[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Cryoscopic Studies on Bases in Sulfuric Acid: The Ionization of Di-ortho Substituted Benzoic Acids[1]

BY HENRY P. TREFFERS AND LOUIS P. HAMMETT

Carbonium and oxonium ions play so important a part as unstable intermediates in current theories of reaction mechanism[2] that their study under conditions which permit their stable existence in large concentrations is especially pertinent. For this purpose solutions in sulfuric acid are most suitable. Once the effect of the large self-ionization of the solvent is appreciated, the medium turns out to be an almost ideal one for the investigation of ionic solutes, the complications due to interionic forces and ion association being of considerably less magnitude than they are even in water.[3] The ratio of the actual freezing point depression per mole to that produced by a non-electrolyte, the van't Hoff factor *i*, is therefore a relatively accurate measure of the number of ions produced by the solution of one molecule of the solute. The results of Hammett and Deyrup,[3a] who did take account of the self-ionization of the solvent, and the earlier results of Hantzsch[4] and of Oddo,[4] who did not, but whose results nevertheless justify broad differentiations with respect to type of ionization, lead to the following conclusions. Most carbonyl compounds act as simple monoacid bases with an *i* factor of 2 and a corresponding conductivity. Typical reactions are those of acetophenone

$$C_6H_5COCH_3 + H_2SO_4 \rightleftarrows C_6H_5COH^+CH_3 + HSO_4^- \quad (1)$$

and of benzoic acid

$$C_6H_5CO_2H + H_2SO_4 \rightleftarrows C_6H_5CO_2H_2^+ + HSO_4^- \quad (2)$$

A large proportion of the ketones, aldehydes, acids, and esters which have been investigated behave in this way.

A few oxygen compounds, all of which are of structural types which would be expected to possess very weak basicity, have *i*-factors of unity and do not increase the conductivity of the solvent. Notable among these are trichloroacetic acid, dimethyl sulfate, and such polynitro compounds as picric acid. A still smaller group show *i*-factors between 1 and 2 and are consequently incompletely ionized. Hantzsch[4] showed this to be true of dichloroacetic acid, and the present work adds nitrobenzene to this class.

The typical alcohol shows a factor of 3, and the aqueous solution obtained by dilution with water of the sulfuric acid solution has been shown by Oddo[4] to contain alkyl sulfuric acid. The reaction is evidently of the type

$$CH_3OH + 2H_2SO_4 \longrightarrow CH_3OSO_3H + OH_3^+ + HSO_4^- \quad (3)$$

It was shown however by Hantzsch[4] and confirmed by Hammett and Deyrup[3a] that triphenylcarbinol gives an *i*-factor of 4 and can be recovered unchanged on dilution with water. Furthermore the colorless carbinol gives rise to an intensely yellow solution in sulfuric acid in the same way that colorless triphenylmethyl chloride gives rise to a yellow solution when it dissolves and ionizes in liquid sulfur dioxide. Hantzsch's conclusion that the reaction is

$$(C_6H_5)_3COH + 2H_2SO_4 \rightleftarrows (C_6H_5)_3C^+ + OH_3^+ + 2HSO_4^- \quad (4)$$

is therefore well-nigh inescapable.

Some unpublished preliminary observations of Deyrup in this Laboratory led to the surprising conclusion that 2,4,6-trimethylbenzoic acid has a factor of 4. This acid therefore seems to behave more like triphenylcarbinol than it does like benzoic acid. It was the chief purpose of the present investigation to determine the conditions for the appearance of this phenomenon.

Experimental

Apparatus.—The earlier part of this work was carried out with the apparatus and technique of Hammett and Deyrup[3a] with satisfactory results. Later serious difficulty due to downward drifts in the freezing point of the acid appeared, apparently simultaneously with the use of a new lot of rubber stoppers. Consequently we designed the all glass magnetically stirred cell shown in Fig. 1. To avoid thermal leakage into the cell the solenoids which acted intermittently on the iron cored stirrer extensions A were immersed in water cooled oil-baths. The main joint between cap and body of the cell and the

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[1] Based upon the dissertation submitted by Henry P. Treffers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University. The material was presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] (a) Lowry, *Chemistry and Industry*, **43**, 1128 (1924); (b) Meerwein, *Ann.*, **453**, 16 (1927); (c) Whitmore, THIS JOURNAL, **55**, 4153 (1933); (d) Roberts and Hammett, *ibid.*, **59**, 1063 (1937).

[3] (a) Hammett and Deyrup, *ibid.*, **55**, 1900 (1933); (b) Hammett and Lowenheim, *ibid.*, **56**, 2620 (1934).

[4] Bibliography in Ref. 3a.

ground joint by which the specially constructed Beckmann thermometer fitted into the cap were lubricated with Lubriseal. A small plug fitting into an opening in the cell cap (not shown) through which portions of solute were introduced was not lubricated. The lower part of the cell fitted into a larger tube to provide an air gap, and this in turn into a Dewar flask which was maintained at a temperature 1 ± 0.3° below the freezing temperature of the system under investigation.

About 60 g. of sulfuric acid was used and this was always allowed to stand overnight in the closed cell to absorb any moisture present before making measurements. A supercooling of about 2.5° was used and seeding was accomplished by touching a piece of solid carbon dioxide to the outside of the apparatus just below the level of the acid. The thermometer was compared with one calibrated by the Bureau of Standards, and all readings were corrected for supercooling, for errors in the scale, exposed stem, and by the setting factor of the thermometer. Duplicate measurements (after application of the corrections) usually checked to about 0.002°. When all precautions were observed no difficulty was experienced with drifts in the freezing points, measurements taken as much as forty-eight hours apart agreeing to within 0.004°.

A medicine dropper with a long stem was used to weigh and introduce liquid solutes; control experiments showed that it would weigh and deliver samples with the required precision. In some cases solid solutes were introduced in the form of pellets made in a hand press, which were shown to withstand the necessary handling without loss. Many of the solutes, however, failed to form adherent pellets when thoroughly dry, and for these a sort of weight buret with a long stem and a wide opening was used successfully with the finely powdered material.

Materials.—All solutes were dried *in vacuo* over phosphorus pentoxide. Melting points are corrected. The ultimate standard for acidimetric titrations was Bureau of Standards potassium acid phthalate.

Sulfuric acid was prepared from C. P. grade 96% acid and fuming acid. Benzophenone was recrystallized three times from alcohol–water mixture, m. p. 48–49°. Benzoic acid was resublimed, m. p. 122°. *o*-Toluic acid was recrystallized from 15% alcohol, m. p. 102°, 99.9% by titration. 2,4-Dimethylbenzoic acid was prepared by acetylation of *m*-xylene and oxidation of the resulting ketone with hypobromite;[5] recrystallized from dilute alcohol, m. p. 120–121°, 99.2%. 2,4,5-Trimethylbenzoic acid was prepared by acetylation of pseudocumene,[6] followed by oxidation with hypobromite,[7] and was purified by recrystallization of the sodium salt from acetone, and also by dissolving in 96% sulfuric acid and precipitating with ice water after two hours; recrystallized from alcohol–water, m. p. 148–149°, 99.7%. 2,4,6-Trimethylbenzoic acid, prepared by the Grignard reaction from bromomesitylene,[8] was recrystallized repeatedly from carbon tetrachloride, m. p. 152–153°, 99.9%. 3,5-Dibromo-2,4,6-trimethylbenzoic acid, prepared by bromination of the trimethyl acid,[9] was recrystallized from alcohol–water, m. p. 211–212°, 99.2%. 3,4,5-Trimethoxybenzoic acid was prepared by methylation of recrystallized gallic acid[10] was recrystallized from 20% alcohol and finally from water, m. p. 167–168°, 99.6%. 2,6-Dibromotrimethoxybenzoic acid was prepared by bromination of the trimethoxy acid[11] and recrystallized from alcohol–water, m. p. 145–146°, 99.1%. 2,6-Dimethylbenzoic acid was prepared (a) by hydrolysis by way of the amide[12] of the nitrile, which was prepared by the Sandmeyer reaction,[13] and recrystallized from water, m. p. 116–117°, 99.8%; (b) by the Grignard reaction[14] from 1-iodo-2,6-dimethylbenzene, which was prepared from *vic-m*-xylidine, m. p. 116–117°, 100.0%. 2-Methyl-6-nitrobenzoic acid was prepared from *o*-toluidine through the acetylated amine, nitrated amine, and nitrile, each of which was purified before proceeding,[15] and purified by dissolving in sulfuric acid and precipitating with ice water and by crystallization from water, m. p. 153–154°, 100.4%. Trimethylacetic acid was purified by fractional freezing, m. p. 35.4°, 100.6%. 2,4,6-Trimethylacetophenone was prepared by acetylation of mesitylene and repeated fractional distillation *in vacuo*, b. p. 105.5–106.5° at 9 mm. Nitrobenzene was twice distilled.

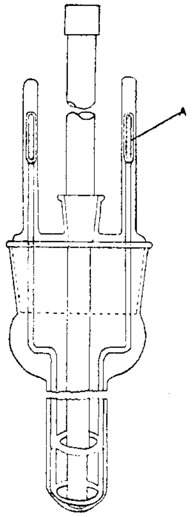

Fig. 1.

Results

In all cases the procedure was to add small increments of water to sulfuric acid containing a small concentration of sulfur trioxide until the freezing point was observed to have passed through the maximum (at 10.5°) and dropped to the point where the freezing point–water content function is linear (below 10.3°). From this point on it may be assumed safely that the self-ionization of the solvent has been repressed so completely by the base water that it does not complicate the behavior of the basic solute subsequently added. The freezing point thus attained by the addition of the water before the introduction of the solute under investigation is listed in Table I under the heading *t*. The items in the table which follow any entry in this column represent a series of experiments in which successive increments in molality of solute listed under the heading Δm are added to an acid of this initial

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[5] Perkin and Stone, *J. Chem. Soc.*, **127**, 2283 (1925).

[6] Noller and Adams, THIS JOURNAL, **46**, 1892 (1924).

[7] Mills, *J. Chem. Soc.*, **101**, 2192 (1914).

[8] Bamford and Simonson, *ibid.*, **97**, 1906 (1910).

[9] Shildneck and Adams, THIS JOURNAL, **53**, 351 (1931).

[10] "Organic Syntheses," John Wiley and Sons, Inc., New York, Coll. Vol. I, 1932, p. 522.

[11] Laire and Tiemann, *Ber.*, **26**, 2023 (1893).

[12] Berger and Olivier, *Rec. trav. chim.*, **46**, 600 (1927).

[13] "Organic Syntheses," Vol. IV, 1925, p. 69.

[14] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1935, p. 72.

[15] Gabriel and Thieme, *Ber.*, **52**, 1079 (1919).

TABLE I

CRYOSCOPIC BEHAVIOR OF BASES

	Δm	$\Delta\vartheta$	μ	
Benzophenone				
10.1	0.0113	0.131	0.06	1.89
	.0113	.137	.07	1.98
	.0243	.306	.10	2.06
	.0355	.472	.14	2.18
	.0319	.441	.17	2.27
Benzoic Acid				
10.2	0.0127	0.137	0.03	1.76
10.0	.0216	.229	.08	1.73
	.0379	.462	.12	1.99
	.0407	.490	.16	1.98
	.0339	.417	.19	2.02
	.0330	.416	.23	2.07
2-Methylbenzoic Acid				
10.0	0.0084	0.104	0.07	2.02
	.0118	.144	.08	1.99
	.0147	.182	.10	2.02
10.0	.0272	.325	.09	1.95
	.0277	.340	.12	2.00
2,4,5-Trimethylbenzoic Acid				
9.6	0.0365	0.446	0.20	2.00
	.0326	.400	.24	2.01
	.0207	.255	.27	2.02
	.0375	.503	.31	2.20
2,4,6-Trimethylbenzoic Acid				
10.1	0.0145	0.336	0.07	3.78
	.0347	.799	.13	3.74
10.3	.0109	.217	.04	3.25
	.0116	.266	.06	3.75
	.0104	.251	.08	3.95
	.00647	.158	.09	3.98
10.2	.0122	.265	.05	3.54
	.0116	.270	.07	3.80
	.0114	.268	.09	3.85
	.0124	.291	.12	3.84
	.0114	.274	.14	3.94
7.2	.0342	.777	.39	3.77
2,6-Dimethylbenzoic Acid				
10.1	0.0158	0.343	0.07	3.53
	.0238	.508	.11	3.49
10.1	.0170	.368	.07	3.53
	.0174	.374	.10	3.51
	.0306	.617	.16	3.31
9.5	.0240	.496	.09	3.38
	.0399	.830	.16	3.41
7.5	.0229	.398	.33	2.87
3,5-Dibromo-2,4,6-trimethylbenzoic Acid				
9.7	0.00516	0.083	0.08	2.62
	.0249	.395	.11	2.59
9.9	.0182	.293	.08	2.63
	.0241	.344	.11	2.33
	.0305	.373	.14	2.00
8.5	.0226	.292	.22	2.12
	.0317	.381	.25	1.98
	.0243	.278	.27	1.89
	.0173	.202	.29	1.93
3,4,5-Trimethoxybenzoic Acid				
9.9	0.0125	0.157	0.07	2.05
	.0307	.386	.10	2.05
2,6-Dibromo-3,4,5-trimethoxybenzoic Acid				
9.9	0.0304	0.336	0.09	1.80
	.0492	.532	.14	1.76
2-Methyl-6-nitrobenzoic Acid				
10.0	0.103	1.191	0.15	1.89
	.0263	0.299	.18	1.87
	.0379	.434	.21	1.88
Trimethylacetic Acid				
9.9	0.152	1.843	0.20	1.99
Nitrobenzene				
10.1	0.0109	0.084	0.04	1.25
	.0161	.114	.05	1.15
	.0168	.124	.05	1.20
10.1	.0104	.085	.04	1.33
	.0183	.133	.05	1.18
2,4-Dimethylbenzoic Acid				
10.0	0.0309	0.375	0.08	1.98
2,4,6-Trimethylacetophenone				
10.2	0.0482	0.604	0.11	2.04

freezing point. Under $\Delta\vartheta$ is listed the further freezing point depression produced by the addition of each increment, corrected as previously noted. The fourth column under the heading μ reports the approximate ionic strength of the solution.

The van't Hoff factor i listed in the last column was calculated by the equation

$$\Delta\vartheta/\Delta m = 6.154\, i\,(1 - 0.0047\,\vartheta) \qquad (5)$$

in which $\Delta\vartheta$ and Δm are increments in freezing point depression and molality and ϑ is the total depression calculated from the freezing point of the pure solvent at a point midway between the initial and final values for the increment in question. This is derived from the exact expression

$$\frac{dT}{dm} = \frac{RT^2}{\Delta H}\,\frac{\partial \ln a_1}{dm} \qquad (6)$$

by the use of the ideal solution law $\partial \ln a_1/\partial \ln N_1 = 1$, of the equation of Brönsted[16] for the heat of fusion of sulfuric acid, $\Delta H = 2485 + 6.1t$, and of the equation

$$N_1 = \frac{10.20 - m_H - m}{10.20 + m_H + m} \qquad (7)$$

in which m_H is the molality of water. The latter equation is correct if all the ionization processes are of the type of equations (1), (2), and (4).

It may be estimated that the uncertainty in ϑ and hence in i due to error in reading of the thermometer and to the supercooling correction varies

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(16) Brönsted, *Z. physik. Chem.*, **68**, 693 (1909).

from 1 to 7%, being smaller the larger the increment Δm and the smaller the total solute concentration including that of the water.

Two solutes 2,4-dimethylbenzoic acid and 2,4,6-trimethylacetophenone react quite rapidly with sulfuric acid. For these substances therefore an extrapolation of the freezing point–time relationship, the data for which are given in Table II, was used to obtain an initial value of i. With all the other substances studied no drift of freezing point with time was observed over periods of several hours and the original solute could be recovered unchanged and in essentially quantitative yields at the end of the freezing point measurements by dilution with water.

TABLE II

DATA FOR EXTRAPOLATION

2,4-Dimethylbenzoic acid Initial f. p. 0.520		2,4,6-Trimethylacetophenone Initial f. p. 0.661	
Time, min.	F. p., °C.	Time, min.	F. p., °C.
0	(0.905)	0	(1.265)
15	.917	30	1.310
25	.921	45	1.328
35	.928	65	1.356
40	.936	90	1.398
110	.980	315	1.589
205	1.022	330	1.692
325	1.070		

Discussion

One of the solutes studied, nitrobenzene, adds another example to the rather small list of bases which are measurably but incompletely ionized in sulfuric acid. This result is of importance in connection with the interpretation of the solubility of organic substances in sulfuric acid–water mixtures.[17]

Benzophenone is an example of a fundamentally monoacid base which is basic enough to be ionized completely in pure sulfuric acid, its ionization being no doubt essentially complete in 80% sulfuric acid–water solution.[18] Nevertheless the values of i show a trend, varying from a value 5% below the ideal figure 2 at low concentrations to one 15% above that figure at high concentrations. The most probable causes for such deviations from the behavior predicted by equation (5) are withdrawal of solvent by solvation of the ions, variation of the partial molal heat content of the solvent with the nature and concentration of the solute, and deviations from ideal solution behavior of the solute ions. The latter factor is probably unimportant, because the direction of the drift is opposite to that predicted to result from interionic forces. Benzoic acid shows the same effect although to a lesser degree and water does not show it at all. Consequently it depends upon the nature as well as the concentration of the solute.

2,4,6-Trimethylbenzoic acid shows a van't Hoff factor in the near neighborhood of 4, and the closely related 2,6-dimethylbenzoic and 3,5-dibromo-2,4,6-trimethylbenzoic acids have values intermediate between 2 and 4. The only reasonable interpretation involves a reaction similar to that proposed by Hantzsch for the triphenylcarbinol case.

$$\mathrm{RCOOH} + 2\mathrm{H_2SO_4} \rightleftharpoons \mathrm{RCO^+} + \mathrm{OH_3^+} + 2\mathrm{HSO_4^-} \qquad (8)$$

Ionization as a diacid base would give a factor of three, ionization as a triacid base is altogether improbable, and it seems quite impossible that any sulfonation or oxidation process should be so rapid and reversible as are the reactions in question.

This interpretation is strongly supported by the fact that the methyl ester of 2,4,6-trimethylbenzoic acid is hydrolyzed completely by dissolving in sulfuric acid and immediately pouring into ice water.[19] Under the same conditions methyl benzoate is not measurably affected. This is a most striking phenomenon because the ester which is thus instantaneously ruptured by concentrated sulfuric acid is typical of those which are especially resistant to the action of dilute acids and alkalies. It is in fact the classical example of a sterically hindered ester. Obviously, however, the linkage of methoxyl group to acyl group in this ester is especially sensitive to the concentrated acid, just as the linkage of hydroxyl to acyl is especially sensitive in the corresponding acid.

The stable existence of acyl ions of the type of the 2,4,6-trimethylbenzoyl ion, $\mathrm{(CH_3)_3C_6H_2CO^+}$, is a matter of considerable interest in connection with problems of reaction kinetics and mechanism. Such ions are possible intermediates in many reactions of esters, acids, acid chlorides, and similar compounds. And even where their independent existence as kinetic intermediates may be excluded, mechanisms in which they play the B part in the typical London–Polanyi substitution process $\mathrm{A} + \mathrm{BC} \longrightarrow \mathrm{AB} + \mathrm{C}$, as in

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[17] Hammett and Chapman, THIS JOURNAL, **56**, 1282 (1934).

[18] Hammett and Deyrup, *ibid.*, **54**, 2721 (1932).

[19] This observation was first made by Dr. Deyrup in this Laboratory.

$$RCOOCH_3 + OH^- \longrightarrow RCOOH + OCH_3^- \quad (9)$$

must be considered.

In two cases, that of 2,6-dimethylbenzoic and that of 3,5-dibromo-2,4,6-trimethylbenzoic acid, the reaction of equation (8) is clearly incomplete. In both cases increase in solute concentration or in water concentration (shown by low value of t in column 1 of Table I) leads to smaller values of i. In the latter case this apparently can be reduced to the neighborhood of 2 but not lower. This suggests strongly that the process of equation (8) occurs not in the single step written but in two non-overlapping steps

$$RCOOH + H_2SO_4 \rightleftharpoons RCO_2H_2^+ + HSO_4^- \quad (10)$$

$$RCO_2H_2^+ + H_2SO_4 \rightleftharpoons RCO^+ + OH_3^+ + HSO_4^- \quad (11)$$

reaction (10) being just as complete with those acids which are capable of further reaction to form the acyl ion as it is with benzoic acid and other acids which show no evidence of the latter process.

The present data clarify many of the structural factors which affect the formation of the acyl ion. The process is favored by substitution of methyl for hydrogen, whereas electron attracting substituents like Br and NO_2 are unfavorable (note especially the effect of bromine substitution on trimethylbenzoic acid). The effect of a methyl group is in the same direction in the ortho and para positions, unlike its effect on the acidic ionization of benzoic acid, and it is so much stronger in the ortho position that the formation of acyl ions has been observed only with derivatives of 2,6-dimethylbenzoic acid. Neither two nor three methyl groups suffice when only one is in the ortho position, but a third methyl in the para position does increase the extent of the effect observed with the 2,6-dimethyl compound. A di-ortho substitution is insufficient when one or both of the groups are of the electron attracting type; the process does not therefore appear to be related to the kinetic steric hindrance which di-ortho substituted compounds in general exhibit. Finally the aliphatic trimethylacetic acid, which possesses many similarities to the di-ortho substituted benzoic acid derivatives, fails to show the effect.

Summary

Further cryoscopic studies of organic oxygen compounds in sulfuric acid have been carried out with an improved apparatus. Nitrobenzene has been found to be incompletely ionized. Completely ionized monoacid bases have been shown to exhibit minor deviations from ideal behavior. An entirely new type of reaction with strong sulfuric acid has been found to occur with 2,6-dimethylbenzoic acid and two of its derivatives. This involves the formation of acyl ions of the type RCO^+ in addition to the normal ionization as a base forming ions of the type $RCO_2H_2^+$. The structural factors which determine the appearance of this ionization process have been clarified. The methyl ester of an acid which forms acyl ions in sulfuric acid has been found to be hydrolyzed instantaneously in sulfuric acid.

NEW YORK, N. Y. RECEIVED JULY 12, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Partial Pressures of Hydrogen Chloride from Benzene Solutions at 30°

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The distribution of hydrogen chloride between benzene and water at 20° has been determined by Knight and Hinshelwood.[1] Wynne-Jones[2] has pointed out that the peculiar shape of the curve expressing their results is not to be expected from theoretical considerations and that the concentrations of the hydrogen chloride in the benzene layer are not even approximately proportional to the partial pressures of the aqueous solutions.

Wynne-Jones carried out a few experiments with benzene at 25° over a small concentration range and found that the behavior of hydrogen chloride in the benzene was quite normal. He also determined the distribution of hydrogen chloride between water and nitrobenzene at 25° and found hydrogen chloride to be a normal solute in the nitrobenzene. He concluded that Knight and Hinshelwood's results are probably subject to some experimental error.

The purpose of the present investigation was to study the behavior of hydrogen chloride in benzene solutions by determining its partial pressure

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[1] Knight and Hinshelwood, *J. Chem. Soc.*, 470 (1927).

[2] Wynne-Jones, *ibid.*, 1064 (1930).