The Kinetics of Ester Hydrolysis in Concentrated Aqueous Acids.

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Measurements are reported on the kinetics of hydrolysis of ethyl acetate and methyl formate in solutions of hydrochloric and sulphuric acid up to 10M, and on the acidity function of concentrated hydrochloric acid solutions. The results show that the reaction velocity is not proportional to the acidity function of the solution, being more closely proportional to the acid concentration. It is concluded that hydrolysis takes place by a bimolecular mechanism involving attack by a water molecule, in agreement with other evidence.

THE kinetics of acid-catalysed reactions in concentrated aqueous solutions of strong acids have been used in several instances to obtain information about reaction mechanisms. If the reaction velocity is proportional to the acidity function of the solution it is believed that the transition state contains only a proton in addition to the substrate molecule, while if a molecule of water is also involved the velocity is more nearly proportional to the hydrogen-ion concentration. This suggestion was originally made by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1932, **54**, 2721), and it was pointed out by Hammett and Paul (*ibid.*, 1934, **56**, 830) that the existing data do not make it possible to apply this criterion with certainty to the acid hydrolysis of carboxylic esters, since the acid concentrations which have been used are not high enough to give a clear distinction between the two types of dependence. The work of Long, McDevit, and Dunkle (*J. Phys. Colloid Chem.*, 1951, **55**, 829) shows that in the hydrolysis of γ-butyrolactone the reaction velocity is proportional to hydrogen-ion concentration in solutions of hydrochloric and perchloric acid up to about 4M. Since the γ-lactones are unstrained internal esters, it is likely that the same is true for simple carboxylic esters. This conclusion is in agreement with the mechanism usually accepted on other grounds, but it would be desirable to have direct evidence. It is difficult to extend the usual titrimetric method to high acid concentrations, since the reactions become inconveniently fast, and the titrations are inaccurate in the presence of a large excess of acid. The present paper describes kinetic measurements on the hydrolysis of ethyl acetate and methyl formate in solutions of strong acids up to 10M, physical methods being used to follow the fast reactions involved. The acidity functions of aqueous 6—10M-hydrochloric acid have also been measured.

EXPERIMENTAL

Hydrolysis of Ethyl Acetate.—This reaction was followed dilatometrically, it having been shown by Galeotti (*Z. physikal. Chem.*, 1911, **76**, 117) that the hydrolysis of a 10% aqueous solution is accompanied by a contraction of about 0·05%. The slower reactions were carried out in a dilatometer of conventional design with a volume of 50 c.c. and a capillary cross-section 0·08 mm.^{2}, thus giving a movement of the meniscus of about 150 mm. for the hydrolysis of a 4% solution of the ester. The course of these reactions was strictly of first order, and velocity constants were obtained either by observing the end-point, or by applying Guggenheim's method (*Phil. Mag.*, 1926, **7**, 538). However, for acid concentrations greater than about 2M the logarithmic plots were no longer strictly linear, especially near the beginning of the reaction. This was traced to the incomplete dissipation of heat evolved in the reaction, and experiments on the thermal characteristics of different types of glass tube showed that the error could be rendered negligible by using thin-walled tube of small diameter. The faster experiments were carried out in a dilatometer having a bulb consisting of a 30-cm. length of thin-walled tubing 1 cm. in diameter, and a capillary of cross-section 0·03 mm.^{2}. This revealed no departures from first-order behaviour for reactions with half-times down to 5 min. All kinetic experiments were carried out at 25°, and blank experiments showed that the temperature of the dilatometers fluctuated by less than 0·003°. Both dilatometers had a single tap.

The ester used was an "AnalaR" preparation redistilled before use. The acids used were

" AnalaR " reagents, and their concentration was related by titration to constant-boiling hydrochloric acid. The acid solution and the ester were both brought to thermostat temperature and degassed for a few minutes before mixing : this caused slight concentration changes (about 1%) in some of the acid solutions, detected by titrating a sample after degassing. Reliable dilatometer readings could be made about 5 min. after mixing. The results of these experiments are given in Table 1.

TABLE 1. *Hydrolysis of ethyl acetate at 25°.*

k = first-order velocity constant in sec.$^{-1}$. Acid concentrations in moles/l. of solution. Ester concentrations 4% unlesss otherwise stated.

Hydrochloric acid.

[HCl]	0·457	0·486	0·722	1·34	1·47	1·59	2·11	3·09
10^5k	5·19 *	5·38	8·10	17·8 †	18·0	20·8	27·4	45·0
H_0	+0·33	+0·29	+0·10	−0·24	−0·35	−0·40	−0·59	−0·94

[HCl]	4·75	5·48	6·51	7·91	8·11	9·06	10·10	10·20
10^5k	81·8	104	143	202	192	217	244	247
H_0	−1·55	−1·77	−2·20	−2·81	−2·89	−3·23	−3·57	−3·60

* Ester concn. 2%. † Ester concn. 8%.

Sulphuric acid.

[H_2SO_4] ...	1·35	1·37	1·87	2·85	3·08	3·63	4·25	4·76	6·75
10^5k	18·8	19·8	30·9	56·1	65·5	79·7	104	128	192
H_0	−0·31	−0·33	−0·62	−1·15	−1·25	−1·50	−1·80	−2·05	−3·03

Hydrolysis of Methyl Formate.—This ester is hydrolysed in acid solution about 40 times as fast as ethyl acetate, and the reaction could therefore not be followed dilatometrically. However, the hydrolysis is endothermic, with $\Delta H \simeq 4$ kcal./mole, and is therefore suitable for study by the thermal-maximum method developed in this laboratory (Bell and Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 16; Bell, Gold, Hilton, and Rand, *Disc. Faraday Soc.*, 1954, **17**, 151), the more usual maximum being replaced here by a temperature minimum. The reaction was carried out by breaking bulbs containing about 2 g. of 17% ester solution into 50 c.c. of hydrochloric acid in a platinum vessel, the sensitivity of the single-junction thermocouple plus amplifier being 3000—4000 mm./degree. When aqueous solutions of methyl formate are mixed with concentrated hydrochloric acid there is a considerable instantaneous heat evolution. In the kinetic experiments this was eliminated by dissolving the ester in sodium nitrate solution instead of in water, heat being absorbed by the dilution of the sodium nitrate solution. For a given acid concentration the correct amount of sodium nitrate was determined by a series of experiments in which varying (insufficient) amounts of sodium nitrate were added to fixed quantities of ester and water in the bulb, and the instantaneous galvanometer deflection observed in each case. The correct amount of sodium nitrate was then estimated by extrapolating to zero galvanometer deflection. Typical plots of this kind are shown in Fig. 1. The temperature change caused by the reaction under adiabatic conditions (T_0; cf. Bell and Clunie, *loc. cit.*) was determined by experiments in a small double-walled glass vessel, in which the slow transfer of heat from the surroundings could be easily allowed for. The temperature was measured by the same amplifier and galvanometer as in the kinetic experiments, and the thermal characteristics of the two systems were directly compared by carrying out the neutralisation of sodium hydroxide by hydrochloric acid in each system. The results obtained for the rates of hydrolysis are given in Table 2, the velocity constants being derived from the observed value of T_m/T_0, and the measured cooling constant k_2 by the expression given by Bell and Clunie (*loc. cit.*) for first-order reactions.

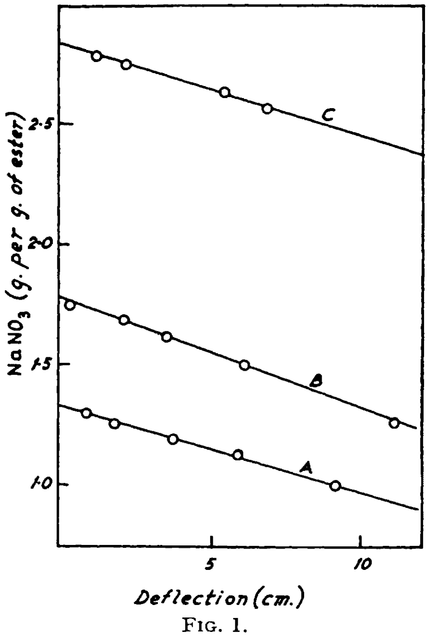


FIG. 1.

A, 2·67N-HCl. *B*, 3·58N-HCl. *C*, 5·79N-HCl.

TABLE 2. *Hydrolysis of methyl formate at* 25°.

Acid concentrations in moles/litre of solution. $k_2 = 0{\cdot}079_5$ sec.$^{-1}$. k_1 = first-order velocity constant in sec.$^{-1}$. Each T_m value is the mean of at least four experiments.

[HCl]	T_m/T_0	10^4k_1	H_0	$\log_{10}\{k_1/[HCl]\}$	$\log_{10} k_1 + H_0$
2·67	0·100	106	−0·79	−2·40	−2·76
3·58	0·130	153	−1·11	−2·37	−2·93
4·48	0·170	223	−1·40	−2·30	−3·05
5·30	0·205	291	−1·72	−2·26	−3·26
6·41	0·270	450	−2·11	−2·16	−3·46

Acidity Functions of Hydrochloric Acid.—The measurements already reported (Hammett and Deyrup, *loc. cit.*) extend only up to a concentration of 6M-hydrochloric acid, and were made with a visual colorimeter. We have therefore made further measurements in the range 2—10M using a Hilger Spekker absorptiometer. The three indicators used were *o*-nitroaniline (m. p. 71·7°), 4-chloro-2-nitroaniline (m. p. 116·0°), and *p*-nitrodiphenylamine (m. p. 133·0°), each after recrystallization from alcohol. The appropriate line of the mercury-discharge lamp was isolated by means of filters, and measurements were made at room temperature. The first two indicators showed a slight absorption at 4047 Å even in 95% sulphuric acid. Since this absorption was unchanged by recrystallisation it must be attributed to the protonated form of the indicator, and a small correction was applied to the optical densities of the more acid solutions, in which higher indicator concentrations had to be used in order to obtain an adequate absorption.

The results obtained are given in Table 3. The pK values of the first two indicators are those derived by Hammett from measurements in hydrochloric acid. The value of −2·35 given for *p*-nitrodiphenylamine was obtained from our own measurements by comparing the results obtained with this indicator with those for 4-chloro-2-nitroaniline in the range [HCl] = 5·0—5·5 : it is in good agreement with the value obtained by Hammett (−2·38) from measurements with sulphuric acid. In the range [HCl] = 2—6 our values of H_0 are in fair agreement with those of Hammett, allowing for the different concentration scales used. The values of H_0 for hydrochloric acid given in Tables 1 and 2 were obtained by interpolation from a plot of both sets of data against concentration. For sulphuric acid Hammett's data were used directly.

TABLE 3. *Acidity functions for aqueous hydrochloric acid.*

(Concentrations in moles/l. of solution.)

o-Nitroaniline, pK = − 0·17.

[HCl]	2·24	2·25	2·52	2·57	2·88	3·63
$\log_{10}\{[I]/[IH^+]\}$	−0·46	−0·45	−0·55	−0·57	−0·70	−0·97
H_0	−0·63	−0·62	−0·72	−0·74	−0·87	−1·14

4-Chloro-2-nitroaniline, pK = − 0·91.

[HCl]	2·68	3·30	5·00	5·39	5·49
$\log_{10}\{[I]/[IH^+]\}$	0·08	−0·13	−0·76	−0·84	−0·86
H_0	−0·83	−1·04	−1·67	−1·75	−1·77

p-Nitrodiphenylamine, pK = − 2·35.

[HCl]	5·04	5·35	5·40	5·67	6·78	6·80	7·30	7·33	7·43	7·56	7·79
$\log_{10}\{[I]/[IH^+]\}$	0·69	0·60	0·58	0·47	0·00	0·03	−0·20	−0·25	−0·28	−0·31	−0·45
H_0	−1·66	−1·75	−1·77	−1·88	−2·35	−2·32	−2·55	−2·60	−2·63	−2·66	−2·80

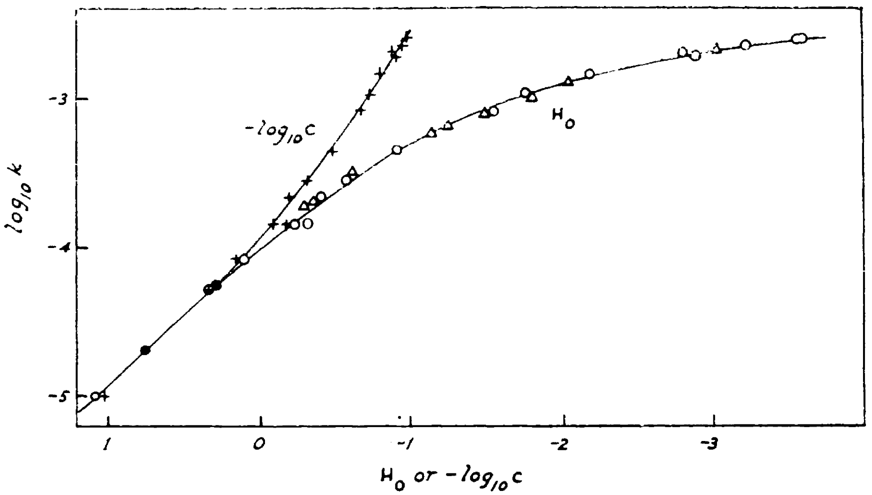
[HCl]	7·87	7·91	8·16	8·46	8·71	8·82	9·01	9·40	9·61	9·90
$\log_{10}\{[I]/[IH^+]\}$	−0·45	−0·48	−0·63	−0·64	−0·75	−0·85	−0·89	−1·01	−1·09	−1·17
H_0	−2·80	−2·83	−2·98	−2·99	−3·10	−3·20	−3·34	−3·36	−3·44	−3·52

DISCUSSION.

Previous kinetic data on the acid hydrolysis of ethyl acetate extend up to [HCl] = 1·4 (Harned and Pfanstiel, *J. Amer. Chem. Soc.*, 1922, **44**, 2199), and our results over the same range are in good agreement with these. Fig. 2 shows plots of $\log_{10} k$ against H_0 and against $-\log_{10}$ [HCl] over the whole concentration range. The points for the two most dilute solutions are taken from the results of Harned and Pfanstiel (*loc. cit.*). In the plot involving H_0 the data for both hydrochloric and sulphuric acids fall on the same curve, but this is far from linear, and its slope varies from close to unity in the more dilute solutions to about 0·1 at the highest concentrations. The plot against $-\log_{10}$ [HCl] is more closely linear, but bends noticeably upwards, its slope varying from unity to about 1·6 with increasing concentration. The results with sulphuric acid when plotted against $\log_{10}$ [H_2SO_4] (not shown in Fig. 2) lie slightly above the corresponding curve for hydrochloric acid : this is reasonable, since at the concentrations involved the first dissociation of sulphuric acid is complete, and the second present only to a small extent.

The data for the hydrolysis of methyl formate show a closely similar behaviour, as may be seen from the last two columns in Table 2. Neither is strictly constant, but there is a closer proportionality to concentration than to acidity function. In these experiments the acidity functions will be modified slightly by the presence of sodium nitrate (up to 0·15M), but Paul's results (*ibid.*, 1954, **76**, 3236) show that the salt effects involved will not be sufficient to alter our general conclusions.

FIG. 2.



○ *and* +, HCl: Δ, H_2SO_4.

The lack of parallelism between reaction velocity and acidity function excludes the unimolecular mechanism, in which the slow step is $R'\cdot CO\cdot\overset{+}{O}HR \longrightarrow R'\cdot\overset{+}{C}O + HOR$, the transition state being formed by simple addition of a proton to the ester. Since acyl-oxygen fission is well established for simple carboxylic esters, the only reasonable alternative is the bimolecular mechanism, involving the slow step $R'\cdot CO\cdot\overset{+}{O}HR + H_2O \longrightarrow R'\cdot CO\cdot\overset{+}{O}H_2 + HOR$ (cf. Datta, Day, and Ingold, *J.*, 1939, 838). According to the usually accepted view this should lead to a proportionality between reaction velocity and acid concentration, since the transition state contains a water molecule as well as a proton. This proportionality is only approximately found in our measurements. However, there are actually no compelling grounds for expecting an exact proportionality to acid concentration over an extended range. The data for the enolization of acetophenone (Zucker and Hammett, *ibid.*, 1939, **61**, 2791) and for the hydrolysis of γ-butyrolactone (Long, McDevit, and Dunkle, *loc. cit.*) extend only up to 4M-acid, and the theoretical interpretation given by Hammett depends upon the plausible but uncertain assumption that the ratio of activity coefficients $f_S f_{H_3O^+}/f_{S\cdot H_3O^+}$ (where S is the substrate) is unity. Further, in the concentrated acid solutions which we have used the choice of concentration scale makes a considerable difference : for example, there is a closer (though still not exact) proportionality between reaction velocity and acid concentration if the latter is expressed in moles per kg. of solvent rather than in moles per litre of solution. We conclude, therefore, that the most important criterion in this type of investigation is the presence or absence of parallelism between reaction velocity and acidity function, and that the exact dependence on acid concentration is a matter for further investigation.

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