[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Relation between the Rates of Some Acid Catalyzed Reactions and the Acidity Function, H_0

BY LOUIS P. HAMMETT AND MARTIN A. PAUL

In the attempt to understand the behavior of such typical acid-catalyzed reactions as sucrose inversion or ester hydrolysis in solutions of acids or other electrolytes which are not extremely dilute, attempts have been made to correlate reaction rates with total acid concentration, with hydrogen-ion concentration calculated from the conductivity ratio, with electrometric *P*H, and with mean ionic activity. Apparently the one method of estimating the acidity of a solution which has not previously been applied to this problem is the only one with which a successful correlation may indeed be obtained, the measurement of acidity by means of suitable indicators. Thus the ratio of the values in 4 molar and in 0.1 molar hydrochloric acid solution of the rate of sucrose hydrolysis is 228,[1] of the molarity is 40, of the hydrogen-ion concentration calculated from the conductivity ratio is 18.7, of the mean ionic activity is 102.2,[2] but the ratio of the values of $a_{H^+}f_B/f_{BH^+}$,[3] the measure of hydrogen-ion concentration or activity given by basic indicators is 204.[4]

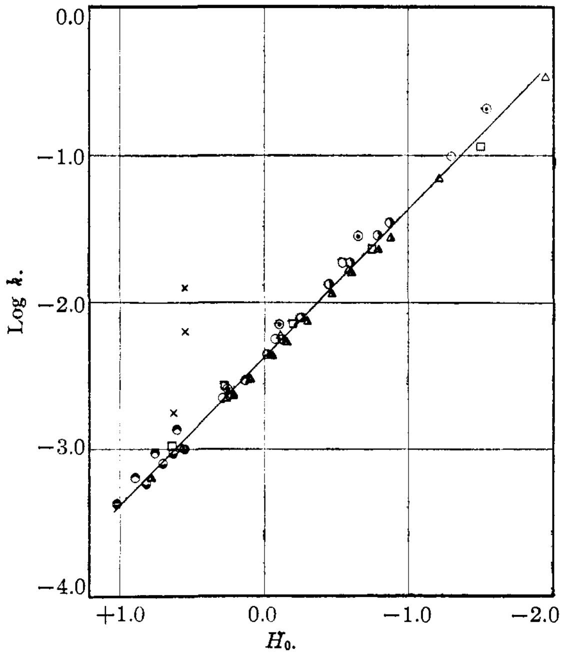

Fig. 1.—Relation between H_0 and velocity constant for hydrolysis of sucrose: ⊙, $HClO_4$ 0.5–4 *M*; □, H_2SO_4 0.25–3.77 *M*; ○, HCl 0.5–4 *M*: △, HNO_3 0.5–6.95 *M*; ×, CCl_3COOH 0.5–4 *M*, all from data of Hantzsch and Weissberger. ◑, HCl 0.28–3.08 *M*; ▲, HNO_3 0.19–3.08 *M*, data of Armstrong and Wheeler and of Worley. ◓, 0.1 *N* HCl + KCl 0–3 *M*; ◒, 0.1 *N* HCl + $BaCl_2$ 0–1.3 *M*. data of Kautz and Robinson.

In Fig. 1 the logarithm of the rate of inversion of sucrose is plotted against the acidity function H_0, which is the negative logarithm of the previously mentioned "acidity in terms of a basic indicator," $a_{H^+}f_B/f_{BH^+}$.[3] This plot includes the rate measurements of four different workers[5] on five different acids at concentrations extending from 0.1 molar to nearly 7 molar, in some cases in the presence of added neutral salt, and it represents a variation in hydrolysis rate of nearly a thousand to one. Figure 2 contains a similar plot of the ethyl acetate hydrolysis data of Harned and Pfanstiehl[6] and of the cyanamide hydrolysis data of Grube and co-workers.[7] The values of H_0 are taken from the work of Hammett and Deyrup[3] and from the article by the present authors immediately preceding this.

The close agreement of the experimental points with the straight line of unit slope amounts to a direct proportionality between reaction rate and the measure of hydrogen-ion concentration or activity given by the indicator method of measurement. It seems clear that this can only result from the fact that both acid catalysis and indicator reaction depend upon the addition of hydrogen ion to a neutral organic molecule of basic properties, the substrate in the one case, the indicator base in the other; and that the change in

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[1] Hantzsch and Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).

[2] These values were obtained from the "International Critical Tables."

[3] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[4] We have omitted any value based upon an electrometric *P*H measurement, because it would be difficult to attach any meaning to such a measurement in a 4 molar hydrochloric acid solution. It has, however, been shown by Fales and Morrell, THIS JOURNAL, **44**, 2071 (1922), that the electrometric measure of acidity does not parallel the sucrose hydrolysis rate in the range from 0.01 to 1.2 molar hydrochloric acid.

[5] Hantzsch and Weissberger, Ref. 1; Armstrong and Wheeler, *Chem. News*, **103**, 133 (1911); Worley, *J. Chem. Soc.*, **99**, 349 (1911); Kautz and Robinson, THIS JOURNAL, **50**, 1022 (1928).

[6] Harned, *ibid.*, **40**, 1461 (1918); Harned and Pfanstiehl, *ibid.*, **44**, 2193 (1922).

[7] Grube and Motz, *Z. physik. Chem.*, **118**, 145 (1925); Grube and Schmid, *ibid.*, **119**, 29 (1926).

medium properties, the salt effect, accompanying the transition from relatively low to relatively high electrolyte concentration alters the equilibrium in the indicator reaction and the rate in the catalysis in identical fashion. The present result is therefore a quantitative verification, at least within limits, of the opinion of Hantzsch[8] that indicator reaction and acid catalysis, being both dependent upon salt formation, are equivalent measures of acidity. A similar correlation has been obtained by Hammett and Deyrup[3] by the comparison of acidity function with the rates of a number of reactions which take place in mixtures of sulfuric acid and water in the range of acid concentration from 70 to 100%.

Of the possible mechanisms of acid catalysis, one, whose theory has been developed by Kastle, Euler and Stieglitz, and is discussed by Brönsted[9] as the "ionization theory," leads immediately to the relation which we have found to hold for the strong acids. According to this the observed rate is the rate of further change of the ion SH^+ formed by the addition of hydrogen ion to the substrate S, and the rate of formation of this ion is so rapid compared with its further reaction that equilibrium exists between ion and substrate. The rate v is then given by

$$v = k_1c_{SH^+} = k_2a_Sa_{H^+}\frac{1}{f_{SH^+}} = k_2c_Sa_{H^+}\frac{f_S}{f_{SH^+}}$$

Since however the ratio f_S/f_{SH^+} may be expected to be the same as the corresponding ratio f_B/f_{BH^+} for any other base including the indicators,[3] at least within the range of medium variation here in question, and since by definition $H_0 = -\log a_{H^+}f_B/f_{BH^+}$ the specific velocity constant $k = v/c_S$ is given by

$$\log k + H_0 = \log k_2$$

which is the equation of the straight line in the figures.

A different reaction mechanism, that of the general acid catalysis of Brönsted,[9] is however strongly suggested by the variant nature of the results for trichloroacetic acid in the sugar hydrolysis. Here the rate of hydrolysis increases rapidly as the acid concentration varies from 0.5 to 4 molar, in spite of the fact that the acidity, as measured by the value of H_0, undergoes very little change. If there is general acid catalysis this deviation may be attributed to the increase in the concentration of catalytically active trichloroacetic acid molecules, a complication which does not arise in the case of the strong acids, because their solutions contain, in the range studied, no appreciable concentration of undissociated molecules,

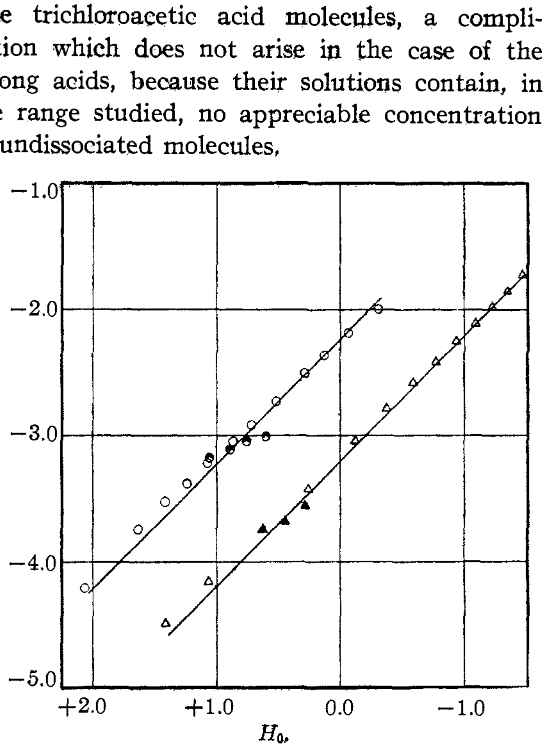

Fig. 2.—Relation between H_0 and velocity constants for hydrolysis of ethyl acetate and for hydrolysis of cyanamide. Ethyl acetate hydrolysis: ○, HCl 0.01–1.50 *M*; ◓, 0.1 *N* HCl + KCl 0–3 *M*. Cyanamide hydrolysis: △, HNO_3 0.05–5.0 *M*; ▲, 0.25 *N* HNO_3 + KNO_3 0–2.7 *M*.

On this theory the catalytic activity of the strong acids depends exclusively upon oxonium ion, and the rate determining step is, not the first order reaction of the ion SH^+, but the second order reaction of S with OH_3^+. According to Brönsted's[9] reaction velocity theory the rate is given by the equation

$$v = k_1c_Sc_{OH_3^+}(f_{OH_3^+}f_S/f_X)$$

where f_X is the activity coefficient of the "critical complex" obtained from the substrate and oxonium ion. Since

$$c_{OH_3^+}f_{OH_3^+} = k_2a_{H^+}a_{H_2O}$$

we have for the specific velocity $k = v/c_S$

$$\log k - \log a_{H^+}(f_S/f_X) - \log a_{H_2O} = \log k_1k_2$$

$$\text{or } \log k + H_0 = \log k_1k_2 + \log a_{H_2O}\frac{f_{BH^+}f_S}{f_Xf_B}$$

In order that this equation may agree with the observed result, it is necessary that the quantity $a_{H_2O}f_{BH^+}f_S/f_Xf_B$ be practically constant. Constancy of the ratio $f_{BH^+}f_S/f_Xf_B$ is not unreasonable, since both BH^+ and X are singly charged, but is difficult to predict with certainty in view of

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[8] Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923); see also Brönsted, *Chem. Rev.*, **5**, 336 (1928); Hammett, THIS JOURNAL, **50**, 2666 (1928).

[9] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

the vagueness with which the concept of critical complex is encumbered. For the relatively small variations in water activity in question, the experimental data do not exclude the possibility that $\log k + H_0 - \log a_{H_2O}$ rather than $\log k + H_0$ is constant, although agreement is definitely less good for the former relation. It is also possible that there is some more or less accidental compensation between the factors a_{H_2O} and $f_{BH^+}f_S/f_Xf_B$ or that the hydration of the sucrose is a complicating factor.

It is to be noted that there is already evidence that some acid catalyses are not capable of correlation with the acidity function. Among these are the hydrochloric acid catalysis of the acetylchloroaminobenzene rearrangement,[10] and the hydrolysis of hydrogen cyanide recently studied by Krieble and Peiker.[11] In these cases there are large and specific effects of individual acids, and the trichloroacetic acid hydrolysis of sucrose can indeed be properly classified with them.

Summary

The rates of the acid catalyzed hydrolysis of sucrose, of ethyl acetate and of cyanamide in aqueous solutions of various strong acids in concentrations extending up to 7 molar can be closely correlated with the acidity function, H_0, which is to say with the measure of acidity given by a simple basic indicator, and with no other measure of acidity.

The variant behavior of trichloroacetic acid in the sucrose hydrolysis suggests the possibility of a general acid catalysis in the Brönsted sense, a catalysis by trichloroacetic acid molecules as well as by oxonium ion.

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[10] Harned and Seltz, THIS JOURNAL, **44**, 1475 (1922).

[11] Krieble and Peiker, *ibid.*, **55**, 2326 (1933).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Adsorption of Wool Violet (4BN) by Lead Sulfate and the Influence of the Adsorbed Dye on the Speed of Kinetic Exchange[1]

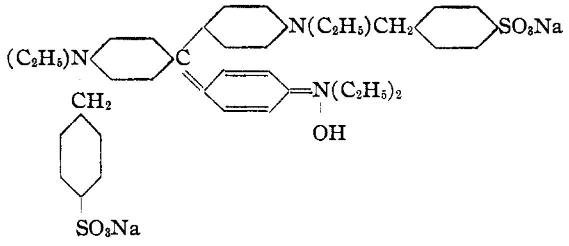
BY I. M. KOLTHOFF, W. VON FISCHER AND CHARLES ROSENBLUM

Ponceau 2R[2] and Ponceau 4R[3] have been used in a study of the adsorbent properties of lead sulfate. In the present work it appeared that wool violet 4BN has distinct advantages over the other dyes. The surface of lead sulfate is saturated with the wool violet at relatively small concentrations of the dye in the supernatant liquid; moreover, the lead salt of the dye is soluble enough to permit a study of the dye adsorption in the presence of a slight excess of lead ions in the solution. One cc. of a 0.5% solution of wool violet in water gives a colored precipitate when added to 5 cc. of 0.01 N lead nitrate, but remains clear with a 0.005 N solution.

Materials Used

Lead Sulfate.—This substance was prepared in a way similar to that described in a previous study,[4] and was used throughout in the air dried state.

Wool Violet 4BN.—A sample was obtained from the National Aniline and Chemical Company and purified by repeated recrystallizations. It was dissolved in alcohol, filtered and an equal volume of ether added to the filtrate. The crystalline precipitate was collected after several hours of standing, and the final product air dried. On heating in a vacuum oven at 65–70° for twelve hours the loss in weight was 0.5%. In Rowe's Colour Index (No. 698) the following formula of the wool violet is given: $C_{41}H_{44}N_3O_6S_2Na$. This corresponds to a molecular weight of 761 and a sodium content of 3.02%. The sodium content of the purified dye was determined according to the procedure of I. M. Kolthoff and J. Lingane[5] and was found to be 5.85 to 6.0%. This shows definitely that the wool violet is not a mono but a disodium salt to which we assign the formula: $C_{41}H_{45}N_3O_7S_2Na_2$. mol. wt. 801.



The nitrogen content of the dye was determined according to Kjeldahl and found to be 5.32, 5.31, 5.34% N. According to the above formula (disodium salt) the calculated percentage of sodium is 5.75 and of nitrogen 5.25.

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[1] Part of the material presented in this paper is taken from the master's thesis of William Von Fischer, University of Minnesota, 1933.

[2] F. Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 480 (1922).

[3] I. M. Kolthoff and Charles Rosenblum, THIS JOURNAL, **55**, 2664 (1933).

[4] Kolthoff and Rosenblum, *ibid.*, **55**, 2656 (1933).

[5] Kolthoff and Lingane, *ibid.*, **55**, 1871 (1933).