The Acidity Function in Aqueous Acetic Acid Solutions

BY DONALD S. NOYCE AND PAUL CASTELFRANCO

Acetic acid has had widespread use as a solvent for a variety of organic reactions.[1,2] The profound effect of small amounts of water on reaction rates has also been observed.[2] It seemed desirable, therefore, to determine the effective acidity of a strong acid in the water–acetic acid solvent pair to make possible a more intelligent evaluation of acid catalyzed reactions carried out in this medium.

Experimental

Materials.—Sulfuric acid was prepared by the method of Brand,[3] m.p. 10.3°. Acetic acid was dried by azeotropic distillation with benzene and fractionation, m.p. 16.3°. *o*-Nitroaniline was purified by crystallization from alcohol, m.p. 71.7°. *p*-Nitroaniline was crystallized from ethanol, m.p. 148–149°. The extinction coefficient in water of *o*-nitroaniline was 4500 at 4120 Å., and of *p*-nitroaniline 12,250 at 3830 Å. Standard solutions of 1 molal sulfuric acid in acetic acid and 1 molal sulfuric acid in water were prepared with added *o*-nitroaniline at a concentration of 60.0 mg./l. Prepared in like manner were solution 0.01 N in sulfuric acid, to which *p*-nitroaniline was added at a concentration of 12.68 mg./l.

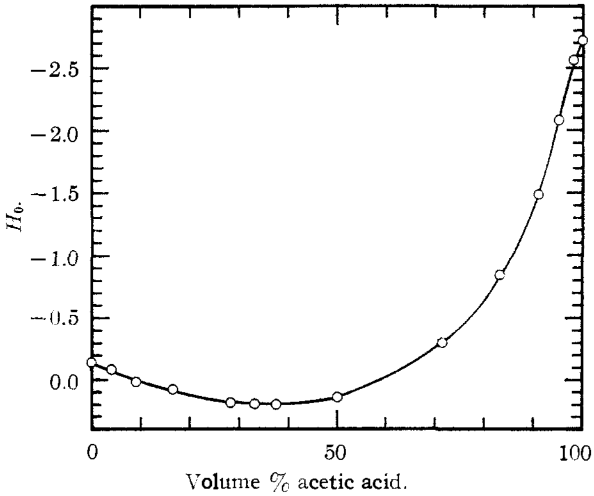

Fig. 1.—H_0 of 1 molal H_2SO_4 in aqueous sulfuric acid.

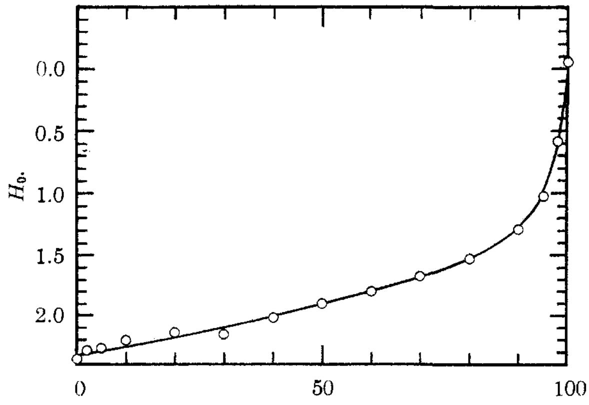

Fig. 2.—H_0 of 0.01 N H_2SO_4 in aqueous acetic acid.

Procedure.—The indicator ratios for various mixtures were determined in the usual manner[4] using a Beckman DU spectrophotometer. From these H_0 was calculated; the results obtained are summarized in Table I.

TABLE I

Vol. % of acetic acid	1 m H_2SO_4, H_0	Vol. % of acetic acid	0.01 N H_2SO_4, H_0
0	−0.14 ± 0.02[a]	0	2.36 ± 0.10[a]
3.9	− .09 ± .02	2	2.29 ± .07
9.1	− .02 ± .02	5	2.27 ± .07
16.7	+ .08 ± .02	10	2.21 ± .06
28.5	.19 ± .02	20	2.14 ± .06
33.3	.19 ± .02	30	2.15 ± .06
37.5	.20 ± .02	40	2.02 ± .05
50.0	.15 ± .02	50	1.90 ± .03
71.3	− .30 ± .02	60	1.80 ± .02
83.3	− .85 ± .02	70	1.67 ± .02
90.9	−1.49 ± .02	80	1.53 ± .02
95.3	−2.08 ± .02	90	1.29 ± .02
98.2	−2.56 ± .02	95	1.02 ± .02
100	−2.72 ± .02	98	0.58 ± .02
		100	−0.06 ± .02

[a] The accuracy of the measurements is estimated, being somewhat less than in the other cases, because of the wide spread of acidity covered by one indicator.

Discussion

Hammett[5] has defined an indicator acidity function H_0 which has proved successful in correlating reaction rates in strongly acidic solution, and also in non-aqueous solvents.[6] Paul[7] has recently shown such a correlation in acetic acid solution, while Mackenzie and Winter[8] have demonstrated a correlation with a similar function in acetic acid–acetic anhydride mixtures.

The results of the determination of the acidity function of 1 molal sulfuric acid in aqueous acetic acid, and of 0.01 N sulfuric acid in the mixed solvents are shown in Figs. 1 and 2, respectively. The values of H_0 for water and for acetic acid extremes agree within the experimental error with values reported in the literature.[9] Values for 50 mole per cent. acetic acid solutions have been reported by Hammett,[10] and these values indicate that the nature of the acidity function curve for the mixed solvent is perhaps similar to Fig. 1 for solutions of higher acid concentration.

The tenfold change in acidity function in going from 100% acetic acid to 92–95% acetic acid is also in rough agreement with the data reported by Djerassi and Scholz and by Fieser[2] on the diminu-

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(1) For typical recent uses, see P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948); R. Criegee, *Ann.*, **560**, 127 (1950); M. S. Newman, S. H. Lee, Jr., and A. B. Garrett, THIS JOURNAL, **69**, 113 (1947); E. D. Hughes, C. K. Ingold and R. T. Reed, *J. Chem. Soc.*, 2406 (1950); H. Huebner and O. Brenken, *Ber.*, **6**, 170 (1873); J. Cason and R. E. Harmon, *J. Org. Chem.*, in press (1951).

(2) C. Djerassi and C. R. Scholz, THIS JOURNAL, **69**, 2404 (1947); L. F. Fieser, *ibid.*, **70**, 3237 (1948).

(3) J. C. D. Brand, *J. Chem. Soc.*, 585 (1946).

(4) (a) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).

(5) Ref. 4(a); L. P. Hammett and M. A. Paul, THIS JOURNAL, **56**, 827, 830 (1934); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 262 *et seq.*

(6) N. C. Deno and M. S. Newman, THIS JOURNAL, **72**, 3852 (1950).

(7) M. A. Paul, *ibid.*, **72**, 3813 (1950).

(8) H. A. E. Mackenzie and E. R. S. Winter, *Trans. Faraday Soc.*, **44**, 171 (1948).

(9) N. F. Hall and W. F. Spengeman, THIS JOURNAL, **62**, 2487 (1940).

(10) M. A. Paul and L. P. Hammett, *ibid.*, **58**, 2155 (1936).

tion in rates occurring on the addition of water to the reaction media in these two cases.

Studies of the acidity function in other mixed solvents have been reported by Braude,[4b] and the general similarity of the results is evident. The only point of difference is the disappearance of the maximum in the value of H_0 in dilute acid (0.01 *N*). Further work is necessary before offering an interpretation of this change.

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Isomerization Accompanying Alkylation. VIII.[1] Reaction of Benzene with 2- and 3-Pentanol

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It has been found that the alkylation of benzene with ethylcyclopropane in the presence of hydrogen fluoride, aluminum chloride or sulfuric acid gives a mixture of amylbenzenes consisting, in each case, of approximately 63% 2-phenylpentane and 37% 3-phenylpentane.[1] The large amount of isomerization occurring during this reaction suggests that the 2- and 3-pentylcarbonium ions are readily interconvertible in the presence of acidic catalysts. Further evidence for this has been obtained from a study of the alkylation of benzene with 2- and 3-pentanol using aluminum chloride and hydrogen fluoride catalysts.

The monoalkylated product from the reaction of 3-pentanol with benzene in the presence of hydrogen fluoride at 0–5° consisted of 56% 2- and 44% 3-phenylpentane. When aluminum chloride was used as the catalyst at 25–35°, the product consisted of 76% 2- and 24% 3-phenylpentane. In the latter case, the aluminum chloride was added to a solution of the alcohol in benzene to avoid an excess of aluminum chloride in contact with the pentylbenzenes.

Similar results were obtained when 2-pentanol was used as the alkylating agent with aluminum chloride as catalyst. Thus, the monoalkylated product consisted of 60% 2-phenylpentane and 40% 3-phenylpentane. This reaction was previously reported to give 2-phenylpentane.[3]

Similar results were obtained previously[4] when 1-pentanol reacted with benzene in the presence of 80% sulfuric acid at 70°.

Infrared spectral analysis was used in each case to determine the product composition; this was done according to the method described in the preceding publication.[1]

Experimental

1. **3-Pentanol. Hydrogen Fluoride Catalyst.**—The procedure for this type of reaction has been described previously.[5] From 10 g. (0.114 mole) of 3-pentanol, 78 g. (1.0 mole) of benzene and 20 g. (1.0 mole) of hydrogen fluoride, there was obtained 13.8 g. (78% yield) of monoalkylated material, b.p. 190–192°, $n^{20}\mathrm{D}$ 1.4875. The infrared spectrum of the product showed it to consist of 56% 2- and 44% 3-phenylpentane.

Aluminum Chloride Catalyst.—Aluminum chloride, 26.6 g. (0.2 mole) was added in small portions to a well-stirred solution of 17.6 g. (0.2 mole) of 3-pentanol in 78 g. (1.0 mole) of benzene. The temperature was maintained below 35° by occasional cooling in an ice-bath. The mixture was stirred for one hour and then allowed to stand overnight at room temperature. The product was poured into ice-water, washed with 10% hydrochloric acid, 10% sodium hydroxide and water until neutral to litmus. After drying over calcium chloride, distillation gave 23.5 g. (80% yield) of monoalkylated product, b.p. 190–193°, $n^{20}\mathrm{D}$ 1.4877. The infrared spectrum showed that the product consisted of 76% 2- and 24% 3-phenylpentane.

2. **2-Pentanol. Aluminum Chloride Catalyst.**—The procedure of Huston and Hsieh was followed.[3] The monoalkylated product, obtained in 40% yield, had the following constants: b.p. 190–193°, $n^{20}\mathrm{D}$ 1.4878. It consisted, according to infrared spectral analysis, of 60% 2- and 40% 3-phenylpentane.

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[1] For paper VII of this series, see H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4343 (1951).

[2] Universal Oil Products Predoctoral Fellow, 1947–1950.

[3] R. C. Huston and T. Y. Hsieh, THIS JOURNAL, **58**, 439 (1936).

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[5] H. Pines, A. Edeleanu and V. N. Ipatieff, THIS JOURNAL, **67**, 2193 (1945).

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The Purity of Diiodofluorescein-I_2^{131}

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Diiodofluorescein containing iodine^{131} is being extensively used as an aid in the location of brain tumors. In a recent paper, Boyack, Moore and Clausen[2] report the preparation of diiodofluorescein-I_2^{131} by iodination of fluorescein with iodine^{131} monochloride. Their method includes a convenient method of preparing iodine^{131} monochloride from dichloramine-T and sodium iodide^{131} with potassium iodide as carrier; they employ a 100% stoichiometric excess of dichloramine-T. When we attempted[3] to adapt this iodinating system to the preparation of 3,5-diiodo-4-pyridone-I_2^{131} the product obtained contained chlorine as well as iodine; it was found necessary to decrease greatly the excess of dichloramine-T in order to obtain the desired chlorine-free diiodopyridone. This observation suggested the possibility that chlorination as well as iodination might also occur in the above-mentioned synthesis of diiodo^{131}-fluorescein. Boyack, Moore and Clausen gave no analysis of their product, stating that a diiodo structure was strongly supported by the fact that all the iodine was consumed in iodination as indicated by the absence of iodine in the filtrate from the reaction product.

We, therefore, prepared samples of diiodofluorescein according to the directions of Moore, *et al.*,[2] (except that no iodine^{131} was used) and analyzed them for chlorine and iodine. The fluorescein used was purified as the diacetate,[4] and the reaction prod-

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[1] Medical Division, Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee.

[2] G. Boyack, G. E. Moore and D. F. Clausen, *Nucleonics*, **3**, No. 4, 62 (1948).

[3] Roe, Hayes and Bruner, *J. Elisha Mitchell Soc.*, **66**, 163 (1950).

[4] W. R. Orndorff and A. J. Hemmers, THIS JOURNAL, **49**, 1272 (1927).