262. *Kinetics of the Depolymerisation of Trioxan in Aqueous Acids, and the Acidic Properties of Aqueous Hydrogen Fluoride.*

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Measurements have been made of the rate of depolymerisation of trioxan at 25° in concentrated aqueous solutions of hydrochloric, perchloric, sulphuric, and hydrofluoric acids, together with the acidity functions (obtained from indicator measurements) of aqueous hydrofluoric acid up to 43 per cent. by weight. For all the catalyst solutions used the rate of depolymerisation is more closly related to the acidity function of the solution than to its concentration, thus indicating that the transition state of the reaction does not involve a water molecule. Although hydrofluoric acid is a weak acid in dilute solution, its acidity increases rapidly with concentration in the range 5—15M, and in the most concentrated solutions it simulates the behaviour of a strong acid. It is shown that this can be accounted for in terms of the successive formation of the species HF_2^-, $H_2F_3^-$, and $H_3F_4^-$.

It has been previously shown [1] that the depolymerisation of paraldehyde in aqueous solutions of strong acids is a first-order reaction whose velocity is closely related to the acidity function of the acid solution. The present paper reports a similar study of the depolymerisation of the related substance trioxan (trioxymethylene). This reaction has previously been investigated by Skrabal, Stockmair, and Schreiner,[2] who used as catalyst only toluene-*p*-sulphonic acid at a single concentration, and also by Walker and Chadwick,[3] who studied a limited range of concentrations of phosphoric acid at 40°. Paul [4] showed that Walker and Chadwick's results could be correlated with the acidity functions of the catalyst solutions, and the same author demonstrated a similar correlation for the rate of depolymerisation in mixtures of perchloric acid and perchlorates.[5] However, the concentration range covered is small, and most of the kinetic results refer to 40°, while the acidity functions were measured at room temperature.

The catalysts studied in the present investigation include aqueous hydrogen fluoride up to 50 per cent. by weight. In dilute aqueous solutions hydrofluoric acid is a weak acid, and the presence of the bifluoride ion does not cause any complications in the catalytic behaviour of these solutions.[6] On the other hand, anhydrous hydrogen fluoride is one of the most strongly acidic media known, and it is therefore of interest to follow the change in acid properties with change of concentration. In addition to the kinetic measurements, the acidity functions of aqueous hydrogen fluoride solutions have been measured by means of indicators.

EXPERIMENTAL

A commercial sample of trioxan (Eastman Organic Chemicals) was used without further purification. It gave no detectable free formaldehyde on dissolving in water, and when set aside overnight with 50 per cent. sulphuric acid produced more than 99% of the theoretical quantity of formaldehyde, as estimated by the method described below. The solutions of hydrochloric, perchloric, and sulphuric acids were made from " AnalaR " reagents, and were titrated with sodium hydroxide solution which had been standardised against constant-boiling hydrochloric acid. Solutions of hydrofluoric acid in the range 40—60% were made by passing hydrogen fluoride gas from a cylinder into the " AnalaR " acid. All solutions containing hydrofluoric acid were kept in Polythene vessels. Acid concentrations are expressed throughout in moles per litre of solution, the percentage of hydrogen fluoride by weight being also given for the solutions of this acid.

In the kinetic experiments, 1—3 g. of trioxan were dissolved in 50 c.c. of the acid solution at 25°, and the reaction was followed by estimating formaldehyde at intervals in 5 c.c. samples.

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[1] Bell and Brown, *J.*, 1954, 774.
[2] Skrabal, Stockmair, and Schreiner, *Z. phys. Chem.*, *A*, 1934, **169**, 177.
[3] Walker and Chadwick, *Ind. Eng. Chem.*, 1947, **39**, 974.
[4] Paul, *J. Amer. Chem. Soc.*, 1950, **72**, 3813.
[5] *Idem, ibid.*, 1952, **74**, 141.
[6] Bell and McCoubrey, *Proc. Roy. Soc.*, 1956, *A*, **234**, 192.

The sample was added to a known excess of N/10- or N/100-iodine solution, and an excess of 2N-sodium hydroxide solution added immediately. After 10—30 minutes (to complete the oxidation of the formaldehyde to formic acid), the solution was acidified with 2N-hydrochloric acid, and the unchanged iodine titrated with N/10- or N/100-sodium thiosulphate solution. In most of the experiments less than 10% of the total reaction was followed, so that no evidence was obtained as to the order of the reaction. However, in the more concentrated solutions of hydrofluoric acid the course of the reaction was accurately of the first order over more than 75% depolymerisation : further, the reaction velocity was proportional to the trioxan concentration over a three-fold range. The first-order velocity constants were obtained from a plot against time of $\log_{10}$ [trioxan], or, for the slowest reactions, by plotting [formaldehyde] against time and dividing the slope of this line by the initial trioxan concentration. The initial formaldehyde content of the trioxan solutions was negligible, but in some experiments the first one or two titres (corresponding to $<0{\cdot}5\%$ of the reaction) showed a slightly more rapid formaldehyde production than the remainder of the reaction. This may be due to the presence in the trioxan of a very small amount of a less stable polymer of formaldehyde, conceivably the less stable conformation of trioxan itself.

TABLE 1. *Depolymerisation of trioxan at 25°.*

c = acid concentration, mole/l. of solution. k = first-order velocity constant (sec.$^{-1}$)

Hydrochloric acid

c	0·0469	0·0778	0·0798	0·220	0·375	0·590	0·755	0·960	1·17
10^8k ...	0·218	0·238	0·275	0·636	1·38	2·67	4·02	6·11	7·75
H_0	+1·42	+1·17	+1·16	+0·67	+0·42	+0·20	+0·08	−0·04	−0·17
c	1·41	1·62	1·75	1·99	2·32	2·70	2·82	3·03	3·27
10^8k ...	10·5	13·7	15·1	22·1	32·4	50·9	55·6	68·1	91
H_0	−0·29	−0·39	−0·44	−0·54	−0·67	−0·82	−0·86	−0·93	−1·02
c	3·50	3·64	3·70	3·81	3·96	4·46	4·92	5·40	5·92
10^8k ...	112	131	132	154	178	283	410	603	1070
H_0	−1·10	−1·15	−1·17	−1·21	−1·26	−1·44	−1·60	−1·77	−1·95

Perchloric acid

c	0·765	1·00	1·24	1·50	1·78	2·23	2·81	3·26	3·75
10^8k ...	3·78	6·22	8·61	14·7	19·3	34·4	75·0	130	262
H_0	+0·08	−0·12	−0·27	−0·44	−0·56	−0·76	−1·01	−1·22	−1·46
c	4·19	4·23	4·93	5·14					
10^8k ...	384	503	1340	2040					
H_0	−1·67	−1·69	−2·07	−2·20					

Sulphuric acid

c	0·260	0·360	0·488	0·760	1·00	1·28	1·48	2·09	2·42
10^8k ...	1·12	1·73	2·64	4·42	6·64	10·4	13·2	33·3	47·9
H_0	+0·54	+0·39	+0·26	+0·03	−0·13	−0·30	−0·41	−0·75	−0·92
c	2·56	3·05	3·48	4·00	4·59				
10^8k ...	59·0	117	197	356	673				
H_0	−0·99	−1·25	−1·45	−1·68	−1·95				

Hydrofluoric acid

%HF	1·44	1·80	2·55	3·91	6·81	8·36	12·4	151	15·5	26·9	30·2
c	0·72	0·91	1·30	2·06	3·50	4·61	6·60	7·95	8·20	14·9	16·9
10^8k ...	0·17	0·19	0·24	0·63	1·15	1·65	4·4	6·9	8·6	70	192
H_0 ...	+1·39	+1·33	+1·25	+1·00	+0·58	+0·48	+0·20	+0·02	−0·02	−0·87	−1·10
%HF	31·0	33·2	36·9	39·2	43·5	48·5	48·8	51·6	53·7	53·8	
c	17·4	18·9	21·2	22·7	25·5	29·6	29·8	31·0	32·6	32·8	
10^8k ...	198	339	870	2300	6590	28,200	30,400	85,700	205,000	223,000	
H_0 ...	−1·16	−1·33	−1·62	−1·81	−2·15	—	—	—	—	—	

The acidity functions given in Table 1 for hydrochloric, sulphuric, and perchloric acids are interpolated from the results of Hammett and his co-workers.[7] Those for hydrofluoric acid are interpolated from our own measurements, which are recorded in Table 2 and shown graphically in Fig. 1. These were made with a Hilger "Spekker" photoelectric absorptiometer, the mercury line 3650 Å being used for the indicator *p*-nitroaniline, and the 4047 Å line for *o*-nitroaniline and 4-chloro-2-nitroaniline. The solutions were made up in a poly(vinyl chloride) weighing bottle, brought to 25°, and transferred for measurement to a cell constructed by

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[7] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827.

TABLE 2. *Acidity functions of aqueous hydrogen fluoride at* 25°.

Indicator, p-*nitroaniline*; pK = 1·11

%HF	2·07	2·17	2·72	2·80	4·66	7·97	9·81	11·1	12·1	13·7	15·0	17·5
c	1·07	1·12	1·40	1·44	2·43	4·10	5·12	5·65	6·30	7·20	7·95	9·35
H_0 ...	+1·33	+1·26	+1·23	+1·11	+0·90	+0·50	+0·38	+0·27	+0·23	+0·09	+0·04	−0·19

Indicator, o-*nitroaniline*; pK = −0·15

%HF	15·1	17·5	22·7	25·3	31·3	33·7	37·1
c	8·00	9·35	12·4	14·0	17·6	19·2	21·3
H_0 ...	−0·03	−0·18	−0·58	−0·82	−1·09	−1·38	−1·65

Indicator, 4-*chloro*-2-*nitroaniline*; pK = −0·91

%HF	32·8	38·9	40·8	42·7
c	18·6	22·5	23·7	25·0
H_0 ...	−1·38	−1·71	−1·97	−2·10

cementing together Perspex sheet with a solution of Perspex in dichloroethylene. Measurements were made as rapidly as possible, and the cell was washed out immediately after use. In this way it could be used a number of times without appreciable optical deterioration, though a check was made by measuring the optical density of the cell filled with water before and after each measurement with acid. The values of the acidity function H_0 were calculated in the usual way, using the pK values given by Hammett[7] for the three indicators.

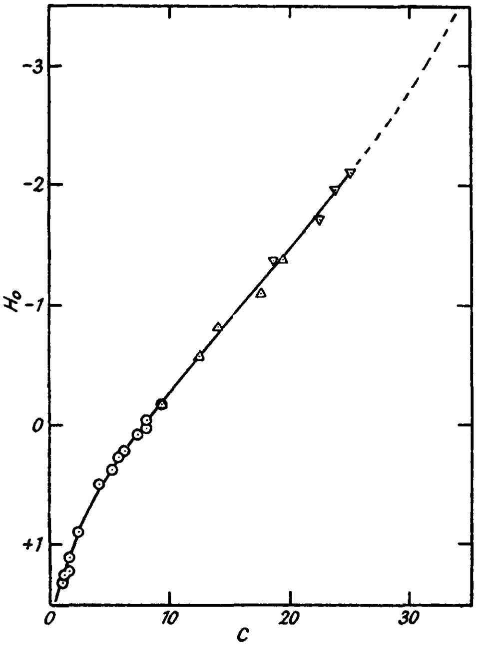


FIG. 1.

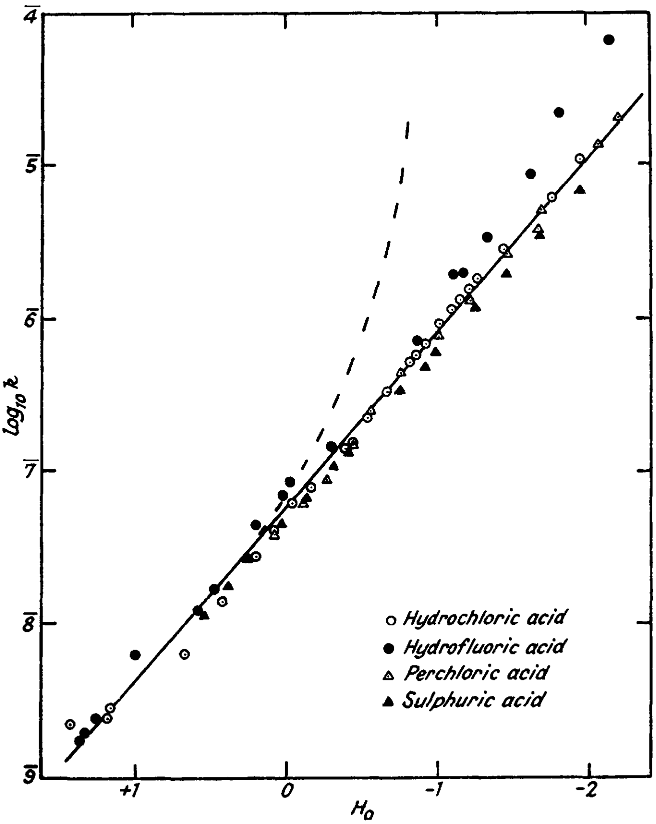
⊙, *p*-Nitroaniline.
△, *o*-Nitroaniline.
▽, 4-Chloro-2-nitroaniline.

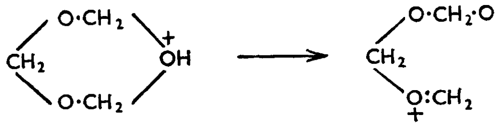
DISCUSSION

Like the analogous reaction of paraldehyde,[1] the depolymerisation of trioxan shows a close relation between the reaction velocity and the acidity function of the catalyst solution. This is shown by Fig. 2, in which $\log_{10}k$ is plotted against H_0. There are small systematic deviations between the results for hydrochloric, perchloric, and sulphuric acids, but on the whole the results are well represented by the straight line drawn in the diagram, which has a slope of 1·2. The broken line in Fig. 2 represents the result of plotting $-\log_{10}c$ in place of H_0 for the experiments with hydrochloric acid. Similar curved plots are obtained for the other strong acids, and it is clear that the reaction velocity follows the acidity function much more closly than it does the acid concentration.

The conclusion to be drawn from this is that in the depolymerisation of trioxan in aqueous solution no water molecule is included in the transition state. The same conclusion had been reached for the depolymerisation of paraldehyde, and there is the further parallel that both reactions can take place as uncatalysed, homogeneous, gas reactions,[8] as acid-catalysed, heterogeneous, gas reactions, and also as acid-catalysed reactions in non-hydroxylic solvents.[9] No water molecules are available under these conditions, and it is also interesting to note that trioxan can be depolymerised by passing its vapour over a sulphonic acid resin catalyst,[10] and paraldehyde by shaking a toluene solution with an " acidic " alumina–silica catalyst.[11] There is a close analogy between the depolymerisation reactions and the hydrolysis of methylal, for which there is again a parallelism between reaction velocity and acidity function.[12] Although a water molecule is of course ultimately involved, the rate-determining step is believed to be $\mathrm{CH_2(OMe){\cdot}\overset{+}{O}HMe \longrightarrow CH_2{:}\overset{+}{O}Me + MeOH}$, the corresponding step in the trioxan depolymerisation being :

FIG. 2.





All these reactions give a slope somewhat greater than unity for the plot of $\log_{10}k$ against H_0. This may be associated with the presence of several equivalent oxygen atoms in these

[8] Bell and Burnett, *Trans. Faraday Soc.*, 1938, **34**, 420.

[9] *Idem, ibid.*, 1939, **35**, 474.

[10] Schnizer, Fisher, and Maclean, *J. Amer. Chem. Soc.*, 1953, **75**, 4347.

[11] T. Spencer, unpublished work in this laboratory.

[12] McIntyre and Long, *J. Amer. Chem. Soc.*, 1954, **76**, 3240.

molecules, thus allowing the attachment of more than one proton, but it more probably arises from the limitations inherent in the concept of the acidity function as a universally valid measure of acidity. Thus, it may be noted that all these reactions involve the attachment of a proton to an oxygen atom, while the indicators used in measuring H_0 are nitrogen bases.

The results for hydrofluoric acid also fit the plot of Fig. 2, although in dilute aqueous solution it is a weak acid with a dissociation constant of about 7×10^{-4}. There is little information available about the acid properties of concentrated solutions of weak acids, but the present finding for hydrofluoric acid contrasts with the results of Bell and Brown [1] for the depolymerisation of paraldehyde in solutions of dichloroacetic and trichloroacetic acids, and of sodium hydrogen sulphate, where the reaction velocity increased with concentration in a range where the acidity function is almost stationary. However, in the present work both the kinetic and the indicator results agree in showing that the acidity of hydrofluoric acid solutions increases very rapidly in the range 10—50% by weight, and it is of interest to seek an interpretation of this behaviour.

The strong acids hydrochloric, hydrobromic, perchloric, and sulphuric (first dissociation) give very similar curves when H_0 is plotted against the molar concentration, c, at least up to acidities of about $H_0 = -2$. At the higher concentrations H_0 is numerically very much greater than $-\log_{10}c$, the discrepancy increasing with increasing concentration. It seems reasonable to regard this behaviour primarily as a property of the hydrogen ion in aqueous solution, probably connected with the associated structure of water. For a weak acid dissociating according to the simple scheme, $HX \rightleftharpoons H^+ + X^-$, the value of $[H^+]$ is approximately proportional to $c^{\frac{1}{2}}$ in concentrated solutions, and if the dissociation constant $K < 0{\cdot}1$, then $[H^+]$ will never appreciably exceed unity in solutions of attainable concentrations. This corresponds with the experimental fact that in concentrated solutions of dichloro-, trichloro-, and trifluoro-acetic acid [1, 13] the acidity varies little with the concentration and barely exceeds $H_0 = 0$. Although the dissociation constant of hydrofluoric acid is only 7×10^{-4}, this acid shows an entirely different type of behaviour, and the acidity rises to about $H_0 = -3{\cdot}3$ at the highest concentrations studied. (In Fig. 1 the part of the curve for concentrations above 43% of hydrofluoric acid is constructed from the kinetic results, it being assumed that the straight line in Fig. 2 can be extrapolated.) We attribute this to the fact that in concentrated solutions its dissociation is not even approximately represented by $HF \rightleftharpoons H^+ + F^-$. There is good evidence for the existence of HF_2^- even in dilute solutions, and the value of the constant $[HF_2^-]/[HF][F^-] = 3{\cdot}97$ (cf. Broene and de Vries [14]) means that there is little free fluoride ion present in any of the solutions which we have used. It is also extremely probable (and supported by evidence from infrared spectra [15]) that larger ions of the general formula $H_{n-1}F_n^-$ are present in the more concentrated solutions, since there exist several series of solid acid fluorides, such as KHF_2, KH_2F_3, KH_3F_4, and KH_4F_5. On the other hand, it is unlikely that polymers of undissociated hydrogen fluoride exist to an appreciable extent in aqueous solutions, though they do so in the vapour. There is no evidence for the presence of H_2F_2 in aqueous solutions known to contain HF_2^- and H^+, and it is commonly described as a strong acid. This can be ascribed to the spread of the negative charge over the two fluorine atoms in the species HF_2^-, thus stabilising the anion relative to the undissociated acid, and the same argument will apply to the ions $H_2F_3^-$, $H_3F_4^-$, etc.

The observed variations of acidity with concentration can be explained along these lines. Suppose for simplicity that one ion, $H_{n-1}F_n^-$, predominates over a certain concentration range. The equilibrium governing the hydrogen ion concentration is then $n\text{HF} \rightleftharpoons H^+ + H_{n-1}F_n^-$, and we have approximately $[H^+] \propto [HF]^{n/2}$. If $n > 2$, $[H^+]$ will at first increase more rapidly than the stoicheiometric acid concentration c, and at high concentrations will tend to a value c/n; *i.e.*, the solution will behave like a strong acid of this concentration. This corresponds closely with the behaviour observed, as shown in Fig. 1. In the more dilute solutions the acidity is low, corresponding to that of

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[13] Randles and Tedder, *J.*, 1955, 1218.

[14] Broene and de Vries, *J. Amer. Chem. Soc.*, 1947, **69**, 1644.

[15] Jones and Penneman, *J. Chem. Phys.*, 1954, **22**, 781.

hydrochloric acid solutions of concentrations about 0·05*c*. In this range the main anionic species is HF_2^-, and we have $[H^+][HF_2^-]/[HF]_2 = \{[H^+][F^-]/[HF]\}\{[HF_2^-]/[HF][F^-]\} = 3 \times 10^{-3}$ (cf. Broene and de Vries[14]), whence $[H^+]/[HF] = (3 \times 10^{-3})^{\frac{1}{2}} = 0{\cdot}055$, independent of concentration. Between $c = 5$ and $c = 15$ the acidity increases rapidly, and above $c = 15$ it is equal to that of hydrochloric acid solutions between $c/4$ and $c/3$. In this higher concentration range the formation of $H_2F_3^-$ and $H_3F_4^-$ will lead to a rapid increase in $[H^+]$, and the behaviour of the most concentrated solutions suggests that here we have essentially a strong acid $H^+ + H_2F_3^-$ or $H^+ + H_3F_4^-$. It is not profitable to attempt a more quantitative treatment in the absence of independent information about the species present in solution and their activity coefficients.

It is noteworthy that the acidity functions of concentrated phosphoric acid solutions show a concentration dependence resembling that of hydrofluoric acid, and unlike the other weak acids.[16] It seems likely that this also is due to the formation of complex anions of strong acids, this time with the elimination of water : thus a typical ionisation scheme might be $nH_3PO_4 \rightleftharpoons H_{n+1}P_nO_{3n+1}^- + (n-1)H_2O + H^+$, with consequences similar to those for hydrofluoric acid.

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[16] Heilbronner and Weber, *Helv. Chim. Acta*, 1949, **32**, 1513.