

821. *The Hammett Acidity Function in Reactions catalysed by Carboxylic Acids. The Hydrolysis of Methylal and the Depolymerisation of Trioxan.*

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Correlation between the acidity function (H_0) and the rates of reactions catalysed by carboxylic acids frequently breaks down at higher acid concentrations. The behaviour of two systems was studied by using various carboxylic acids and with acetic acid-sulphuric acid mixtures. In the hydrolysis of methylal it was demonstrated that the non-linearity of the H_0 -log (reaction rate) plot was caused by a "salting-in" effect. In the depolymerisation of trioxan, although this effect is doubtless a factor, far greater deviations were caused by catalysis by undissociated molecules. This could be most clearly demonstrated by using acetic acid-sulphuric acid mixtures.

A LINEAR relation between the Hammett acidity function¹ (H_0) and log (reaction rate) is well established for catalysis by strong acids in aqueous solution.² Only a few investigations have been made into this relation in the case of carboxylic acids. It has been found, however, that in more concentrated solutions of these acids the reaction rate is sometimes greater than that expected for the appropriate acidity function value.^{3,4} Long and Paul² suggested that this deviation may be due to factors arising in the determination of H_0 by the indicator method. They suggested a "salting-in" effect by the carboxylic acid on the base, varying with each base and acid used. In contrast, Satchell⁵ determined an acidity-function scale for dichloroacetic acid and claimed a linear correlation with the rates of a deuterium-exchange reaction and the depolymerisation of paraldehyde (data of Bell and Brown⁴). However, the gradient of the log rate-(acidity function) plot was only 0.65 compared with that of 1.0 obtained with strong acids. Bascombe and Bell⁶ have since pointed out that certain basic indicators are unsuitable for use in the determination of H_0 values in solutions of some carboxylic acids.

It appeared that a wider range of kinetic measurements on acid-catalysed reactions using solutions of carboxylic acids would be useful. This paper describes investigations of the rates of hydrolysis of methylal and trioxan in aqueous solutions of carboxylic acids and sulphuric acid-acetic acid mixtures.

RESULTS

Hydrolysis of Methylal.—The kinetic results obtained for the hydrolysis of methylal with aqueous solutions of various acids at 25° are summarised in Table 1 and the plots of log (hydrolysis rate) against acidity function are given in Fig. 1. The H_0 values for trifluoroacetic and trichloroacetic acids were interpolated from the results of Randles and Tedder⁷ corrected to a pK value for *p*-nitroaniline of 1.02. The values for sulphuric acid and dichloroacetic acid are from the results of Bascombe and Bell,⁶ and the H_0 values for acetic acid-sulphuric acid mixtures are taken from Table 3.

In the case of sulphuric acid alone the plot of log rate against H_0 gave a linear graph and this was used as the reference line. As expected, the gradient was 1.0, and individual points are not shown.

The results obtained by using trifluoroacetic acid and trichloroacetic acid followed this reference curve very closely. When they were considered individually there was a slight

¹ Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 4239.

² Long and Paul, *Chem. Rev.*, 1957, 935.

³ Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 827.

⁴ Bell and Brown, *J.*, 1954, 774.

⁵ Satchell, *J.*, 1958, 3904.

⁶ Bascombe and Bell, *J.*, 1959, 1096.

⁷ Randles and Tedder, *J.*, 1955, 1218.

upward curvature detectable towards higher acidities. This is similar to Satchell's findings⁵ for the hydrogen-exchange reaction. In dilute solutions the points obtained by using dichloroacetic acid follow the reference line, but in the more concentrated solutions there is a pronounced and increasing deviation above the reference line. Finally, the group of results obtained by using various mixtures of acetic acid with 0.73M-sulphuric

TABLE 1. *Acid-catalysed hydrolysis of methylal at 25°.*

<i>Trifluoroacetic acid.</i>								
[Acid] (mole/l.) ...	0.231	0.667	1.646	2.72	4.86	6.03	7.31	8.05
10^3k (min. ⁻¹)	25.3	67.0	139	190	276	339	621	718
H_0	0.63	0.24	-0.11	-0.25	-0.44	-0.55	-0.71	-0.81
<i>Trichloroacetic acid.</i>								
[Acid] (mole/l.) ...	0.589	0.850	1.437	2.87	5.03	5.52	6.42	7.58
10^3k (min. ⁻¹)	63	82.5	108	128	181	202	284	555
H_0	0.29	0.13	-0.025	-0.065	-0.135	-0.18	-0.31	-0.61
<i>Dichloroacetic acid.</i>								
[Acid] (mole/l.) ...	0.155	0.40	0.754	1.35	2.40	3.58	4.75	6.16
10^3k (min. ⁻¹)	7.7	13.9	18.4	21.2	21.9	24.6	34.4	57.4
H_0	1.0	0.85	0.73	0.66	0.66	0.665	0.65	0.57
<i>Sulphuric acid (0.73M)-acetic acid (temp. = 24.7°).</i>								
[Acetic acid] (mole/l.)	0	0.35	1.07	1.75	2.42	3.49	5.20	
10^3k (min. ⁻¹)	136.2	132.6	125.4	118.8	116.4	114.0	114.0	
H_0	-0.125	-0.105	-0.06	-0.02	+0.02	+0.08	+0.13	

acid show a decrease in rate of hydrolysis with increasing acetic acid concentration. There is an increasing deviation from the line as the acetic acid concentration increases.

Depolymerisation of Trioxan.—A series of measurements of the rate of depolymerisation of trioxan with the same acids is summarised in Table 2 and the plots of log rate against H_0 are given in Fig. 2. The sources of the H_0 values are those quoted in the above section.

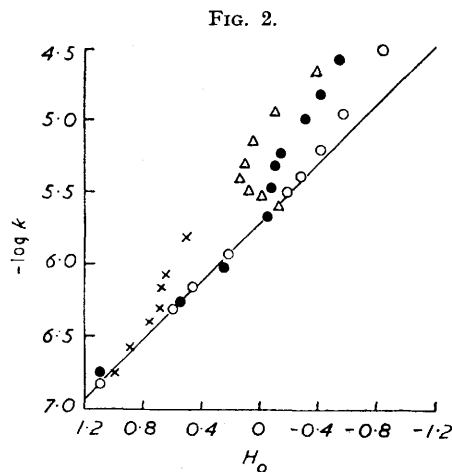
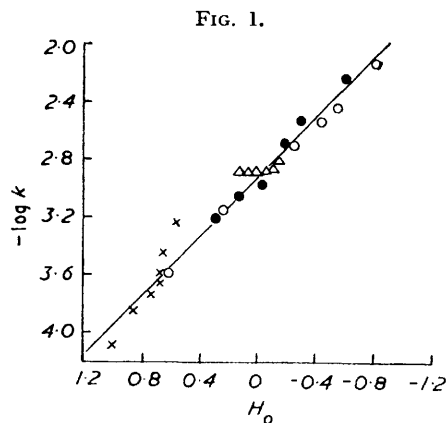


FIG. 1. *Hydrolysis of methylal.* FIG. 2. *Depolymerisation of trioxan.* Continuous lines are those obtained in hydrolysis with sulphuric acid alone, slope 1.0. The other symbols are experimental points obtained in catalysis with: ○ trifluoroacetic acid, ● trichloroacetic acid, × dichloroacetic acid, △ acetic acid in 0.73M-sulphuric acid.

In Fig. 2 the reference line again refers to the reaction rate in the presence of sulphuric acid alone and is of slope 1.0. At the lower concentrations the points obtained for all the carboxylic acids follow this line but at higher concentrations all the acids show marked deviations, the rates being greater than expected for the particular H_0 values. There is

also a considerable deviation for acetic acid-sulphuric acid mixtures, as the acetic acid concentration is increased.

DISCUSSION

Methylal.—It has been well established that the hydrolysis of methylal is catalysed only by hydrogen ions. It must be assumed therefore that divergence in the relation between H_0 and log rate reflects faults in the H_0 scales for carboxylic acids and does not indicate catalysis by other components. This inexactness of the acidity function scale can be explained by the "salting-in" effect during the determination of the scale by means of

TABLE 2. *Depolymerisation of trioxan by acids at 25°.*

<i>Trifluoroacetic acid.</i>									
[Acid] (mole/l.)	0.082	0.150	0.272	0.380	0.540	0.600	0.711	1.72	
10^7k (min. ⁻¹)	1.51	2.96	4.80	7.15	9.56	9.42	11.48	25.02	
H_0	1.11	0.79	0.59	0.46	0.37	0.29	0.21	-0.12	
[Acid] (mole/l.)	1.748	2.180	3.00	4.56	5.60	6.28	8.26		
10^7k (min. ⁻¹)	27.0	32.88	41.40	63.0	89.16	112.0	324.7		
H_0	-0.14	-0.19	-0.28	-0.42	-0.52	-0.58	-0.85		
<i>Trichloroacetic acid.</i>									
[Acid] (mole/l.)	0.096	0.21	0.318	0.502	0.676	1.584	1.762	3.56	
10^7k (min. ⁻¹)	1.73	3.62	5.40	8.52	10.95	21.48	22.50	33.80	
H_0	1.11	0.71	0.54	0.25	0.21	-0.04	-0.05	-0.07	
[Acid] (mole/l.)	4.760	5.32	6.23	6.49	6.94	7.49	7.77		
10^7k (min. ⁻¹)	47.58	57.72	92.58	105.7	152.4	268.2	344.4		
H_0	-0.11	-0.15	-0.28	-0.32	-0.41	-0.56	-0.69		
<i>Dichloroacetic acid.</i>									
[Acid] (mole/l.)	0.160	0.368	0.716	1.33	2.20	3.62	5.04	6.85	
10^7k (min. ⁻¹)	1.69	2.70	4.11	5.05	5.90	7.02	8.34	15.60	
H_0	1.0	0.87	0.74	0.66	0.66	0.67	0.64	0.51	
<i>Sulphuric acid (0.73M)-acetic acid.</i>									
[Acetic acid] (mole/l.)	0	1.75	3.49	5.20	6.92	8.59	10.38	12.04	
10^5k (min. ⁻¹)	2.65	2.97	3.30	4.01	5.06	7.14	11.70	22.2	
H_0	-0.13	-0.01	+0.08	0.13	0.11	0.05	-0.11	-0.39	
<i>Sulphuric acid (1.83M)-acetic acid.</i>									
[Acetic acid] (mole/l.)	0	0.35	0.85	1.69	2.62	3.41	4.35	5.24	7.05
10^5k (min. ⁻¹)	1.47	1.53	1.59	1.72	1.94	2.13	2.47	2.88	4.20
H_0	-0.84	-0.82	-0.78	-0.71	-0.64	-0.58	-0.54	-0.53	-0.57
									8.75
									7.38

TABLE 3. *Acidity functions of aqueous sulphuric acid-acetic acid mixtures.*

(a) <i>Sulphuric acid concentration = 0.73 mole/l.</i>									
Indicator, <i>p</i> -nitroaniline, $pK = 1.02$. Optical density (β) of indicator solution (54 mg./l.) = 0.494.									
[Acetic acid] (mole/l.)	0	0.35	1.05	1.75	3.49	4.16	5.20		
β	0.033	0.035	0.038	0.041	0.051	0.052	0.058		
H_0	-0.13	-0.10	-0.06	-0.02	0.08	0.09	0.14		
[Acetic acid] (mole/l.)	5.92	6.92	7.63	8.59	10.38	12.04	13.79		
β	0.057	0.053	0.052	0.047	0.034	0.018	0.008		
H_0	0.13	0.10	0.09	0.04	-0.11	-0.40	-0.76		
(b) <i>Sulphuric acid concentration = 1.83 moles/l.</i>									
Indicator <i>o</i> -nitroaniline, $pK = -0.29$. Optical density of indicator solution (117 mg./l.) = 0.370.									
[Acetic acid] (mole/l.)	0	0.35	1.06	1.71	2.40	3.25	3.28	4.14	5.10
β	0.081	0.084	0.094	0.103	0.113	0.115	0.127	0.126	0.130
H_0	0.84	0.82	0.76	0.70	0.65	0.64	0.57	0.58	0.56
[Acetic acid] (mole/l.)	5.35	6.08	6.795	7.605	8.53	8.67	10.40	12.18	13.79
β	0.140	0.140	0.136	0.129	0.099	0.113	0.075	0.040	0.014
H_0	0.50	0.50	0.53	0.56	0.73	0.65	0.88	1.21	1.60

indicators.⁸ This explains the apparent decrease in acidity when acetic acid is added to sulphuric acid solutions,⁹ and also the feature reported above, *i.e.*, that the rate of hydrolysis

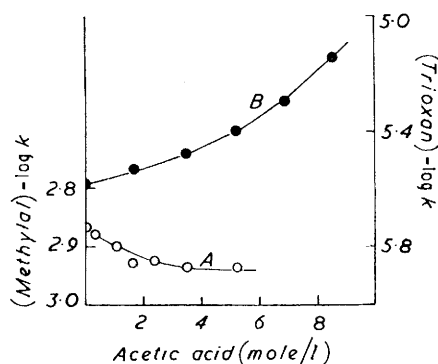
⁸ Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

⁹ Noyce and Castelfranco, *J. Amer. Chem. Soc.*, 1951, **73**, 4482.

of methylal in sulphuric acid is decreased by the addition of acetic acid. The salting-in effect in this last case is much smaller with methylal than with the indicator base since the non-correlation of H_0 and reaction rate becomes greater as more acetic acid is added, the rate values all being higher than expected (Table 1; Fig. 1). The failure of the plot of log rate against H_0 to give linearity in the case of the carboxylic acids is covered by the same theory. The divergence in behaviour is not marked with trifluoroacetic or trichloroacetic acid except in the most concentrated solutions, in contrast to the behaviour of the weaker dichloroacetic acid.

Trioxan.—Trioxan would be expected to show similar salting-in effects. Indeed a comparison of Figs. 1 and 2 shows that with trioxan the rate of depolymerisation is much higher than expected from the appropriate acidity function, particularly at higher concentrations of all the carboxylic acids. From a consideration of these binary mixtures alone then it appear that, if these reactions are subject only to hydrogen-ion catalysis, there is a salting-in effect in the order: indicator > methylal > trioxan. Fig. 3 illustrates the effect of increasing amounts of acetic acid on the rates of reaction of methylal and

FIG. 3. Effect of changing acetic acid concentration on the hydrolysis of methylal (curve A, left-hand scale) and the depolymerisation of trioxan (curve B, right-hand scale), both in solution in 0.73M-sulphuric acid.



trioxan in 0.73M-sulphuric acid. As already discussed, in the case of methylal the reaction rate is decreased and this is explained on the basis of the salting-in effect. However, with trioxan the rate rises steadily with increasing acetic acid concentration. Hence, while there may also be a salting-in effect with trioxan, there is some more important effect which results in an increase, not a decrease, in rate: since under these conditions the acetic acid will be practically undissociated, this is probably catalysis by undissociated acetic acid, supplementing that by hydrogen ions. If so, one would not expect a correlation between H_0 and log rate for trioxan in the binary systems of aqueous carboxylic acids since, added to the deviation caused by the salting-in effect, will be the contribution from catalysis by undissociated carboxylic acid. Very recently Kresge and Chiang¹⁰ showed that the nuclear hydrogen exchange in 1,3,5-trimethoxybenzene is also catalysed by undissociated acetic acid and hence a non-linear H_0 -log rate plot would again be expected (cf. Satchell⁵).

There is no evidence to indicate how undissociated molecules facilitate depolymerisation of trioxan. Possibly they assist decomposition of a proton-trioxan complex, but a wider survey of the kinetics is required before further speculation.

EXPERIMENTAL

Trioxan was prepared by the slow distillation of a 60% solution of formaldehyde containing approximately 2% of sulphuric acid; it was extracted from the distillate with methylene chloride and crystallised from this solvent,¹¹ and was finally recrystallised from water and dried

¹⁰ Kresge and Chiang, *J. Amer. Chem. Soc.*, 1959, **81**, 5509.

¹¹ Frank, U.S.P. 2,304,080/1942.

for 3—4 weeks over fused calcium chloride; it had m. p. 61°. A further supply of trioxan, from Dr. W. Cule Davies, Associated Chemical Companies, Ltd., Leeds, was similarly recrystallised. Methylal was purified by treatment with sodium wire followed by fractional distillation; it had b. p. 42.0°.

Trifluoroacetic acid was obtained from Kodak, Ltd., and dichloroacetic acid from Hopkin and Williams, Ltd.; both were used without further treatment. Trichloroacetic, sulphuric, and acetic acids were "AnalaR" grades, as were all volumetric reagents used. *o*-Nitroaniline and *p*-nitroaniline were recrystallised three times each from ethyl alcohol, and had m. p. 73° and 147°, respectively.

Kinetic Measurements.—The hydrolysis of methylal was followed by estimating the formaldehyde liberated. Methylal was delivered into the acid solution by calibrated pipette. The mixture was kept in a thermostat, and 5 ml. samples were removed at intervals for analysis. The formaldehyde content of the samples was determined by the sulphite method,¹² thymolphthalein being used as indicator. The methylal concentration was calculated, and first-order rate constants obtained by the usual plot (Table 1).

Trioxan depolymerises in acid with the liberation of 3 moles of formaldehyde per mole of trioxan. 1.3—1.7 g. of trioxan and the appropriate acid solution in a 50 ml. stoppered flask were kept in a thermostat; 5 ml. samples were taken as required, and the formaldehyde estimated by the iodometric method.¹² First-order rate constants were then calculated (Table 2).

Acidity-function Measurements in Sulphuric Acid–Acetic Acid Mixtures.—Measured volumes of concentrated sulphuric acid and glacial acetic acid were run from burettes into water in 50 ml. graduated flasks, 5 ml. of a stock indicator solution (*p*-nitroaniline, 54 mg./l.; or *o*-nitroaniline, 117 mg./l.) were added to each flask, and the contents made up to 50 ml. and kept at 25° for several hours. The optical density of each solution was then determined with a Unicam S.P. 500 spectrophotometer, aqueous sulphuric acid being used in the reference cell. The wavelengths used were: *p*-nitroaniline, 380 m μ ; *o*-nitroaniline, 411 m μ . The optical density of a solution of 5 ml. of stock indicator solution diluted to 50 ml. was also measured. If β is the optical density of this indicator solution, and β_1 that of the acidic solution, then the ratio $[B]/[BH^+]$ is given by $\beta_1/(\beta - \beta_1)$. The acidity function was then calculated from $H_0 = pK_B + \log [B]/[BH^+]$ with the pK values: *p*-nitroaniline, 1.02; *o*-nitroaniline, -0.29. With *p*-nitroaniline, measurements of the ratio $[B]/[BH^+]$ at wavelengths in the range 360—400 m μ showed that H_0 was independent of wavelength in this region.⁶ Finally, 5 ml. samples of each acid mixture were titrated with standard sodium hydroxide solution. The acetic acid content of the solutions was calculated from the difference between the titres and the titre obtained for the solutions containing sulphuric acid only. The results obtained are given in Table 3(a) and (b).

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¹² Walker, "Formaldehyde," Reinhold Publ. Corp., New York, 2nd edn., 1953.