

Kinetics of the Depolymerisation of Paraldehyde in Aqueous Solution.

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Kinetic measurements are reported on the depolymerisation of paraldehyde at 25° in aqueous solutions of hydrochloric, perchloric, sulphuric, nitric, dichloroacetic, and trichloroacetic acids and of potassium hydrogen sulphate. The reaction is of the first order with respect to paraldehyde, and in solutions of the first four acids the rate depends simply upon the acidity function H_0 . Less simple behaviour is shown by solutions of the other three acids, where there appears also to be catalysis by undissociated species. The mechanism of depolymerisation is discussed in terms of these and earlier results.

THE depolymerisation of paraldehyde has previously been studied as a homogeneous gas reaction (Coffin, *Canadian J. Res.*, 1932, **7**, 75; Bell and Burnett, *Trans. Faraday Soc.*, 1938, **34**, 420), as an acid-catalysed gas reaction (Bell and Burnett, *ibid.*, 1937, **33**, 555), and as a reaction catalysed by solutions of both proton acids and Lewis acids in non-aqueous solvents (Bell, Lidwell, and Vaughan-Jackson, *J.*, 1936, 1792; Bell and Skinner, *J.*, 1952, 2955). The present paper extends this study to catalysis by aqueous solutions of acids. Measurements of this kind were reported by Skrabal, Stockmair, and Schreiner (*Z. physikal. Chem.*, 1934, **A**, **169**, 177), but were confined to solutions of toluene-*p*-sulphonic acid at a single concentration. Recent work (Walker and Chadwick, *Ind. Eng. Chem.*, 1947, **39**, 974; Paul, *J. Amer. Chem. Soc.*, 1950, **72**, 3813; 1952, **74**, 141) on the depolymerisation of the related substance trioxymethylene (trioxan) in concentrated aqueous acids at 40° indicates that the reaction velocity depends upon the Hammett acidity function of the catalyst solution, but the range of acids and concentrations used was somewhat limited. The present study embraces seven acids over a wide concentration range.

EXPERIMENTAL

Paraldehyde was redistilled (b. p. 121–122°) and used within a few days of distillation. Small amounts of acetaldehyde were formed on storage, but had no effect on the rate of depolymerisation. Older samples also contained traces of acetic acid, but this never exceeded 0.05%, and could thus be neglected in the catalyst solutions used. The acids used were "AnalaR" or pure laboratory reagents, and the concentration of their solutions was related by titration to constant-boiling hydrochloric acid.

All kinetic measurements were carried out at 25° ± 0.01°, and two different methods were used for following the reaction. In the first, the acetaldehyde formed was estimated by the method of Friedemann, Cotonio, and Shaffer (*J. Biol. Chem.*, 1927, **73**, 342). 0.2–0.3 g. of paraldehyde was dissolved in 100 c.c. of catalyst solution, and from time to time 5 c.c. were pipetted into 10 c.c. of *m*/5-sodium hydrogen sulphite solution. After the solution had stood for 15 min. most of the excess of hydrogen sulphite was removed with *N*/5-iodine solution, and the removal completed with *N*/30-iodine (starch indicator). The bisulphite compound was then decomposed by adding about 1 g. of sodium hydrogen carbonate, and the titration completed with *N*/30-iodine.

Titrations carried out after a long period of time gave titres corresponding to 94–98% depolymerisation. The deficiency is partly due to loss of acetaldehyde by evaporation, and perhaps also to formation of some polymer other than paraldehyde. These effects will only be appreciable in the final stages of the reaction, and we have calculated first-order velocity constants by plotting $\log(\alpha_\infty - \alpha_t)$ against t , where α_t is the observed titre at time t , and α_∞ is the titre for complete reaction calculated from the weight of paraldehyde taken. These plots were linear over at least 70% of the reaction, except in the experiments with nitric acid solutions. With these solutions there was certainly a secondary oxidation of the acetaldehyde formed, and in some instances the observed titres passed through a maximum. The velocity constants recorded for nitric acid solutions are therefore obtained from the first 20–25% of the reaction, and are less accurate than those for the other acids.

The second method used was dilatometric. The depolymerisation of paraldehyde in aqueous solution gives rise to an expansion of about 75 mm.³/g., compared with about

200 mm.³/g. for the pure liquid or for solutions in non-hydroxylic solvents (Bell, Lidwell, and Vaughan-Jackson, *loc. cit.*). The lower value in aqueous solution is attributable to the hydration of about 60% of the acetaldehyde, with a consequent decrease in volume (Bell and Clunie, *Trans. Faraday Soc.*, 1952, **48**, 439). The volume change is, however, ample for accurate kinetic measurements, and these were carried out in two conventional dilatometers, with capacities of 30 and 50 c.c. and capillaries of cross-sections 0.23 and 0.08 mm.² respectively. The paraldehyde concentration was chosen so as to give a total movement of 10–20 cm. in the capillary. The catalyst solution was de-gassed by suction just before the addition of the paraldehyde and the filling of the dilatometer, and reliable readings could be obtained 5 min. after mixing. First-order velocity constants were obtained graphically by Guggenheim's method (*Phil. Mag.*, 1926, **7**, 538) and no departures from first-order kinetics were detected. The dilatometric method is more convenient and accurate than the analytical one and was therefore employed in the majority of experiments: however, the results recorded later show that there is substantial agreement between the two methods.

There are no recorded data on the acidity functions of solutions of hydrogen sulphates or of dichloroacetic acid, and these were therefore measured by Hammett and Deyrup's indicator method (*J. Amer. Chem. Soc.*, 1932, **54**, 2721), *p*-nitroaniline being used. A visual Klett colorimeter was used, with a blue filter, and in calculating the value of H_0 the pK of the *p*-nitroanilinium ion was taken as 1.11 (Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 830). The values obtained are given in Table 1: their accuracy is estimated as ± 0.02 .

TABLE 1.

k = first-order velocity constant (sec.⁻¹). Acid concentrations are in moles/l. of solution.

* denotes that the analytical method was used for determining k .

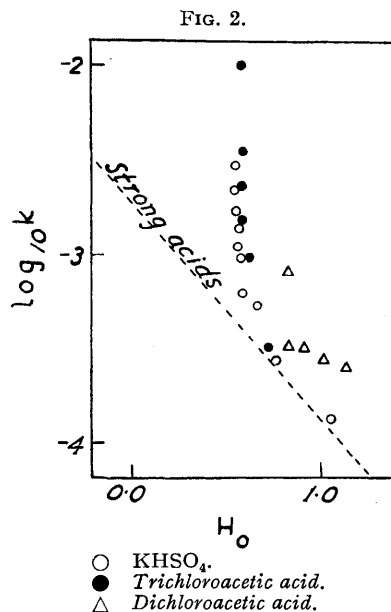
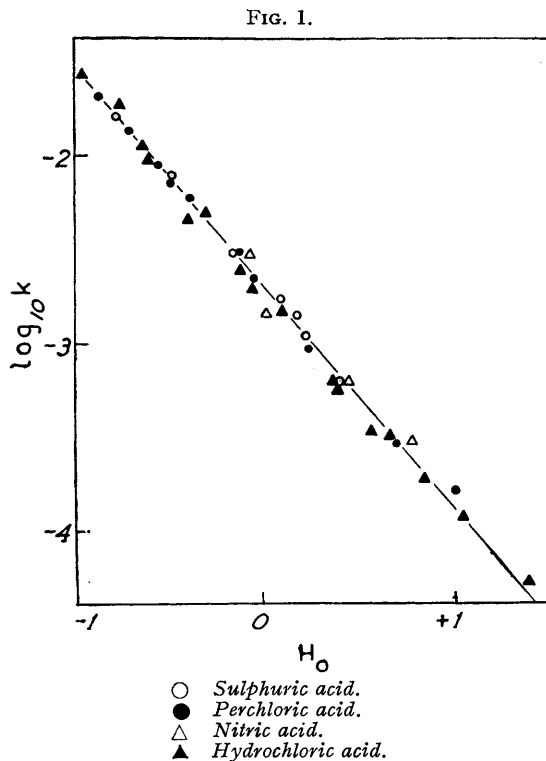
<i>Hydrochloric acid</i>										
[Acid] ...	0.0217	0.049	0.097	0.145	0.217	0.252	0.388	0.425	0.723	
10^5k	0.297	0.545 *	1.19 *	1.85 *	3.30	3.45 *	5.68	6.37 *	15.0	
H_0	1.74	1.39	1.05	0.84	0.67	0.56	0.39	0.35	0.10	
[Acid] ...	0.969	0.97	1.39	1.58	2.08	2.17	2.36	2.50	3.08	
10^5k	19.3	19.8 *	49.0 *	45.0 *	94.5 *	116	136 *	188	280 *	
H_0	-0.06	-0.06	-0.30	-0.39	-0.61	-0.64	-0.70	-0.76	-0.95	
<i>Perchloric acid</i>										
[Acid] ...	0.101	0.202	0.505	0.92	1.01	1.01	1.33	1.52	1.67	2.02
10^5k	1.63	2.98	9.75	22.2 *	31.5	24.3 *	60.2	70.2	89.8	138 *
H_0	1.00	0.69	0.23	-0.05	-0.13	-0.13	-0.38	-0.48	-0.55	-0.70
<i>Sulphuric acid</i>										
[Acid] ...	0.352	0.528	0.703	1.06	1.58	2.11				
10^5k	6.08	8.80	16.3	30.0	74.0	158				
H_0	0.40	0.22	0.09	-0.16	-0.48	-0.78				
<i>Nitric acid</i>										
[Acid] ...	0.186	0.372	0.558	0.744	0.930					
10^5k	3.07 *	6.30 *	14.0 *	19.7 *	31.3 *					
H_0	0.78	0.43	0.19	0.02	-0.07					
<i>Trichloroacetic acid</i>										
[Acid] ...	0.294	0.490	0.980	1.95	1.96	2.44	3.42	5.58		
10^5k	3.17	5.20 *	9.55 *	15.6	15.0 *	22.7	34.5	97.3		
H_0	0.72	0.66	0.62	0.58	0.58	0.58	0.58	0.58		
<i>Dichloroacetic acid</i>										
[Acid] ...	0.535	0.780	1.17	2.34	4.68					
10^5k	2.47	2.72	3.17	3.17	7.75					
H_0	1.13	1.01	0.91	0.82	0.82					
<i>Potassium hydrogen sulphate</i>										
[Acid] ...	0.241	0.510	1.02	1.33	1.52	1.70	2.04	2.28	2.66	
10^5k	1.31	2.67	6.07	9.38	10.7	13.3	16.8	21.7	29.2	
H_0	1.04	0.75	0.58	0.57	0.56	0.56	0.55	0.54	0.54	

Results.—The results of the kinetic measurements are given in Table 1. The acidity functions (H_0) given for hydrochloric, nitric, and trichloroacetic acids are taken from the work of Hammett and Paul (*loc. cit.*). Those for perchloric and sulphuric acid are from Hammett and Deyrup's measurements (*loc. cit.*), with allowance for the revision of the acidity scale made by Hammett and Paul. The concentrations recorded by these authors are in moles/1000 g. of solvent or in weight %: they have been converted to moles/l. by using the densities of the

solutions, and the values in the table obtained by graphical interpolation. The acidity functions for potassium hydrogen sulphate and dichloroacetic acid solutions are from our own measurements.

DISCUSSION

We shall consider first those acids which are substantially completely dissociated in the concentration range considered, *i.e.*, hydrochloric, perchloric, nitric, and sulphuric (first dissociation). In dilute solutions the reaction velocity is directly proportional to acid concentration, and independent of which acid is being used. The value given by Skrabal *et al.* (*loc. cit.*), $k = 0.68 \times 10^{-5} \text{ sec.}^{-1}$ in 0.05M-toluene-*p*-sulphonic acid, is also



concordant with ours. In more concentrated solutions the reaction velocity increases more rapidly than the concentration, and is in fact roughly proportional to the square of the concentration above about 0.5M. Over the whole concentration range the reaction velocity runs closely parallel with the Hammett acidity function. This is illustrated in Fig. 1, which shows a plot of $\log_{10} k$ against H_0 for the four strong acids. There is some tendency for the plot to curve upwards at higher concentrations, and the straight line in the figure has a slope a little greater than unity (1.16): however, these deviations are much more marked if $\log_{10} [\text{acid}]$ is plotted in place of H_0 .

The remaining acids (trichloroacetic, dichloroacetic, and the hydrogen sulphate ion) are incompletely dissociated at the concentrations employed, and for these solutions there is no parallelism with the acidity function. Fig. 2 shows a plot of $\log_{10} k$ against H_0 , the broken line representing the relation found for the four strong acids. The velocity is in each case considerably greater than would be expected from the acidity function, as was also found in the inversion of sucrose by solutions of trichloroacetic acid (Hammett and Paul, *loc. cit.*). This behaviour suggests that in these solutions there is catalysis not only by hydrogen ions, but also by other acidic species; or, expressed in other words, that the transition state of the reaction can associate specifically with the anions $\text{CCl}_3\text{CO}_2^-$,

$\text{CHCl}_2 \cdot \text{CO}_2^-$, and SO_4^- in a manner not paralleled by the cation produced in the indicator measurements of H_0 .

There is no reliable information about the degree of dissociation of the concentrated solutions of di- and tri-chloroacetic acid used, but an estimate can be made for the hydrogen sulphate solutions. Young and Blatz (*Chem. Reviews*, 1949, **44**, 98) have re-interpreted Rao's measurements (*Indian J. Phys.*, 1940, **14**, 143) on the Raman effect in 3–10M-sulphuric acid, and deduce values for the concentration dissociation constant of HSO_4^- (K'_2) in this range. Davies, Jones, and Monk (*Trans. Faraday Soc.*, 1952, **48**, 921) have critically considered various measurements on solutions of sulphuric acid and hydrogen sulphates, and give a table of K'_2 for sulphuric acid solutions up to 0.05M. By combining these two sets of results we can interpolate roughly the value of K'_2 for intermediate concentrations, and if it is assumed that K'_2 has the same value in solutions of H_2SO_4 and KHSO_4 of the same concentration it is possible to calculate the composition of the KHSO_4 solutions used in the present work. The results obtained are given in the first three columns of Table 2: they are approximate only, but show clearly that the reaction velocity increases much more rapidly than the hydrogen-ion concentration.

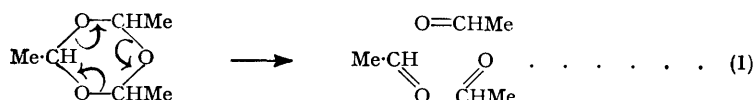
TABLE 2. *Catalysis by hydrogen sulphate solutions.*

[KHSO ₄]	[HSO ₄ ⁻]	[H ⁺]	10 ⁵ <i>k</i>	10 ⁵ <i>k</i> (H ⁺)	10 ⁵ { <i>k</i> - <i>k</i> (H ⁺)} / [HSO ₄ ⁻] ²
0.241	0.153	0.088	1.31	1.1	(14)
0.510	0.360	0.150	2.67	2.0	5.2
1.02	0.77	0.25	6.07	3.3	4.7
1.33	1.03	0.30	9.38	4.2	4.9
1.52	1.19	0.33	10.7	4.7	4.2
1.70	1.33	0.37	13.3	5.2	4.6
2.04	1.61	0.43	16.8	6.7	3.9
2.28	1.79	0.47	21.7	7.3	4.5
2.66	2.11	0.55	29.2	8.8	4.6

We can make an approximate allowance for catalysis by hydrogen ions by subtracting the velocity observed in a hydrochloric solution of concentration equal to $[\text{H}^+]$: these velocities are shown as $k(\text{H}^+)$ in col. 5 of Table 2. The constancy of the ratio given in the last column of the table shows that the remaining velocity is closely proportional to $[\text{HSO}_4^-]^2$. This conclusion cannot claim much quantitative weight, but there seems no doubt that the concentration of hydrogen sulphate ion enters the kinetic expression to a power greater than unity. It is likely that the same is true for catalysis by undissociated di- and tri-chloroacetic acids, though reliable data are lacking on the degree of dissociation of their aqueous solutions: an apparent kinetic order greater than unity (1.5–2.5) is also found when the depolymerisation of paraldehyde is catalysed by solutions of proton acids or of Lewis acids in non-dissociating solvents (Bell, Burnett, and Vaughan-Jackson, *loc. cit.*; Bell and Skinner, *loc. cit.*). Quite apart from any kinetic considerations, it is strange that the acidity functions of all three acids (dichloroacetic, trichloroacetic, and potassium hydrogen sulphate) should become almost independent of concentration in their more concentrated solutions, in spite of considerable variations in hydrogen-ion concentration. We cannot suggest any explanation for this behaviour.

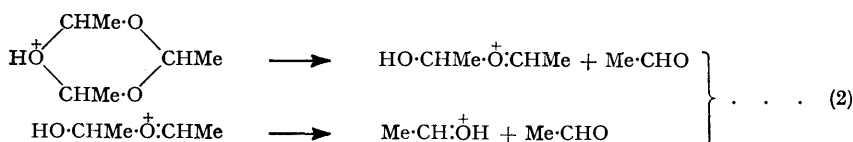
We shall now consider the bearing of these results on the mechanism of depolymerisation. The proportionality between $-\log_{10} k$ and H_0 for the four strong acids suggests that the transition state is formed by the simple addition of a proton to a paraldehyde molecule, without the intervention of a water molecule (Hammett and Deyrup; Hammett and Paul, *loc. cit.*). The same conclusion had already been reached by Paul (*loc. cit.*) for the analogous depolymerisation of trioxymethylene, though on less complete evidence. As mentioned on p. 774, the depolymerisation of paraldehyde takes place readily under a variety of conditions in the absence of water or any similar molecule: for example, as a gas reaction (catalysed and uncatalysed) and in solutions of either proton acids or electron-acceptor molecules in aprotic solvents. This suggests that even in aqueous solution the water molecule is not concerned in any stage of the reaction: this contrasts with the view of Skrabal, Stockmair, and Schreiner (*loc. cit.*), who regard the reaction as analogous to the hydrolysis of acetals and ethers, taking place through the intermediate semiacetal $\text{HO} \cdot \text{CHMe} \cdot \text{O} \cdot \text{CHMe} \cdot \text{O} \cdot \text{CHMe} \cdot \text{OH}$. However, it should be noted that cyclic trimeric

aldehydes such as paraldehyde differ structurally from other ethers and acetals in that they can break down by a simple electronic re-arrangement, *e.g.*,



and it therefore seems natural to assume that this type of mechanism operates both in the presence and in the absence of water.

If the non-hydrolytic mechanism is accepted, we must explain the part played by the acid catalyst. Since the change represented in (1) involves the passage of electrons from one side of the oxygen atom to the other, it may be supposed that the presence of a positive charge on the oxygen (produced by a proton or other acceptor molecule) will facilitate this change. An alternative view is as follows. In the absence of a catalyst the removal of a single acetaldehyde molecule from the paraldehyde ring would leave behind an unstable species (either a di-radical or the ion $\text{O}^-\text{CHMe}\cdot\text{O}^+\text{CHMe}$), and it is more probable that depolymerisation takes place in a single step. In the catalysed reaction, on the other hand, it is easy to picture successive steps such as



and the function of the catalyst may be to enable the reaction to take place in stages.

The kinetic orders of reaction reported in this and earlier papers suggest strongly that depolymerisation can be effected by the attachment of a single hydrogen ion to the paraldehyde molecule, while in catalysis by uncharged acids and by HSO_4^- the simultaneous action of two catalyst molecules is much more effective. This behaviour is reasonably accounted for by the fact that the ring has to be broken in two places in order to complete depolymerisation. In catalysis by hydrogen ions simultaneous attachment to two oxygens will be hindered by the mutual repulsion of the positive charges, and a step-wise mechanism such as (2) is more feasible, while with the other types of catalyst the proximity of an anion (*e.g.*, $\text{R}\cdot\text{CO}_2^-$, SO_4^-) will partly neutralise the repulsion between the positive charges.

There is, however, some ambiguity in assigning a kinetic order to this reaction. The results for aqueous solutions of strong acids could be represented in the form $k = k_1[\text{acid}] + k_2[\text{acid}]^2$, the second term dominating at higher concentrations, though we have preferred here to interpret them in terms of a reaction depending upon the first power of the acidity function.* Conversely, the high catalytic orders assigned to solutions of carboxylic acids in non-aqueous solvents (Bell, Lidwell, and Vaughan-Jackson, *loc. cit.*) might disappear if the results were interpreted in terms of acidity functions. No data are available on the acidities of such solutions, though some indicator and e.m.f. measurements suggest that in hydrocarbon solvents the acidity increases more rapidly than the concentration (La Mer and Downes, *J. Amer. Chem. Soc.*, 1931, **53**, 888; Griffiths, *J.*, 1938, 818). However, the following facts are unaffected by these uncertainties: (a) in dilute aqueous solutions of strong acids the reaction velocity is proportional to the first power of the catalyst concentration, and (b) in dilute solutions of hydrogen chloride and of Lewis acids in non-dissociating solvents the reaction velocity is proportional to the square of the catalyst concentration. These facts demand an explanation of the type given in the last paragraph.

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* The fact that the line in Fig. 1 has a slope slightly greater than unity may indicate a small contribution proportional to the square of the acidity function.