which are more consistent than later ones by the same authors, show deviations from ours on $\Lambda-\sqrt{C}$ plots of 2.1% for potassium bromide, 3.2% for potassium iodide and 0.1% for sodium bromide. Values of $K$, as computed by Kraus and Bray,[20] do not deviate so greatly; this is probably due to compensation of errors arising from a faulty theoretical basis for the computation of $K$ by errors in $\Lambda_0$.

More recently, Monosson and Pleskov[4] measured the conductance of the series of alkali metal nitrates at −40°. While a direct comparison cannot be made with the present work, the difference between the conductance of the sodium and potassium ions may be compared. On the basis of Monosson and Pleskov's measurements and values of $\Lambda_0$ for potassium nitrate and sodium nitrate, as derived by extrapolation of $\Lambda-\sqrt{C}$ plots, the difference in the conductance of the two ions is 38. From our values for the limiting conductance of potassium bromide and sodium bromide, the difference is 32.47. If Monosson and Pleskov's values were corrected approximately 6% to a 6° higher temperature, their difference would be 40.

We have analyzed the data of Monosson and Pleskov by the method of Fuoss and, while the data are not sufficiently consistent for accurate evaluations of $\Lambda_0$, we have obtained the approximate values 331.1 and 296.7 for potassium nitrate and sodium nitrate, respectively. This yields 34.4 for the difference in the conductance of the potassium and sodium ions at −40° and 36.4 at −34°. At −34°, Monosson and Pleskov's value thus differs from ours by approximately 3.9 Λ-units.

## VI. Summary

1. Apparatus and techniques have been developed which permit of measuring the conductance of salts in liquid ammonia solution with a high degree of precision.
2. The conductance of sodium bromide and of potassium chloride, bromide and iodide have been measured to low concentrations at −34°.
3. The experimental values have been analyzed by the method of Fuoss and values of the limiting conductance and the dissociation constant have been derived.
4. In the dilute region over a considerable range of concentration, the values conform to the Fuoss relation with mean deviation varying between 0.011 and 0.034%.
5. An improved seal is described by means of which platinum electrodes may be introduced into apparatus constructed of Pyrex glass.
6. An effective manostat is described for controlling the temperature of a liquid ammonia bath.
7. The solubility of potassium chloride in liquid ammonia at −34° was determined to be 0.01651 as determined by the specific conductance of its solution.

PROVIDENCE, R. I. RECEIVED NOVEMBER 15, 1948

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

# Ionization of Organic Esters in Sulfuric Acid. II. Alkyl Oxygen Fission[1,2]

BY LESTER P. KUHN[3]

Previous workers have shown that organic acids and esters of the formula RCOOR′, where R is a substituted or unsubstituted alkyl or aryl group and R′ is H or a substituted or unsubstituted alkyl group, may ionize in concentrated sulfuric acid either according to equation I[4] or equation II[5,6]

$$\mathrm{RCOOR' + H_2SO_4 = RCOOR'H^+ + HSO_4} \qquad \mathrm{I}$$

$$\mathrm{RCOOR' + 3H_2SO_4 = RCO^+ + H_3O^+ + R'OSO_3H + 2HSO_4^-} \qquad \mathrm{II}$$

The former has been called normal and the latter complex ionization, or acylization. Evidence has been presented[7] which indicates that the acyl cation formed in II may combine with a bisulfate anion to yield an acyl sulfate, in which case II is replaced by equation III.

$$\mathrm{RCOOR' + 3H_2SO_4 = RCOOSO_3H + H_3O^+ + R'SO_3H + HSO_4^-} \qquad \mathrm{III}$$

In the present work we have studied the ionization of esters of isopropyl and *t*-butyl alcohol and we are led to the conclusion that these esters do not ionize according to either of these equations but in a manner which has hitherto not been observed in concentrated sulfuric acid.

Two methods were used to measure the extent of the ionization. The first was the determination of the van't Hoff "*i*" factor from freezing point depression measurements which tells the number of molecules and ions formed from each molecule of solute. Thus the "*i*" factors for equations I, II, and III when R′ is not H, are 2, 5 and 4, respec-

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[1] From the doctoral dissertation of Lester P. Kuhn, The Johns Hopkins University.

[2] Presented at the New York Meeting of the American Chemical Society, September, 1947.

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[4] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); **65**, 4 (1909).

[5] (a) Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933); (b) Treffers and Hammett, *ibid.*, **59**, 1708 (1937); (c) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 45–48, 54–56, 277–285.

[6] (a) Newman, THIS JOURNAL, **63**, 2431 (1941); (b) Newman, Kuivila and Garrett, *ibid.*, **67**, 1704 (1945).

[7] Kuhn and Corwin *ibid.*, **70**, 3370 (1948).

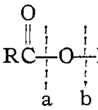
tively. The second method may be called the hydrolysis method. It depends upon the observation first made by Hammett and co-workers[5] that esters which exhibit complex ionization are converted into the corresponding free acids when their sulfuric acid solutions are poured into ice water whereas esters which undergo normal ionization are recovered unchanged. It is of course possible that esters which do not ionize according to the equations II or III may also be converted to their acids by this treatment. The results of these measurements are given in Table I. In the column containing the "*i*" factors two or three values are given for each substance. They were obtained by successive measurements of the freezing point because as will be pointed out shortly the ionization of certain compounds is not constant but increases with time. The last column contains the yield of acid obtained by dissolving the ester in approximately 100% sulfuric acid and, after several minutes, pouring the solution into ice water.

TABLE I

MEASUREMENT OF IONIZATION IN SULFURIC ACID

| Compound | "*i*" Factor | | | Yield of acid, % |
|---|---|---|---|---|
| Isopropyl alcohol | 3.11 | 3.78 | | |
| *t*-Butyl alcohol | 3.19 | 3.42 | 3.97 | |
| Acetic acid | 1.89 | 1.90 | | |
| Methyl acetate | 1.99 | 1.99 | | 0 |
| Ethyl acetate | 1.91 | 1.94 | | 0 |
| Isopropyl acetate | 3.11 | 3.52 | | 59 |
| *t*-Butyl acetate | 3.48 | 3.95 | | 73 |
| Benzoic acid | 1.97 | 1.96 | | |
| Ethyl benzoate | 1.95 | 1.95 | | 0 |
| Isopropyl benzoate | 3.14 | 3.40 | | 36 |
| *t*-Butyl benzoate | 3.44 | 3.55 | | 74 |
| Anisic acid | 3.38 | 3.38 | | |
| Methyl anisate | 3.25 | 3.62 | | 48 |
| Ethyl anisate | 2.88 | 3.02 | | 19 |
| Isopropyl anisate | 4.21 | 4.32 | | 76 |

Isopropyl and *t*-butyl alcohols differ from primary alcohols in that they have "*i*" values greater than 3. The sulfuric acid solutions of these alcohols turn yellow and the color darkens as the solutions stand. They smell strongly of sulfur dioxide indicating that oxidation reduction reactions are taking place, hence it is not surprising that the "*i*" values of these alcohols and their esters increase with each reading. Previous workers[8] have obtained "*i*" values of 3 for secondary alcohols and 2 for *t*-butyl alcohol which are obviously in disagreement with the results presented here. It is beyond the scope of this paper to discuss the mechanism of the ionization of these alcohols or to explain the reason for the discrepancy between our results and those of the previous workers. This problem has been studied by Newman and co-workers.[9] It is clear that because of the time dependence of the "*i*" values of these alcohols and their ester no precise quantitative meaning can be attached to our measurements. It is believed, however, that because the procedure used with each compound was the same the relative magnitudes of the values obtained are significant.

Table I clearly shows that the effect of R′ upon the magnitude of the "*i*" factor of the ester and upon the tendency of the ester to yield its free acid in the hydrolysis experiment is in the order H > methyl > ethyl < isopropyl < *t*-butyl. This irregular order strongly suggests that the last two members of the series ionize in a different manner from the first three, and is reminiscent of results obtained by previous workers in alcoholic and aqueous sytems. It is well-known[10] that in the acid catalyzed hydrolysis or alcoholysis of  $\underset{a}{\overset{\overset{O}{\|}}{RC}}\vdots O \underset{b}{\vdots} R'$ the cleavage may take place at either a or b, the former being called acyl oxygen fission and the latter alkyl oxygen fission. Cleavage "a" is favored by electron attraction by R′ and cleavage at "b" is favored by electron release from R′. In general the former predominates for esters of primary and secondary aliphatic alcohols and the latter predominates for esters of tertiary alcohols.[11] The esters of some secondary alcohols which contain electron releasing aromatic substituents have been shown to hydrolyze with cleavage at "b".[12]

We propose that in approximately 100% sulfuric acid esters of isopropyl and *t*-butyl alcohol ionize with alkyl oxygen fission in contrast to the complex ionization which involves acyl oxygen fission. The ionization of these esters may proceed according to the sequence

$$R\overset{O}{C}—O—R' + H_2SO_4 = RC(OH)—O—R'^{+} + HSO_4^{-}$$

$$RC(OH)—O—R'^{+} = RCOOH + R'^{+}$$

$$R'^{+} = ?$$

$$RCOOH + H_2SO_4 = RCOOHH^{+} + HSO_4^{-}$$

The fate of R′ was not investigated. Upon the suggestion of Dr. Newman the "*i*" values of *t*-butyl benzoate were measured as a function of time and extrapolated back to zero time. The value obtained was close to 3 which indicates that either or both of the following reactions take place immediately

$$R'^{+} + HSO_4^{-} = R'OSO_3H$$

$$R'^{+} + HSO_4^{-} = \text{olefin} + H_2SO_4$$

These products then react further to give the increasing "*i*" values.

It is very difficult to distinguish between alkyl oxygen fission and acyl oxygen fission in sulfuric acid by chemical means. In the anisic acid series the reaction products are the same for either mechanism. In the benzoic acid and acetic acid series acyl oxygen fission would yield the acyl sulfates whereas in alkyl oxygen fission they would

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[8] Oddo and Schandolar, *Gazz. chim. ital.*, **39**, 1 (1909).

[9] Newman, Craig and Garrett, THIS JOURNAL, **71**, 869 (1949).

[10] Day and Ingold, *Trans. Faraday Soc.*, **37**, 694 (1941).

[11] Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).

[12] Balfe, Downer, Evans, Kenyon, Poppett, Searle and Tarnoky, *J. Chem. Soc.*, 797 (1946).

yield benzoic and acetic acid, respectively. No difference in chemical behavior was found between sulfuric acid solutions of these acyl sulfates and the free acids. In one case evidence for alkyl oxygen fission was obtained. When *t*-butyl benzoate which is a liquid is added carefully to 100% sulfuric acid a white solid is formed which will quickly dissolve if the mixture is agitated. This solid was isolated and found to be benzoic acid indicating that this ester is first converted to benzoic acid rather than to the benzoyl ion which is in agreement with the proposed mechanism. More convincing evidence might be obtained by using esters with labelled oxygen and determining whether this oxygen is retained or lost by the benzoic acid which is recovered in the hydrolysis experiments.

## Experimental

**Preparation of Esters.**—The methyl and ethyl esters were obtained from commercial sources and were carefully fractionated before use. The isopropyl and *t*-butyl esters were prepared by the method used by Cohen and Schneider.[10] The only new ester is isopropyl anisate, b. p. 112–113 (2 mm.), $n^{25}\text{D}$ 1.5107, $d^{25}_4$ 1.060. *Anal.* Calcd.: C, 68.0; H, 7.22. Found: C, 67.62; H, 7.18.

The freezing point depression measurements were made according to the method of Newman, *et al.*,[6b] except that a Beckmann thermometer was used instead of a resistance thermometer. Table II contains the results of the freezing point depression measurements for those compounds which have not been previously measured. In the first column is the weight of the sample, the second column gives the molality of the solution, the third column shows the observed freezing points as measured with a Beckmann thermometer, the fourth column gives the freezing point depression and the last column gives the "*i*" value calculated from the equation

$$``i" = \Delta T/\Delta m \times 6.154\ (1 - 0.0047t)$$

where *t* is the difference between the freezing point of 100% sulfuric acid and the observed freezing point.

Table II

| Wt., g. | Δ*m* | F. p., °C. | | Δ*T* | "*i*" |
|---|---|---|---|---|---|
| | | Isorpropyl Alcohol | | | |
| 0.1184 | 0.0267 | 3.757 | 3.140 | 0.507 | 3.11 |
| | | 3.250 | | .617 | 3.78 |
| | | *t*-Butyl Alcohol | | | |
| .2305 | .0417 | 4.394 | 3.374 | .813 | 3.19 |
| | | 3.581 | | .874 | 3.42 |
| | | 3.520 | | 1.020 | 3.97 |
| | | Isopropyl Acetate | | | |
| .0988 | .0132 | 4.440 | 4.155 | 0.252 | 3.11 |
| | | 4.188 | | .285 | 3.52 |
| | | *t*-Butyl Acetate | | | |
| .1795 | .0211 | 4.530 | 4.015 | .452 | 3.48 |
| | | 4.078 | | .515 | 3.95 |
| | | Isopropyl Benzoate | | | |
| .1402 | .0122 | 3.734 | 3.480 | .235 | 3.14 |
| | | 3.499 | | .204 | 3.40 |
| | | *t*-Butyl Benzoate | | | |
| .1972 | .0150 | 3.786 | 3.460 | .316 | 3.44 |
| | | 3.470 | | .326 | 3.55 |
| | | Isopropyl Anisate | | | |
| .2299 | .0159 | 4.100 | 3.680 | .410 | 4.21 |
| | | 3.690 | | .420 | 4.32 |

The hydrolysis experiments were carried out as previously described.[7]

## Summary

In a series of compounds of the general formula RCOOR′, the tendency to cleave and the magnitude of the "*i*" values in sulfuric acid depends upon R′ in the manner H > methyl > ethyl < isopropyl < *t*-butyl. It is suggested that isopropyl and *t*-butyl esters ionize by a mechanism which differs from that of the other members of the series and that this mechanism which has not been observed before in sulfuric acid involves alkyl oxygen fission. The "*i*" values and the yield of ionization products for a number of esters in sulfuric acid are given.

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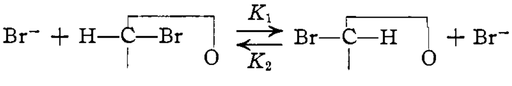
[Contribution from the Department of Chemistry of Stanford University]

# The Action of Some Lithium Salts on Acetobromoglucose

By William A. Bonner

Recently it was observed[1] that a solution of lithium bromide and acetobromoglucose in acetic acid underwent a marked mutarotation which was unaffected by the presence of diphenyl disulfide. This note describes several additional observations of this and related phenomena.

Since the heterogeneous reaction of silver chloride with polyacetyl-α-D-glycosyl halides is known[2] to yield the anomeric polyacetyl-β-D-glycosyl chlorides, it seemed reasonable that the following inversion might explain the present reaction



$$\text{Br}^- + \text{H—C—Br} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \text{Br—C—H} + \text{Br}^- \quad (1)$$

An attempt was made to establish this mechanism kinetically by observing the effect of lithium bromide concentration on the mutarotation.

The rate expression for (1) is given by

$$dx/dt = K_1a(c - x) - K_2ax \qquad (2)$$

where *c* is the initial concentration of α-acetobro-

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(1) Bonner, This Journal, **70**, 3496 (1948).

(2) Schlubach, *Ber.*, **59**, 840 (1926); Schlubach, Stadler and Wolf, *ibid.*, **61**, 287 (1928); Haworth, Hirst and Steacy, *J. Chem. Soc.*, 2864 (1931).