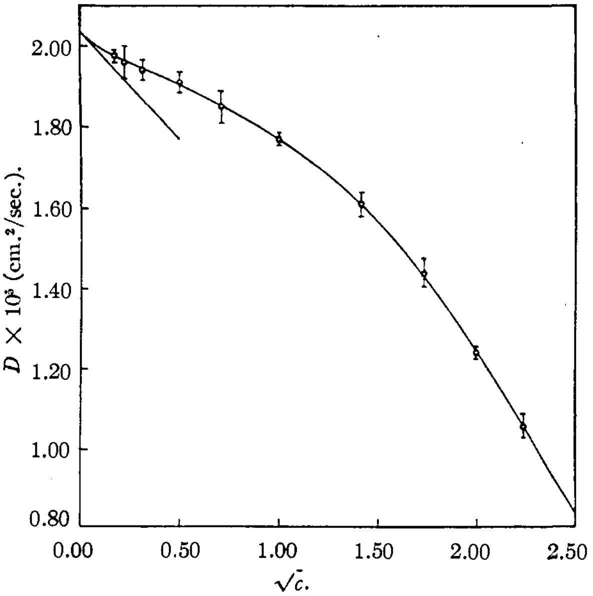

Fig. 1.—Self-diffusion coefficient of Cl^- in aqueous sodium chloride solutions at 25°.

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[2] H. S. Harned and D. M. French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945); H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947); *ibid.*, **71**, 1406 (1949); H. S. Harned and A. L. Levy, *ibid.*, **71**, 2781 (1949); H. S. Harned and C. A. Blake, *ibid.*, **72**, 2265 (1950); *ibid.*, **73**, 2448 (1951); *ibid.*, **73**, 4255 (1951); H. S. Harned and C. L. Hildreth, Jr., *ibid.*, **73**, 650 (1951); *ibid.*, **73**, 3292 (1951); H. S. Harned and R. M. Hudson, *ibid.*, **73**, 652 (1951); *ibid.*, **73**, 3781 (1951); *ibid.*, **73**, 5083 (1951).

[3] J. H. Wang, *ibid.*, **74**, 1182 (1952).

[4] J. H. Wang, *ibid.*, **74**, 1611 (1952).

[5] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Appendix A.

ficient approaches Nernst's limiting value of 2.033 × 10^{-5} cm.^{2}/sec. at infinite dilution. In contrast to Jehle's values for the self-diffusion of chloride ion in aqueous sodium chloride solutions at 35°, the D *vs.* $\sqrt{c}$ curve obtained in the present work shows that the self-diffusion coefficient of chloride ion continues to decrease with increasing salt concentration in the range between 0.03 to 5.00 formular-weight per liter.

It is also seen from Fig. 1 that in contrast to the D *vs.* $\sqrt{c}$ curves for the diffusion of tracer amount of sodium ion in aqueous potassium chloride and sodium chloride solutions, respectively, the D *vs.* $\sqrt{c}$ curve obtained in the present work does not possess a maximum in the whole concentration range studied. This absence of maximum for the D *vs.* $\sqrt{c}$ curve for the tracer-diffusion of chloride ion does not, however, contradict the qualitative explanation suggested earlier[3] if the effect of size of hydrated ion is taken into consideration.

It has been pointed out[7] that the degree of "distortion" that exists in the semi-crystalline structure of "solvent" water in the immediate neighborhood of a hydrated ion seems to increase with decreasing size of the hydrated ion. If this is true, the degree of "distortion" in the structure of solvent water immediately surrounding a smaller chloride ion at infinite dilution should be larger than that for a larger sodium ion. Consequently as the salt concentration increases the increase in the degree of distortion (*i.e.*, the distortion due to finite salt concentration in addition to the distortion that already exists at infinite dilution in the structure of the immediately surrounding solvent water molecules) and, hence, the increase in self-energy should be smaller for chloride ion than for sodium ion in the same sodium chloride solution at moderate concentrations. Since it is the increase in self-energy, as concentration increases, rather than the absolute value of self-energy that makes the tracer-diffusion coefficient increase with increasing salt concentration, it is clear that we should expect Hückel's saturation effect to be smaller for chloride ion than for sodium ion in the same solution at moderate concentrations. Accordingly we should expect the peak in D *vs.* $\sqrt{c}$ curve to be less pronounced for the chloride ion than for the sodium ion which is not in disagreement with the curves obtained experimentally.

The fact that at infinite dilution the degree of distortion that exists in the structure of solvent water in the immediate neighborhood of a hydrated ion increases with decreasing size of the hydrated ion is clearly demonstrated by computing the activation energy for tracer-diffusion of various ions at infinite dilution. If we assume that the activation energy, E, for tracer-diffusion can be calculated by

$$-E/R = \mathrm{d}(\ln D)/\mathrm{d}(1/T) \qquad (4)$$

and that at infinite dilution D is given by equation (1) as

$$D = RT\,\lambda^0/|Z|\,\mathfrak{F}^2 \qquad (5)$$

we may calculate the activation energy for tracer-diffusion from conductance data by

$$E/R = -\,\mathrm{d}[\ln(T\lambda^0)]/\mathrm{d}(1/T) \qquad (6)$$

Individual ionic conductances at infinite dilution for the alkali and halide ions between 5 and 55° have been accurately measured.[6,8] The activation energies for the tracer diffusion of several ions in their aqueous solution at infinite dilution calculated by means of equation (6) from these conductance data are listed in Table II.

TABLE II

ACTIVATION ENERGY FOR TRACER-DIFFUSION OF SEVERAL IONS IN INFINITELY DILUTE AQUEOUS SOLUTION AT 25°

Ion or molecule	E, kcal./mole	Ion or molecule	E, kcal./mole
Li^+ (aq.)	4.56	Cl^- (aq.)	4.17
Na^+ (aq.)	4.39	Br^- (aq.)	4.07
K^+ (aq.)	3.99	I^- (aq.)	4.05
Rb^+ (aq.)	3.95	H_2O	4.6
Cs^+ (aq.)	3.86		

Values in Table II show that as the size of hydrated ion increases from Cs^+(aq.) to Li^+(aq.), the activation energy for tracer-diffusion increases and approaches that for the self-diffusion of pure water. This tendency indicates that the actual activation mechanism for tracer-diffusion of various ions in infinitely dilute aqueous solution probably involves the activation of the immediately surrounding solvent water molecules to get out of the way of the tracer-ion. Since the self-diffusion and viscous flow in pure liquid water involve essentially the same activation mechanism,[9] values in Table II also indicate that when the size of the hydrated diffusing molecule becomes large as compared to water molecules its mobility D/RT should be inversely proportional to the viscosity of solvent water, a relationship that is well known in the case of large spherical molecules as Stokes' law. The fact that the smaller hydrated ions have smaller activation energy for tracer-diffusion than for the self-diffusion or viscous flow of pure water is a microscopic analog of the "slip" phenomena in viscosity measurements.

It may also be noticed from Table II that the activation energy for the tracer-diffusion of the halide ions also increases with increasing size of ion. However, since the water molecule is not symmetrical with respect to polarity, direct comparison of the activation energies for the tracer-diffusion of anions with that of the cations is difficult.

A remark on the definition of activation energy as

$$E = -R\mathrm{d}(\ln D)/\mathrm{d}(1/T) = -R\mathrm{d}[\ln(\lambda^0 T)]/\mathrm{d}(1/T)$$

instead of simply as $E = R\,\mathrm{d}(\ln\lambda^0)/\mathrm{d}(1/T)$ seems desirable. If we accept Eyring's transition-state theory of rate processes for tracer-diffusion in dilute aqueous solutions, the tracer diffusion coefficient D is given by

$$D = \lambda^2\left(\frac{kT}{h}\right)\left(\frac{f^{\ddagger}_{\text{trans}}}{f_{\text{trans}}}\right)\left(\frac{f^{\ddagger}_{\text{rot}}}{f_{\text{rot}}}\right)\left(\frac{f^{\ddagger}_{\text{vib}}}{f_{\text{vib}}}\right)e^{-E/RT} \qquad (7)$$

where λ is a constant characteristic of the system under consideration and reduces to the distance between successive equilibrium sites in the special case of self-diffusion of pure liquid water. f_{trans}, f_{rot}, f_{vib} are, respectively, the translational, rotational and vibrational partition functions of the normal state of the molecule or ion the activation of which determines the rate of the diffusion process

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(7) J. H. Wang, THIS JOURNAL, **73**, 510 (1951).

(8) B. B. Owen, private communication.

(9) J. H. Wang, THIS JOURNAL, **73**, 4181 (1951).

under consideration. $f^{\ddagger}_{\text{trans}}, f^{\ddagger}_{\text{rot}}, f^{\ddagger}_{\text{vib}}$ are the corresponding partition functions of the activated state of the ion or molecule, with the understanding that the translational degree of freedom of the activated state in the direction of diffusion has been removed. It is generally assumed that $(f^{\ddagger}_{\text{vib}}/f_{\text{vib}}) = 1$ for transport processes. If we consider the intermolecular translational motion as free translation in a "cage," $(f^{\ddagger}_{\text{trans}}/f_{\text{trans}})$ should be approximately equal to $h/[(2\pi mkT)^{1/2}V_f^{1/3}]$, where V_f is equal to the "free-volume" of each "cage." This consideration would suggest to us the definition of activation energy as $-R\text{d}[\ln(D/T^{1/2})]/\text{d}(1/T)$ according to equation (7). On the other hand if the intermolecular translational motion can be considered as harmonic oscillation with frequency ν such that $h\nu \ll kT$, then $(f^{\ddagger}_{\text{trans}}/f_{\text{trans}})$ becomes $(1 - e^{-h\nu/kT}) \cong h\nu/kT$ which suggests defining the activation energy as $-R\text{d}(\ln D)/\text{d}(1/T)$ according to equation (7). Since the actual intermolecular translational motion in liquid water is neither free translation nor a harmonic oscillation of frequency ν such that $h\nu \ll kT$, it appears that a correct definition of activation energy should be $-R\text{d}[\ln(DT^{\gamma})]/\text{d}(1/T)$ with $-1/2 < \gamma < 0$. Actually the value of $h\nu/kT$ for liquid water at 25° is about 0.97. Thus if we consider the intermolecular translational motion as harmonic oscillation we would get a value of γ that is very close to $-1/2$. However, because of the semi-crystalline structure of liquid water the potential barrier hindering the rotation of a water molecule in its normal state must be higher than that for the activated state. This would mean that the exponential index of T in f_{rot} may be higher than that in $f^{\ddagger}_{\text{rot}}$ which suggests that the unknown index γ in the above discussion may be higher than the value estimated above. Thus it is clear from these considerations that an exact determination of the activation energy for tracer-diffusion is still beyond our reach, but the definition $E = -R\text{d}(\ln D)/\text{d}(1/T)$ appears to be more plausible than the definition $E = -R\text{d}[\ln(D/T)]/\text{d}(1/T)$.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT
RECEIVED NOVEMBER 19, 1951

The Use of Chlorine Trifluoride as a Fluorinating Agent

BY EUGENE G. ROCHOW AND IRA KUKIN

The commercial availability of chlorine trifluoride[1] made it desirable to investigate the possibility of using this compound instead of elementary fluorine in a number of reactions in which that element customarily is used. In the only published work concerning the use of chlorine trifluoride as a fluorinating agent[2] HgF_2, AgF_2, CuF_2, TiF_3, PtF_4 and PbF_3 (not PbF_4) were prepared by heating the free metal with chlorine trifluoride for three hours at 120°; CoF_3 is reported from Co_3O_4 and from $CoCl_2$ without details.[3]

Experimental

Preparation of Metal Fluorides.—Cobalt(III) fluoride, nickel(II) fluoride and silver(II) fluoride were prepared from cobalt(II) chloride, nickel(II) chloride and silver chloride, respectively. Fifty grams of the chloride first was heated in a porcelain dish for several hours at 250° to dry it, and then the anhydrous chloride was ground to pass a 30 mesh screen, and the powder was spread on a monel tray shaped to fit within a monel tube. The monel reaction tube (see Fig. 1) was similar in design to that used by Priest,[4] who designed it for the preparation of anhydrous metal fluorides by the action of free fluorine on metal chlorides.

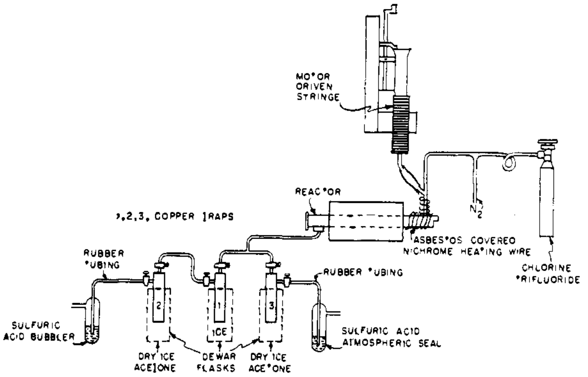

Fig. 1.—Complete apparatus assembly for preparation of fluorocarbons.

Nitrogen was passed through the reactor assembly of Fig. 1 and the furnace was heated to 250°. The flow of nitrogen was discontinued, the safety seal[4] was put in place, and the flow of chlorine trifluoride begun. During the fluorination, chlorine passed through the cold copper trap 3, and then bubbled out through the sulfuric acid outlet. The valve leading to copper trap 1 was kept closed during this fluorination cycle. The completion of the reaction was observed by the discontinuation of bubbles in the sulfuric acid outlet, since the trap was maintained at a temperature sufficiently low to condense the chlorine trifluoride (b.p. +11.3°) but not the chlorine (b.p. −33.7°).

The chlorine trifluoride then was purged from the system with dry nitrogen, and the reactor assembly was cooled. In the case of the cobalt(III) fluoride, the product was used directly for the fluorination of hydrocarbons. Its oxidizing value was determined by the oxidation of potassium iodide in caprylene[5] and was found to correspond to 90% CoF_3; the impurity was shown to be cobalt difluoride by a negative chloride test on the product. Prolonged fluorination with the chlorine trifluoride beyond the point of disappearance of chlorine at the outlet resulted in a product having an oxidizing value equal to that calculated for CoF_3.

It was found that the same reactor assembly could be used for fluorinating hydrocarbons. To do this, the valve leading to trap 3 was closed and the valves to traps 1 and 2 were opened; the hydrocarbons could then be introduced through a separate opening on the inlet tube of the reactor, by way of a metal valve. Several methods[6] for the introduction of the hydrocarbons were tried, but the use of a motor-driven syringe[7] proved most expedient. Alternation of the hydrocarbon feed and the chlorine trifluoride then allowed the same sample of cobalt fluoride to be used repeatedly without removing it.

The copper tubing and that portion of the reactor which extended in front of the electric furnace were wound with nichrome resistance wire to ensure volatilization of the hy-

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[1] Harshaw Chemical Company, Cleveland, Ohio.

[2] W. Huckel, *Nachr. Akad. Wiss. Gottingen Math. physik-Klasse*, 36 (1946).

[3] J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950.

[4] "Inorganic Syntheses," Vol. III, p. 171-183. See also Vol. VII-1 of the National Nuclear Energy Series, "Fluorine Technology," edited by Slesser and Schram (McGraw-Hill Book Co., Inc., New York, N. Y., 1951).

[5] Private communication from the Harshaw Chemical Company.

[6] R. D. Fowler and W. B. Burford: "Fluorocarbons," O.T.S. Report, Department of Commerce, Washington, D. C., 1947; *Ind. Eng. Chem.*, **39**, 292, 319, 329, 338, 350 (1947).

[7] This device is based in part on the automatic titrator designed by J. J. Lingane, *Anal. Chem.*, **20**, 285 (1948).

drocarbons before reaching the layer of cobalt trifluoride. The amount of hydrocarbon introduced during each cycle necessarily was somewhat less than the theoretical amount which could be fluorinated completely, based on the amount of cobalt trifluoride present, its oxidizing value, and the particular hydrocarbon used. The spent cobalt difluoride then was reoxidized with chlorine trifluoride, after the system had been flushed thoroughly with nitrogen. In this cycle the valve leading to trap 1 was kept closed while the valve to trap 3 was opened. Passing the chlorine trifluoride over the cobalt difluoride for only five minutes resulted in a conversion to the cobalt III fluoride, with an oxidizing value greater than 90% of theoretical.

It might be thought possible to mix the vapors of chlorine trifluoride and hydrocarbon and to pass the mixture over cobalt trifluoride to effect fluorination. However, it was found that if the chlorine trifluoride were mixed directly with the hydrocarbon, either as vapor in the reactor tube or as liquid in the copper traps at Dry Ice temperature, only tarry and carbonaceous material resulted. The repetitive batch process of fluorination with CoF_3 must therefore be used.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.
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COMMUNICATIONS TO THE EDITOR

THE ORIGINS OF GLUCURONIC ACID

Sir:

The observations that three-carbon compounds, such as lactate and pyruvate, stimulate glucuronic acid synthesis *in vitro* to a greater extent than six-carbon compounds, such as glucose, suggests that the former are either precursors of glucuronic acid or that their oxidation supplies energy for the reactions by which conjugated glucuronides are synthesized from other sources.[1]

In an attempt to clarify this problem, the synthesis of menthol glucuronic acid by liver slices of fasted guinea pigs was studied using, as substrates, glucose, and lactate, in each of which a single carbon was labeled with C^{14} as indicated in the table below. In each experiment the slices were incubated in the same modified Ringer's solution containing glucose, lactate, menthol and a sodium bicarbonate:carbon dioxide buffer system. Only one substrate was labeled in each experiment. The menthol glucuronic acid synthesized by such a system was isolated, purified to constant radioactivity and oxidized, either with periodate (which gave carbon 1, carbons 2-3-4, and carbons 5-6 as three separate fractions), or with 12% hydrochloric acid (which gave carbon 6 as a separate fraction).[2] Each fraction was isolated, specifically converted to carbon dioxide, and plated and counted as barium carbonate. The results are summarized as

Substrate	Labeled position of substrate	C-1	C-2,3,4	C-5,6
	Counts per minute per mM. carbon			
Glucose-1-C^{14}	53.8 × 10^5	56,500	3,200	1,320
Lactate-3-C^{14}	11.7 × 10^5	4,150	2,060	6,540
	8.8 × 10^5	830	470	1,270

It is apparent from the data with glucose-1-C^{14} that this compound enters the glucuronic acid molecule with no major redistribution of C^{14} from the 1-position of the glucose molecule. This might be interpreted as evidence for the direct conversion of glucose to glucuronic acid. However, if glucose were the sole source of glucuronic acid, it would be expected, in accordance with current concepts of glycogenesis, that symmetrical labeling of the glucuronic acid would occur when lactate-3-C^{14} was the labeled substrate. Contrary to this expectation, the average specific activity of carbons 5 and 6 of the glucuronic acid is higher than that of carbon 1, indicating that this substrate is converted to the distal portion (carbons 4, 5, 6) of the glucuronic acid molecule to a greater extent than to the proximal portion. Decarboxylation of the menthol glucuronic acid obtained with lactate-3-C^{14}, resulting in the isolation of carbon 6 as a discrete fraction, shows that practically all the radioactivity in the C-5,6 fraction resides in C-6, the specific activity of the latter being approximately 2.5 times than of C-1. It would appear from these results that the entire glucose molecule is not the sole source of the glucuronic acid. Since lactate is rapidly metabolized by pathways other than anabolic reactions, it is to be expected that considerable dilution and redistribution of the radioactivity of the original substrate will occur and will be apparent in the labeling of the menthol glucuronic acid even though lactate were a precursor.

These data, therefore, do not exclude the possibility that, in the biosynthesis of conjugated glucuronic acid, a triose, produced from lactate, condenses with another triose formed from glucose and that, in this manner, carbons 1, 2 and 3 of the glucuronic acid originate predominantly from carbons 1, 2 and 3 of glucose while carbons 4, 5 and 6 originate from a three-carbon compound. Further work, designed to test these possibilities, is in progress.

This work was done while the author was a Postdoctoral Fellow of the National Institutes of Health, U.S.P.H.S., and, subsequently, with the aid of a grant from the Nutrition Foundation, Inc. The continued guidance and assistance of Dr. Ernest Bueding and the interest of Drs. Warwick Sakami

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(1) W. L. Lipschitz and E. Bueding, *J. Biol. Chem.*, **129**, 333 (1939).

(2) C. F. Huebner, R. Lohmar, R. J. Dimler, S. Moore and K. P. Link, *ibid.*, **159**, 503 (1945).