than the A surface, and they may very possibly make the calculated rate on the B surface equal to the observed rate.

Summary

These calculations indicate that the high temperature thermal decomposition of ammonia on "aged" tungsten occurs uniformly on its dodecahedral faces and at such a rate that almost every vibration of underlying tungsten atoms with the energy of activation leads to reaction. The obvious factors which have been neglected in the calculation affect it in a way which supports this conclusion.

Cleveland, Ohio Received February 26, 1934

[Contribution from the Department of Chemistry, Columbia University]

The Solubilities of Some Organic Oxygen Compounds in Sulfuric Acid–Water Mixtures

By Louis P. Hammett and Ray P. Chapman

The fact that most organic oxygen compounds are very soluble in concentrated sulfuric acid, and that some, notably ethyl ether and cellulose, possess a largely increased solubility in very concentrated aqueous hydrochloric acid, is reasonably familiar. The phenomenon has indeed received technical application in such processes as the purification of anthraquinone,[1] in the preparation of parchment paper,[2] and probably in the zinc chloride process for vulcanized fiber.[3] The eminently reasonable hypothesis that the increased solubility results from salt formation between the basic oxygen compound and the strong acid has been suggested for particular groups of compounds by a number of investigators.[4] This hypothesis has especial interest because of the possible application of the solubility method to the determination of the strength of very weak bases, and is open to quantitative investigation now that there is available a series of indicators by means of which a measure of acidity may be obtained over the whole range of sulfuric acid–water mixtures.[4e,5] We have therefore undertaken the determination of the solubility of some typical oxygen compounds in sulfuric acid–water mixtures of a much wider range of compositions than was accessible to the analytical methods used by previous workers.

Methods and Materials

All measurements were at 25 ± 0.02°.

Sulfuric acid–water mixtures of the desired concentrations were standardized by titration, using Bureau of Standards benzoic acid or potassium acid phthalate as ultimate standards. These solutions together with an excess of the organic solute were rotated in a water thermostat. The containers were bottles with accurately ground stoppers, which were protected by a paraffin seal and by rubber tubing. It was found in a number of cases that no further increase in solubility took place after twenty hours, and this period of rotation was adopted as a minimum. In the case of the solid solutes, the saturated solution was filtered without removal from the thermostat through an immersion filter of the fritted glass type. With nitrobenzene, the saturated aqueous layer was separated carefully.

In the experiments on benzoic acid and on phenylacetic acid the concentration of the saturated solutions was determined by the continuous extraction method previously described by us.[6] Experiments on known amounts of phenylacetic acid showed the method to have the same precision (about 1%) with this acid as with benzoic. The concentration of the nitro compounds was determined by reduction with titanous sulfate using essentially the method of Callan and Henderson,[7] which we have found to be capable of a precision of about 1% by experiments on known amounts of the three compounds in question. The concentration of benzoyldiphenyl was determined by colorimetric comparison of the saturated solution with a solution of known concentration of the compound in sulfuric acid of the same concentration as was used in the preparation of the saturated solution.

Experiments with indicators showed that not even at the highest acid concentrations studied was the solubility of benzoic acid sufficiently large to have a measurable effect upon the acidity function, H_0,[5] of the sulfuric acid–water solution.

In the analysis of the wet solid phase, the organic acid was determined by the same method as was used with the solutions, and the sulfuric acid was determined either by difference from a determination of total acidity or by titration of the residual acid in the extractor after the removal of the organic acid.

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(1) Ullmann, "Enz. d. techn. Chem.," 2d ed., Vol. I, p. 200.

(2) Ullmann, *ibid.*, Vol. VIII, p. 290.

(3) Frey and Elöd, *Ber.*, **64B**, 2556 (1931).

(4) (a) Jüttner, *Z. physik. Chem.*, **38**, 56 (1901); (b) Sackur, *Ber.*, 35, 1242 (1902); (c) Knox and Richards, *J. Chem. Soc.*, **115**, 508, 850 (1919); (d) Kendall and Andrews, This Journal, **43**, 1545 (1921); (e) Hammett, *Chem. Rev.*, **13**, 61 (1933).

(5) (a) Hammett and Deyrup, This Journal, **54**, 2721 (1932); (b) Hammett and Paul, *ibid.*, **56**, 827 (1934).

(6) Chapman and Hammett, *Ind. Eng. Chem., Anal. Ed.*, **5**, 346 (1933).

(7) Callan and Henderson, *J. Soc. Chem. Ind.*, **41**, 157T (1922).

The sulfuric acid was a reagent grade; benzoic acid was resublimed; nitrobenzene was redistilled shortly before use; the other acids were purified by several recrystallizations. Benzoic and phenylacetic acids had the theoretical acidimetric titer, the nitro compounds the theoretical titanometric titer within the precision of the respective determinations. Benzoyldiphenyl was prepared and purified as previously described.[5] The corrected melting points were as follows: *o*-nitrobenzoic acid, 146–147°, *p*-nitrobenzoic acid, 240–241°, phenylacetic acid, 78–79°.

Results and Discussion

The solubilities in moles of solute per 1000 g. of sulfuric acid–water mixture, together with the percentage composition of the solvent mixture, are listed in Table I and plotted in Fig. 1. Each point is the average of at least two concordant determinations.

TABLE I

SOLUBILITIES IN SULFURIC ACID–WATER MIXTURES

% H_2SO_4	*m*	% H_2SO_4	*m*	% H_2SO_4	*m*
		Benzoic Acid			
0.0	0.0276	46.74	0.00517	70.37	0.01052
11.28	.0161	48.72	.00499	72.46	.01371
19.79	.01034	50.55	.00500	74.59	.01804
28.51	.00708	52.76	.00501	79.28	.0593
35.82	.00581	58.15	.00541	81.75	.0937
39.24	.00530	60.83	.00610	83.61	.1020
41.90	.00505	64.30	.00681	85.13	.1254
44.54	.00496	67.38	.00848	85.91	.1356
		Phenylacetic Acid			
0.0	0.1267	50.55	0.0258	70.27	0.0530
11.28	.0801	52.01	.0266	72.46	.0630
28.51	.0330	52.76	.0275	74.54	.0904
37.61	.0283	58.67	.0287	77.40	.1947
46.74	.0260	64.30	.0343		
48.89	.0259	68.03	.0431		
		o-Nitrobenzoic Acid			
0.0	0.0435	52.01	0.0080	79.28	0.0310
11.28	.0192	56.35	.0080	81.75	.0469
19.79	.0139	60.83	.0088	83.61	.0737
31.23	.0095	65.07	.0095	85.13	.1017
41.90	.0080	72.46	.0141		
46.74	.0076	76.75	.0207		
		p-Nitrobenzoic Acid			
0.0	0.00166	77.40	0.00316	83.61	0.01197
31.23	.00068	79.28	.00452	85.13	.01908
52.01	.00079	80.41	.00540	90.05	.0983
72.46	.00179	81.75	.00708		
		Nitrobenzene			
0.0	0.0158	48.89	0.0155	70.37	0.0478
19.79	.0097	52.76	.0193	74.54	.0729
35.82	.0098	58.15	.0255	79.28	.1482
44.54	.0134	64.30	.0340		
		p-Benzoyldiphenyl			
70.34	0.000017	77.40	0.00076	79.77	0.00802
75.55	.000214	78.70	.00168		

TABLE II

COMPOSITION OF WET SOLID PHASE

Soln. % H_2SO_4	Solid phase % H_2SO_4	% org. acid	Soln. % H_2SO_4	Solid phase % H_2SO_4	% org. acid
		Benzoic Acid			
74.59	64.84	12.9	83.41	68.21	19.8
	60.17	18.6			
			85.13	67.05	22.4
79.28	66.45	16.3		73.79	14.7
	64.93	17.6			
		p-Nitrobenzoic Acid			
77.40	53.21	31.37	85.13	56.04	34.29
81.75	58.00	29.67		55.74	34.63

The general features of the curves are much the same (except possibly in the case of benzoyldiphenyl, whose solubility is too small for measurement at acid concentration below 70%). As the acid concentration increases, there is an initial decrease in solubility which is obviously of the nature of a salting-out effect.[8] This is followed by an approximately level portion, after which

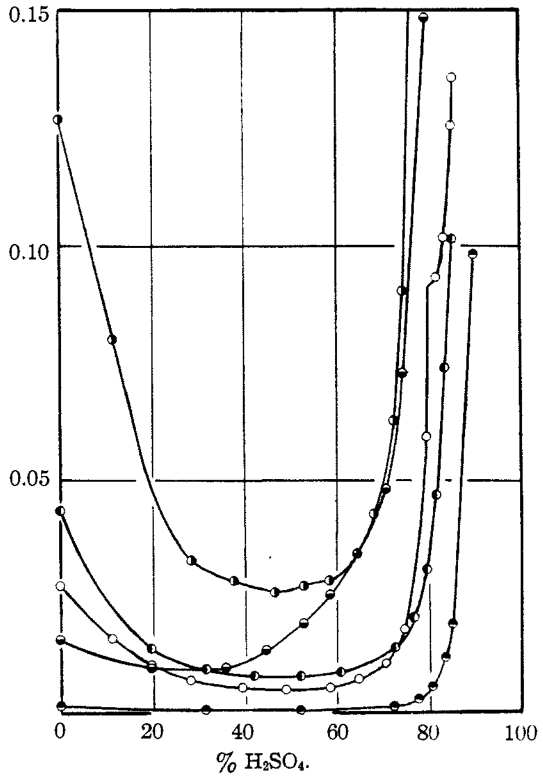

Fig. 1.—○, benzoic acid; ◒, nitrobenzene; ◑, phenylacetic acid; ◐, *o*–nitrobenzoic acid; ◓, *p*–nitrobenzoic acid.

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[8] *Cf.* Kendall, Ref. 4d.

the solubility rises very sharply.[9] In the case of benzoic acid, the shape of the curve strongly suggests a change of phase, a suspicion which is verified by the data on the composition of the wet solid phase given in Table II. The application to these data of the usual triangular plot does not lead to entirely satisfactory results because of the small solubility of the solute, and of the viscous and hygroscopic nature of the solutions. Nevertheless, it is beyond question that the solid phase is benzoic acid up to 79.28% sulfuric acid and that there is a transition between this point and 83.41% sulfuric acid to a new phase containing both benzoic and sulfuric acids. This may be the 1:1 compound observed in the binary system,[10] although the not very concordant data suggest a higher proportion of sulfuric acid. In the case of *p*-nitrobenzoic acid the data on the wet solid phase clearly demonstrate that the solid phase is the pure component over the entire range. With the other solutes, there is no evidence from discontinuities of a change of phase in the range studied. At higher sulfuric acid concentrations, the stable phase in the case of benzoyldiphenyl is an intensely yellow liquid, the transition occurring at about 80% sulfuric acid.

The cryoscopic work of Hantzsch,[11] of Oddo and Casalino[12] and of Hammett and Deyrup[13] has shown that benzoic, *o*-nitrobenzoic and *p*-nitrobenzoic acids and benzoyldiphenyl behave as strong bases in sulfuric acid which is anhydrous or nearly so, and it is extremely probable that the same is true of phenylacetic acid. Further cryoscopic work now in progress in this Laboratory has shown that nitrobenzene on the other hand is a weak electrolyte in sulfuric acid. Since the solubility increase in this case appears in solutions which indicator measurements show to have a tendency for salt formation with a neutral base from 10^4 to 10^8 times smaller than that of pure sulfuric acid,[5] it is clear that it bears no relation whatsoever to salt formation between nitrobenzene and sulfuric acid, although it may depend upon the formation of a non-ionized compound of the two.[14] Similarly the sharp solubility increase which Hough, Savage and van Marle[15] found to occur with dinitrobenzene and trinitrotoluene at high sulfuric acid concentrations may be compared with Hantzsch's[11] demonstration that these nitro compounds possess no measurable ionization in sulfuric acid.

Ionization or salt formation due to basic properties in the solute is therefore not the sole cause of the solubility increase; that it may be an important factor is suggested by the fact that the solubility curve breaks more rapidly and rises more sharply in the case of the organic acids than in the case of nitrobenzene and by the fact that the solubility of benzoyldiphenyl increases very rapidly in the range of acid composition in which it has been shown to ionize by colorimetric methods.

The solubility of a neutral base, B, which can react with acids to form the ion BH^+, but which is also affected by the same sort of influences which cause the large increase in solubility in the case of nitrobenzene, may conveniently be represented by the exact equation.

$$S = \frac{a_S}{f_B}\left\{1 + \frac{a_{H^+}f_B}{K'f_{BH^+}}\right\}$$

in which the first term on the right gives the concentration of the neutral base, B, in the saturated solution, the second that of the ion BH^+. a_S is the activity of the solid base and is equal therefore to the solubility in some reference solvent in which ionization is negligible and in which f_B is by definition unity, the f's are activity coefficients, a_{H^+} is the activity of hydrogen ion, and $K' = a_{H^+}a_B/a_{BH^+}$ is the acidity constant of the ion BH^+. For the acid–water mixtures in question it has been shown by indicator measurements[5] that the ratio f_B/f_{BH^+} is independent of the particular organic base used. The quantity $a_{H^+}f_B/f_{BH^+}$ and its negative logarithm, the acidity function, H_0, are therefore functions only of the composition of the acid–water mixture, and are the most satisfactory measures of the acidity of the system both for the equilibrium and for the rates of homogeneous reactions in which uncharged organic bases are concerned.[5,16] We are led therefore to the equation

$$S = \frac{a_S}{f_B}\left\{1 + \frac{\log^{-1}(-H_0)}{K'}\right\}$$

in which H_0 is known from the indicator measurements.[5]

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(9) Such a sharp rise was found by Deyrup in unpublished experiments in this Laboratory to be a very general property of organic oxygen compounds. It is well exhibited in the experiments of Reburn and Shearer, THIS JOURNAL, **55**, 1774 (1933), on the solubility of higher aliphatic alcohols in aqueous halogen acids.

(10) Kendall and Carpenter, THIS JOURNAL, **36**, 2498 (1914).

(11) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); **65**, 41 (1908).

(12) Oddo and Casalino, *Gazz. chim. ital.*, **47**, II, 200 (1917).

(13) Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(14) Cherbuliez, *Helv. Chim. Acta*, **6**, 281 (1923); Masson, *J. Chem. Soc.*, 3200 (1931).

(15) Hough, Savage and van Marle, *Chem. Met. Eng.*, **23**, 666 (1920).

(16) Hammett and Paul, THIS JOURNAL, **56**, 830 (1934).

If f_B were approximately constant over a range of acid concentrations a plot of $S/\log^{-1}(-H_0)$ against $1/\log^{-1}(-H_0)$ would be a straight line whose x-intercept equals $-1/K'$. In the case of the four acids studied, these plots do have this property and lead to the following values of the constant pK': benzoic −5.9, phenylacetic −5.8, *o*-nitrobenzoic −7.0, *p*-nitrobenzoic −6.9. Because of the behavior of nitrobenzene, and because the solubility increase with benzoyldiphenyl completely disagrees with this theory, it is quite improbable that the assumption of constant f_B is justified; and these figures are therefore devoid of any absolute significance. It is however possible that they do give a measure of some value of the base strengths relative to each other of these acids. In order for this to be true, it is only necessary that the variation with changing medium of the f_B coefficients should be the same for this group of closely related substances. Such a hypothesis is supported by the fact that the base strengths thus obtained are in the inverse order of the strengths of the acidic ionizations of the same substances, but its verification must await the determination by an independent method of the base strengths in question.

We wish to express our appreciation for the very helpful assistance in this work of Mr. Henry P. Treffers, who purified the organic compounds and made the solubility measurements on phenylacetic acid, and of Mr. Harry Parver.

Summary

The solubilities in a wide range of sulfuric acid–water mixtures of benzoic acid, phenylacetic acid, *o*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-benzoyldiphenyl and nitrobenzene have been determined.

It has been shown that the sharp increase in solubility at high sulfuric acid concentrations may possibly be related in some cases to ionization or salt-formation arising from basic properties in the organic oxygen compound, but that this is not the sole cause of such solubility increases.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Conductivities of Dilute Sulfuric Acid Solutions in Anhydrous Acetic Acid

BY BRUCE V. WEIDNER, A. WITT HUTCHISON AND G. C. CHANDLEE

The conductivities of dilute sulfuric acid solutions in anhydrous acetic acid have been reported recently by several investigators.[1] Some variation in the specific conductances of the solvent used as well as in the molar conductances of the solutions is found in these results. This variation is presumably due to differences in the very small amount of water which may have been present.

In part of this work we have studied the conductances of solutions in acetic acid having essentially the same specific conductance for the solvent as that used by Hall and Voge[1b] and the results are in excellent agreement. In addition we have prepared acid with a somewhat lower specific conductance and data have been obtained for the conductance of the more dilute solutions prepared with it.

Experimental

The bridge assembly and thermostat described by Lasselle and Aston[2] was used in this work. The cell constants of the two type A Washburn cells were determined using Parker[3] solutions prepared from equilibrium water and purified potassium chloride.

Acetic acid was prepared by the method of Hutchison and Chandlee.[4] Acid with a specific conductivity of 0.56 × 10^{-8} mhos at 25° was obtained in quantity. The melting point determined with a thermometer calibrated against one certified by the Bureau of Standards was 16.60 ± 0.02°. No difference could be detected between the melting point of this acid and other samples with specific conductivities as great as 1.0 × 10^{-8} mhos. The more concentrated solutions were prepared by the use of weight pipets and the others by dilution. The volume concentrations were calculated using the densities of the solutions.[4]

Discussion of Results

In Table I are listed the data obtained for the conductivities of the sulfuric acid solutions.

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[1] (a) Hantzsch and Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932); (b) Hall and Voge, THIS JOURNAL, **55**, 239 (1933); (c) Eichelberger and La Mer, *ibid.*, **55**, 3635 (1933).

[2] Lasselle and Aston, *ibid.*, **55**, 3067 (1933).

[3] Parker and Parker, *ibid.*, **46**, 332 (1924).

[4] Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931).