

889. *Kinetics of the Acid and Alkaline Hydrolysis of Potassium Ethoxycarbonylmethanesulphonate.*

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The rate of hydrolysis of potassium ethoxycarbonylmethanesulphonate has been measured in acid and in alkaline solution. The sulphonate group, although bearing a net negative charge, behaves as a weakly electron-attracting group. Supporting evidence for this statement is quoted, and an explanation given in terms of the structure of the sulphonate group. In concentrated acid solution the velocity of hydrolysis follows the acid concentration more closely than the acidity function, in agreement with previous findings for ester hydrolysis.

PREVIOUS papers <sup>1,2</sup> on the hydrolysis of ethoxycarbonylmethyltriethylammonium iodide dealt with the effect of a positively charged substituent upon the kinetics of ester hydrolysis, and the present work was planned to give corresponding information about the effect of a negative group. For alkaline hydrolysis this information is available from the rates of successive stages of hydrolysis of dicarboxylic esters, but this approach is not possible for acid hydrolysis since the carboxylate group does not retain its negative charge in acid solution. This difficulty does not arise with sulphonates, which are derived from strong acids: however, it will be seen that the sulphonate group does not behave as a simple negative pole.

#### EXPERIMENTAL

Potassium ethoxycarbonylmethanesulphonate (subsequently referred to as "ester") has been prepared by Andreasch <sup>3</sup> from ethyl monochloroacetate and potassium sulphite and by Vieillefosse and Vieillefosse <sup>4</sup> by esterifying sulphoacetic acid and isolating the barium salt. We used a modification of the former method. Equivalent quantities of the two reactants were dissolved in the minimum quantity of water containing 20% of ethanol and refluxed for 30 mins. After evaporation to dryness the solid mass was extracted with boiling 90% ethanol from which the ester crystallised on cooling. After further recrystallisation from 90% ethanol or from ethanol-glycol (19 : 1) the ester (yield 25%) had m. p. 212°. Andreasch <sup>3</sup> gives m. p. 183°. Quantitative hydrolysis by acid or alkali, as described in the kinetic experiments, indicated a purity of 100 ± 1%. Other reagents used were "AnalaR."

In most kinetic measurements the reaction was followed by titration, but this was not practicable for acid concentrations greater than about 2M, for which dilatometry with two conventional dilatometers having volumes of 25 and 50 c.c. and capillaries of 0.1 mm.<sup>2</sup> cross-section was used. The ester concentrations were in the range 0.1—0.5M so as to give a movement of 8—15 cm. in the capillary for complete reaction. First-order kinetics were observed, and velocity constants were obtained graphically by use of an observed end-point for fast reactions and Guggenheim's method <sup>5</sup> for slow ones. There was good agreement between the dilatometric and titration methods in the concentration range where they overlap. In the titration method for acid hydrolysis the product SO<sub>3</sub><sup>-</sup>·CH<sub>2</sub>·CO<sub>2</sub>H (pK 4.1) <sup>6</sup> was titrated (together with the catalyst acid) with standard alkali, Phenol Red being used as indicator. The first-order velocity constants were obtained graphically by use of the calculated titre for complete hydrolysis. For alkaline hydrolysis approximately equal concentrations (0.005M) of ester and sodium hydroxide were used. Samples were added at intervals to an excess of 0.01N-hydrochloric acid, and the excess of acid titrated with 0.006N-sodium hydroxide (Phenol Red). The second-order velocity constants were obtained graphically from a plot of log  $\{(a - x)/(b - x)\}$  against time. In all titrations the solution was kept free from carbon dioxide by a stream of nitrogen.

<sup>1</sup> Bell and Waind, *J.*, 1950, 1979.

<sup>2</sup> Bell and Lindars, *J.*, 1954, 4601.

<sup>3</sup> Andreasch, *Monatsh.*, 1926, **46**, 639.

<sup>4</sup> Vieillefosse and Vieillefosse, *Bull. Soc. chim. France*, 1947, 256.

<sup>5</sup> Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

<sup>6</sup> Backer, *Proc. Acad. Sci. Amsterdam*, 1922, **25**, 359; 1923, **26**, 83.

The results of the kinetic measurements are given in Tables 1—3,  $k_1$  being the first-order velocity constant ( $\text{sec.}^{-1}$ ) and  $k_2$  the second-order one ( $\text{l. mole}^{-1} \text{sec.}^{-1}$ ). Some solutions contained high concentrations both of acid and of ester, and in these there is a considerable difference between the molality  $m$  and the molarity  $c$  of the catalyst. Both are given, the measured densities of the solutions being used to inter-relate them.

TABLE 1. *Acid hydrolysis at 25°, by dilatometry.*

HCl	{	$c$	$m$	$10^7 k_1$	{	HCl	$c$	$m$	$10^7 k_1$	{	$\text{H}_2\text{SO}_4$	$c$	$m$	$10^7 k_1$
		1.94	2.16	148			7.18	8.69	861			1.54	1.74	142
		1.95	2.16	144			7.54	9.29	1180			3.44	4.12	390
		3.08	3.36	276			7.78	9.52	1020			4.72	5.99	589
		4.45	5.22	430			8.87	12.21	1270			5.71	7.79	793
5.94	7.22	677	10.39	15.44	1690									

TABLE 2. *Acid hydrolysis, by titration at 25° (except those marked,\* which are at 45°).*

HCl				HCl			$\text{H}_2\text{SO}_4$		
$10^2 c$	$10^2 m$	$10^2 [\text{KCl}]$	$10^7 k_1$	$10^2 c$	$10^2 m$	$10^7 k_1$	$10^2 c$	$10^2 m$	$10^7 k_1$
2.59*	2.59*	—	16.6*	4.7	5.1	3.88	11.0	11.6	11.3
5.19*	5.19*	—	31.0*	9.4	10.0	7.94	22.0	23.2	19.1
1.24	1.24	—	1.34	22.8	23.8	17.6	44.0	45.9	48.5
1.24	1.24	1.34	1.22	57.9	60.4	48.7	211	248	224
1.24	1.24	2.68	1.18	99.4	105	70.7			
1.24	1.24	4.53	1.14	191	216	121			

TABLE 3. *Alkaline hydrolysis, by titration.*

At 0°			At 25°			At 35°			At 45°		
$10^3 [\text{KCl}]$	$10^3 I$	$10^3 k_2$	$10^3 [\text{KCl}]$	$10^3 I$	$10^3 k_2$	$10^3 [\text{KCl}]$	$10^3 I$	$10^3 k_2$	$10^3 [\text{KCl}]$	$10^3 I$	$10^3 k_2$
—	9.41	35.9	—	9.6	146	—	9.6	255	—	9.4	438
21.1	30.6	39.2	21.1	30.8	167	52.8	62.5	331	21.1	30.6	504
52.8	62.3	41.2	52.8	62.5	193	106	115	372	52.8	62.3	557
106	115	48.3	106	115	215				62.3	71.7	586
106	115	51.1							84.5	93.9	658
									106	115	634

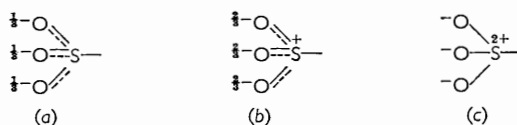
## DISCUSSION

The results show the large salt effects to be expected for reactions between two ions. The data are most extensive for alkaline hydrolysis, and the Figure shows plots of  $\log k_2$  against  $I^{1/2}/(1 + I^{1/2})$  at four temperatures. The lines are drawn with the theoretical slope of unity (the small temperature-dependence of the dielectric constant being neglected): this is in good agreement with experiment, and the velocity constants can be readily extrapolated to zero ionic strength. The extrapolated values at 0°, 25°, 35°, and 45° are  $k_2^0 = 0.0275, 0.120, 0.209, \text{ and } 0.363 \text{ l. mole}^{-1} \text{sec.}^{-1}$ , which are well represented by the Arrhenius equation  $k_2^0 = 2.30 \times 10^6 \exp(-9920/RT)$ . The results for hydrolysis by dilute acid show a similar salt effect in the opposite direction, and the results in 0.0124M-hydrochloric acid can be extrapolated by using the theoretical slope to give  $k^0/c = 1.44 \times 10^{-5} \text{ l. mole}^{-1} \text{sec.}^{-1}$  at zero ionic strength at 25°.

Although the salt effects show the behaviour expected for an ester containing a negatively charged substituent this is not so for the actual values of the velocity constants. Previous comparisons<sup>1,2</sup> of the ester  $^+\text{NET}_3 \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Et}$  with ethyl acetate showed that the presence of the group  $^+\text{NET}_3$  increases the rate of alkaline hydrolysis 200-fold and decreases that of acid hydrolysis 2000-fold, and the group  $-\text{SO}_3^-$  might be expected to show effects of similar magnitude in the opposite direction, especially since  $\text{CO}_2 \text{Et} \cdot \text{CH}_2 \cdot \text{CO}_2^-$  is hydrolysed by alkali 65 times more slowly than  $\text{CH}_2(\text{CO}_2 \text{Et})_2$ .<sup>7</sup> Actually, however, our results show that at 25° the species  $\text{SO}_3^- \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Et}$  is hydrolysed by alkali about 1.2 times as fast as ethyl acetate, and by acid about eight times more slowly. The key to this behaviour is to

<sup>7</sup> International Critical Tables, Vol. VII, p. 135.

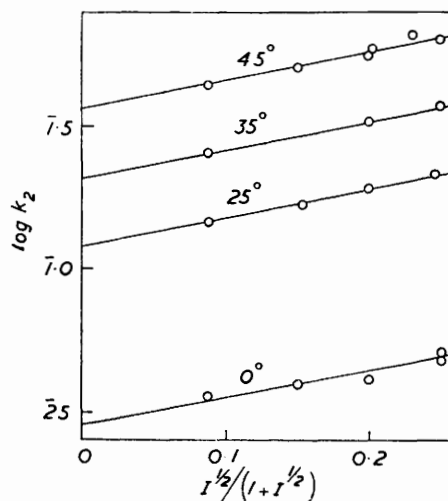
be found in the electronic structure of the sulphonate group. Various views have been expressed about the nature of sulphur-oxygen links, corresponding to the annexed formulations of the group  $-\text{SO}_3^-$ . It has been maintained<sup>8</sup> on the basis of observed bond-lengths that compounds of this class contain essentially double bonds between sulphur and oxygen, corresponding to structure (a), but this conclusion has been doubted<sup>9</sup> and the question appears to be open. In the present context structure (a) should certainly act as a strongly electron-repelling group, but structure (c) [and to a less extent (b)] could well act as an



electron-attracting group at short distances, since the positive charge on sulphur will then be more important than the more distant negative charge on oxygen. The kinetic results obtained here can therefore be accounted for if it is supposed that the bonds in the sulphonate group are essentially single, with a large positive charge on the sulphur atom. This explanation is not inconsistent with the observed salt effects in dilute solution, which depend upon long-range interionic forces and this involves only the net charge on the molecule.

Other evidence exists for the electron-attracting power of the sulphonate group at short distances. The  $\text{p}K$  of  $\text{SO}_3^-\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  is 4.05, compared with 4.75 for acetic acid and 5.36 for  $\text{CO}_2^-\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ : similarly  $\text{p}K$  for  $\text{CH}_3^+\cdot\text{NH}_3$  is 10.63 but  $\text{p}K$  for  $\text{SO}_3^-\cdot\text{CH}_2^+\cdot\text{NH}_3$  is 5.75,<sup>10</sup> the greater effect in the second case being due to the smaller distance between the sulphonate group and the dissociating proton. It is also relevant that the sulphonate group is weakly *meta*-directing in benzene substitution,<sup>11</sup> in contrast to the *ortho-para*-directing effect of other negatively charged groups.

It is of interest to consider how the effect of the sulphonate group should vary with its distance from the part of the molecule being considered, its structure being assumed to resemble (c). It follows from simple electrostatics that, as the distance increases, its electron-attracting power should decrease and change to repulsion at a distance of a few Ångström units. The electron-repulsion should then at first increase with increasing distance, but should soon pass through a maximum and finally decrease to zero. Data are not available for the series  $\text{SO}_3^-\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$  or the corresponding esters, but the acid strengths of the series<sup>10</sup>  $\text{SO}_3^-\cdot[\text{CH}_2]_n\cdot\text{NH}_3$ , with  $\text{p}K$  in parentheses following, are  $n$ : 1 (5.75), 2 (9.20), 3 (10.05), 4 (10.65), 5 (10.95), 10 (11.35). Since  $\text{p}K$  in the series  $\text{CH}_3\cdot[\text{CH}_2]_n\cdot\text{NH}_3$  is almost constant at  $10.62 \pm 0.03$ , these figures show the expected changes of sign in effect of the sulphonate group at about  $n = 4$ . The effective distance between the groups probably does not continue to increase for large values of  $n$ , since the chain is flexible and the oppositely charged ends will tend to approach one another. An analogous increase in electron-repelling power with distance is observed



<sup>8</sup> Hunter, Phillips, and Sutton, *J.*, 1945, 146.

<sup>9</sup> Wells, *J.*, 1949, 55.

<sup>10</sup> Rumpf, *Bull. Soc. chim. France*, 1938, 5, 87.

<sup>11</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Methuen, London, 1953, p. 235.

in the compounds  $\text{SeO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  ( $pK$  5.43) and  $\text{SeO}_2 \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$  ( $pK$  5.99)<sup>12</sup> and can be explained similarly.

The kinetic measurements in concentrated acid solution (cf. Table I) show that the reaction velocity increases somewhat more rapidly than the acid concentration (whether expressed as molality or molarity), but a great deal more slowly than the acidity function  $H_0$ . Since the ester has a negative charge the appropriate acidity function is  $H_-$  rather than  $H_0$ , but the meagre evidence available suggests that these two functions do not differ greatly.<sup>13</sup> The lack of parallelism between velocity and acidity function indicates that the transition state is not formed by the simple addition of a proton to the ester but probably also contains a water molecule: the same conclusion has been reached for the acid hydrolysis of uncharged esters.<sup>14</sup>

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[Received, July 28th, 1958.]

<sup>12</sup> Backer and van Dam, *Rec. Trav. chim.*, 1930, **49**, 482.

<sup>13</sup> Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

<sup>14</sup> Chmiel and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 3326; Bell, Dowding, and Noble, *J.*, 1955, 3106.

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