399. *Acid Catalysis in Non-aqueous Solvents. Part IV. The Depolymerisation of Paraldehyde.*

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BOTH acetaldehyde and paraldehyde can be kept indefinitely at the ordinary temperature, but at high temperatures or in the presence of a catalyst an equilibrium mixture of the two substances is formed. In the pure liquid at the ordinary temperature the equilibrium mixture contains about 80% paraldehyde, while in the gas above 200° paraldehyde changes almost completely to acetaldehyde. The latter change has been studied kinetically (Coffin, *Canadian J. Res.*, 1932, **7**, 75) and shown to be homogeneous and unimolecular. At the ordinary temperature the attainment of equilibrium is reported to be catalysed by hydrochloric, sulphuric, nitric, phosphoric, and trichloroacetic acids and by carbonyl chloride and sulphur dioxide (see especially Turbaba, " Aus dem Gebiet der Katalyse," Tomsk, Verlag d. Techn. Hochschule, 1901), which suggests that there is general acid catalysis. However, the only kinetic measurements on the catalysed reaction are those of Hatcher and Brodie (*Canadian J. Res.*, 1931, **4**, 574) and Hatcher and Kay (*ibid.*, 1932, **7**, 337), who studied the polymerisation of acetaldehyde in benzene solution in presence of syrupy phosphoric acid. The present paper describes a preliminary investigation of the depolymerisation of paraldehyde, which goes almost to completion in dilute solution and should be kinetically simpler than the reverse change. In aqueous solution the position is complicated by the irreversible polymerisation of acetaldehyde to give aldol, crotonaldehyde and other products. The present work was therefore carried out with solutions of acids in a number of non-dissociating organic solvents. This type of solvent has the additional advantage that there are no complications due to the formation of fresh catalytic species by protolytic reaction between the acid and the solvent (cf. Bell, *Proc. Roy. Soc.*, *A*, 1934, **143**, 377).

EXPERIMENTAL.

Measurement of Reaction Velocity.—Two different methods were used for following the reaction, the first dilatometric and the second analytical. The first method is only practicable for temperatures which can be controlled to within 0·01°.

Dilatometric method. The conversion of paraldehyde into acetaldehyde is accompanied by a volume increase of about 20%, so that in 20 c.c. of 1% solution the volume change is 40 cu. mm., which is ample for accurate measurement. More dilute solutions would still give a sufficient volume change, but owing to the high coefficient of expansion of the solvents used, the effect of very small temperature fluctuations would become appreciable. It is not possible to use taps with these solvents, and the dilatometers were therefore sealed : this made it difficult to measure any but slow reactions. Rough comparison of the observed and the calculated volume changes showed that in 1% solution the end-point corresponds to about 80% acetaldehyde. In each experiment 20—30 readings were taken over the first 50—70% of the reaction, and unimolecular constants calculated by the method of plotting devised by Guggenheim (*Phil. Mag.*, 1926, **7**, 538). These plots gave good straight lines, showing that the reverse reaction can be neglected over the range measured. The unimolecular nature of the reaction is illustrated by Table I, which gives the data for a typical experiment.

TABLE I.

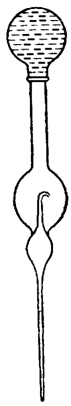
0·0824*N*-Trichloroacetic acid in nitrobenzene at 20°. $k = 0·0117$. Interval between first and second sets of readings = 90 mins. Calculated values from the equation

$$\log_{10}(r_2 - r_1) = 0·895 - 0·0117t.$$

t	$\log_{10}(r_2 - r_1)$.		Diff.	t	$\log_{10}(r_2 - r_1)$.		Diff.	t	$\log_{10}(r_2 - r_1)$.		Diff.
(mins.).	Obs.	Calc.	$\times 10^3$.	(mins.).	Obs.	Calc.	$\times 10^3$.	(mins.).	Obs.	Calc.	$\times 10^3$.
20	0·661	0·661	± 0	37·5	0·455	0·456	− 1	55	0·250	0·251	− 1
22·5	0·633	0·632	+ 1	40	0·427	0·427	± 0	57·5	0·223	0·222	+ 1
25	0·602	0·603	− 1	42·5	0·400	0·398	+ 2	60	0·193	0·193	± 0
27·5	0·571	0·573	− 2	45	0·367	0·368	− 1	62·5	0·167	0·164	+ 3
30	0·544	0·544	± 0	47·5	0·337	0·339	− 2	65	0·137	0·135	+ 2
32·5	0·513	0·515	− 2	50	0·310	0·310	± 0	70	0·076	0·076	± 0
35	0·489	0·485	+ 4	52·5	0·281	0·281	± 0				

In some of the slower reactions a small correction was applied for loss of liquid by evaporation from the capillary. Experiments with pure solvents showed that there was no measurable " spontaneous " change at the temperatures employed (20° and 30°).

Analytical method. The amount of acetaldehyde formed was determined by the bisulphite method of Friedmann, Cotonio, and Schaffer (*J. Biol. Chem.*, 1927, **73**, 342), which was shown by preliminary tests to give accurate results in the presence of paraldehyde and the solvents used. Most of the experiments carried out by this method were with anisole solutions of carboxylic acids between 50° and 150° and a paraldehyde concentration of 0·2%. Under these conditions it is difficult to extract samples of solution without losing acetaldehyde by evaporation, and the reactions were therefore carried out in sealed bulbs which could be broken under bisulphite solution. In each experiment 10—15 bulbs were charged with identical amounts of reaction mixture by using the pipette shown in the figure, which will deliver 1—2 g. with an accuracy of 0·2%. The bulbs were then transferred to a thermostat at 50°, or to vapour-baths containing water (100·5°) or tetrachloroethane (146·2°). The liquids in the vapour-baths boiled under a small excess pressure which was regulated by hand to counteract variations in atmospheric pressure. The temperature variations did not exceed 0·05°. At intervals a bulb was removed and broken under 30 c.c. of $M/5$-potassium bisulphite solution. After standing for 15 minutes to ensure complete reaction of the acetaldehyde, most of the excess bisulphite was removed by adding $N/5$-iodine solution, and the removal completed exactly with 0·037N-iodine (starch indicator). About 1 g. of sodium bicarbonate was then added, and the bisulphite liberated from the acetaldehyde bisulphite compound was titrated with 0·037N-iodine solution (microburette). Experiments without added catalyst showed that solutions of paraldehyde in anisole were completely stable at the temperatures employed.



The same technique could not be employed with hydrogen chloride solutions on account of the loss of hydrogen chloride during the filling of the bulbs. On the other hand, at the lower temperatures used with this catalyst (0° and 25°) no appreciable error is introduced by loss of acetaldehyde. These experiments were therefore carried out in the reaction vessels described by Bell and Levinge (*Proc. Roy. Soc.*, *A*, **1935**, **151**, 211), and samples pipetted out from time to time. To avoid a large air space, the vessel was almost completely filled with solution, and only a small fraction of the total volume was removed for estimation. The concentration of hydrogen chloride was determined at the beginning and the end of each experiment and the mean of the two values (which differed by a few units %) taken. Owing to the various sources of error the results for hydrogen chloride are less accurate than those for the carboxylic acids.

In some experiments the end-point was determined experimentally. In 14 experiments with various concentrations of the three carboxylic acids at 50°, 100°, and 146°, the percentage of acetaldehyde found at the end-point varied only between 93% and 98%. The initial paraldehyde concentration was approximately 0·2% throughout.

It is clear that the reverse reaction will be negligible except very near the end. This is confirmed by the unimolecular course of each experiment. The velocity constants were calculated from the slope of the plot of $\log_{10}(a - x)$ against t, where x is the titre per g. of solution at time t, and a the titre corresponding to complete conversion into acetaldehyde (calculated from the initial paraldehyde concentration). Straight lines were obtained throughout, and experiments with different paraldehyde concentrations (see Table IVa) give further evidence that the reaction is of the first order with respect to paraldehyde. The data for a typical experiment are given in Table II, where $k = 1/t \, . \log_{10} a/(a - x)$.

TABLE II.

0·294N-*Monochloroacetic acid in anisole* (146·2°).

t (mins.).	x (c.c.).	$a-x$.	10^3k.	t (mins.).	x (c.c.).	$a-x$.	10^3k.	t (mins.).	x (c.c.).	$a-x$.	10^3k.
0	0·00	1·88	—	70	0·58	1·30	2·29	170	1·14	0·74	2·38
15	0·14	1·74	(2·20)	90	0·71	1·17	2·29	200	1·29	0·59	2·51
35	0·27	1·61	(1·92)	110	0·84	1·04	2·56	260	1·42	0·46	2·35
50	0·43	1·45	2·26	140	1·01	0·87	2·38	6000	1·76	—	—

Mean $k = 2{\cdot}38 \times 10^{-3}$. From graph, $k = 2{\cdot}41 \times 10^{-3}$.

Difficulties were encountered in attempting to use very dilute solutions of trichloroacetic acid ($< 0{\cdot}01N$). Unimolecular plots were not obtained, and in attempting to measure the end-point the titre was found to pass through a maximum and then to decrease slowly. A similar decrease in titre was found on heating solutions of acetaldehyde in anisole with trichloroacetic acid. The nature of the reaction responsible for the disappearance of acetaldehyde was not discovered, but it appears to be roughly of the first order with respect to trichloroacetic acid. Since the rate of depolymerisation of paraldehyde varies approximately as the second power of the acid concentration (see below), the unknown reaction is negligible at higher acid concentrations.

Materials.—Paraldehyde was dried over sodium and redistilled. For some experiments oxygen was removed by distillation over molten sodium in a current of nitrogen: this treatment had no effect on the results.

Solvents were pure products dried over sodium or phosphoric oxide and fractionally distilled. Trichloroacetic acid was a pure commercial product. Dichloroacetic acid was distilled in an all-glass apparatus; b. p. 190—191°. Monochloroacetic acid was twice recrystallised from benzene. Hydrogen chloride was prepared from pure sodium chloride and sulphuric acid and dried with phosphoric oxide.

Results.—In the following tables c = acid concentration, moles per 1000 g. of solution; k = unimolecular velocity constant, $\log_{10}$, minutes.

Results of dilatometric measurements. The results are given in Table III. The paraldehyde concentration was approximately 1% throughout.

TABLE III.

(a) *Trichloroacetic acid in benzene.*

At 20°.

c	0·737	0·589	0·422	0·369	0·245	0·180	0·147	0·126
$k \times 10^4$	202	146	78·3	50·6	30·8	15·6	11·5	8·80
c	0·0984	0·0733	0·0524	0·0348	0·0209			
$k \times 10^4$	6·30	3·08	2·48	2·14	0·76			

At 30°.

c	0·737	0·516	0·369	0·0958	0·0752	0·0240
$k \times 10^4$	464	234	121	11·8	8·05	1·20

(b) *Dichloroacetic acid in benzene.*

At 20°.

c	1·03	0·827	0·689	0·482	0·344	0·207
$k \times 10^4$	7·71	5·20	4·07	2·19	1·16	0·595

At 30°.

c	0·980	0·790	0·786	0·553	0·395	0·262	0·197	0·131
$k \times 10^4$	25·4	16·7	17·2	9·54	5·75	2·49	1·40	1·04

(c) *Trichloroacetic acid in nitrobenzene at* 20°.

c	0·128	0·0965	0·0824	0·0450	0·0321	0·0193	0·0128
$k \times 10^4$	328	158	117	25·7	12·4	3·95	1·73

(d) *Trichloroacetic acid in anisole at* 20°.

c	0·569	0·285	0·203
$k \times 10^4$	6·4	0·98	0·35

Many attempts were made to measure the catalytic effect of hydrogen chloride in benzene at 20° by the dilatometric method. It was impossible to avoid loss of hydrogen chloride while filling the dilatometers, but there was no loss during the course of the reaction, and unimolecular plots were obtained. The actual hydrogen chloride concentration was determined by opening the dilatometer under water at the end of the reaction and titrating the chloride present (micro-electrometric titration with $N/50$-silver nitrate solution). 0·01—0·001N-Solutions of hydrogen chloride were found to give measurable reaction rates, but the velocity constants were unreproducible by a factor of about 3. It is believed that this is due to the inhibiting effect of traces of water, which is likely to be present at concentrations comparable with that of the acid. This is confirmed by the observation that there is no measurable reaction with a moist hydrogen chloride solution prepared by shaking benzene with concentrated hydrochloric acid. Water also has an inhibiting effect with trichloroacetic acid as catalyst, as is shown by the following data.

Trichloroacetic acid in benzene at 20°.

c	0·737	0·737	0·492	0·492
c_{H_2O}	0	0·250	0	0·250
$k \times 10^4$, obs.	202	103	97·5	30·6
$k \times 10^4$, calc.	—	97	—	28

The values of k in the last line are calculated from Table III(a), and represent the velocity when the concentration of trichloroacetic acid is $c - c_{H_2O}$. Each molecule of water thus appears to render inactive one molecule of trichloroacetic acid: this may be compared with the evidence from other sources that trichloroacetic acid forms a stable monohydrate in benzene solution (Bell, *Z. physikal. Chem.*, 1930, **150**, *A*, 20; Bell and Arnold, J., 1935, 1432).

Attempts were also made to measure the reaction velocity in amyl acetate solution. With solutions of trichloroacetic acid 0·002—0·2*N* there was no detectable volume change over a period of 24 hours, whereas with solutions of hydrogen chloride there was a slight *decrease* in volume, but no evidence of acetaldehyde formation.

Results of analytical measurements. These are given in Table IV. Unless otherwise stated, the paraldehyde concentration was approximately 0·2% throughout.

TABLE IV.

(a) *Trichloroacetic acid in anisole.*

At 146·2°.

c	0·0560	0·0420	*0·0320	0·0280	0·0210	†0·0120
$k \times 10^3$ ...	43·8	29·0	20·5	18·1	10·6	4·34

* Paraldehyde concentration 0·4%. †Paraldehyde concentration 0·1%.

At 100·5°.

c	0·102	0·0750	0·0600	0·0420	0·0350	0·0260	0·0210	0·0130	0·0100
$k \times 10^4$ ...	78·8	46·5	24·2	12·8	8·40	6·00	4·30	1·92	1·00

At 50·0°.

c	0·241	0·154	0·112	0·0950	0·0690	0·0570
$k \times 10^5$ ...	109	41·7	20·4	14·5	7·50	5·00

(b) *Dichloroacetic acid in anisole.*

At 146·2°.

c	0·239	0·190	0·146	0·124	0·0990	0·0720	0·0590
$k \times 10^3$ ...	52·9	27·8	17·3	13·7	7·0	3·9	2·5

At 100·5°.

c	0·492	0·314	0·169	0·140	0·098
$k \times 10^4$ ...	140	49	12·0	8·0	3·7

At 50·0°.

c	0·377	0·278	0·177	0·108
$k \times 10^6$ ...	180	82	27·5	8·8

(c) *Monochloroacetic acid in anisole.*

At 146·2°.

c	0·688	0·575	0·399	0·294	0·190	0·106
$k \times 10^4$ ...	179	124	55·0	24·1	10·2	2·90

At 100·5°.

c	1·23	0·995	0·715	0·565	0·315
$k \times 10^4$ ...	32·2	18·5	8·7	4·71	1·40

(d) *Hydrogen chloride in anisole.*

At 25°.

c	0·172	0·110	0·057	0·037	0·029
$k \times 10^4$ ...	166	58·9	13·8	7·00	3·85

At 0°.

c	0·298	0·181	0·118	0·050
$k \times 10^4$ ...	113	44·0	24·1	9·08

DISCUSSION.

Order of the Reaction.—It was shown above that the reaction is of the first order with respect to paraldehyde. The data in Tables III and IV show that the variation of velocity with acid concentration cannot be exactly expressed by any integral order. The results are most conveniently summarised by means of the "apparent order" p, defined as $d \log_{10} k / d \log_{10} c$. (Plots of $\log_{10} k$ against $\log_{10} c$ were in all cases linear.) The values of p are given in Table V.

TABLE V.

Apparent order with respect to acid.

	Anisole.						Benzene.		Nitrobenzene
	146·2°.	100·5°.	50°.	25·°.	20°.	0°.	20°.	30°.	20°.
Trichloroacetic acid ...	1·6	1·9	2·1	—	2·4	—	1·5	1·6	2·3
Dichloroacetic acid	2·1	2·3	2·5	—	—	—	1·6	1·6	—
Monochloroacetic acid	2·2	2·3	—	—	—	—			
Hydrogen chloride	—	—	—	2·0	—	1·9			

Although a second-order reaction appears to be most prominent, the apparent order varies from 1·5 to 2·5 in different cases. In general there is a tendency for it to decrease on increasing the temperature or on passing from a weaker to a stronger acid. It may be mentioned that catalytic depolymerisation of paraldehyde vapour by gaseous hydrogen chloride or hydrogen bromide at 100—150° takes place as a wall reaction of the first order with respect to both reactants (work in this laboratory by R. le G. Burnett, to be published shortly).

This behaviour indicates a composite mechanism for the reaction, and is probably connected with the presence of three oxygen atoms in the paraldehyde ring, constituting three possible points of attack for the catalyst molecules. Thus we may suppose that there is a small probability of decomposition when one oxygen atom is attacked by an acid molecule, a greater probability when two are so attacked, and a still greater probability when three acid molecules attack all three oxygen atoms. Provided that the concentrations of any complexes formed are small, this picture will always lead to an equation of the form

$$k = k_1c + k_2c^2 + k_3c^3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

independently of any particular assumptions as to the nature of the rate-determining steps. Further, the temperature coefficients of k_1, k_2, and k_3 will be different, decreasing in the order given. The experimental data are not sufficiently accurate or extensive for a critical test of equation (1): in fact, it is not possible to calculate reliable values for the three empirical constants involved. The observed variation of k with concentration can actually in all cases be represented within the experimental error by two-constant equations. Thus all the results for anisole solutions conform to equations of the type

$$k = Ac^2(1 + Bc) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where A and B depend on the acid and the temperature. Equation (2) would formally represent a bimolecular reaction (with respect to acid) having a linear medium effect. We do not, however, believe that this is a true description of the kinetics of the reaction, since the coefficient B varies rapidly (and even changes sign) with change of temperature, while the variations of A with temperature deviate considerably from the Arrhenius equation. It is therefore probable that equation (2) is only empirical, and that the composite mechanism expressed by equation (1) is necessary for a complete description of the reaction.

The Relation between Catalytic Power and Acid Strength.—The results show that for a given solvent at a given temperature the order of catalytic power is always qualitatively the same as the order of acid strength. As a rough quantitative measure of the catalytic power of the acids studied in anisole solution we can use the values of the constant A in equation (2). These constants are not identical with the true bimolecular constants k_2 in equation (1), but since the second-order reaction is the most prominent throughout, they will serve for comparing different acids. The values are given in Table VI together with the dissociation constants of the acids in water at the ordinary temperature (K_d). In the case of trichloroacetic acid no reliable value for K_d can be obtained by direct measurement, and the value given is obtained by multiplying the value for ethyl-alcoholic solution by $6{\cdot}4 \times 10^5$ (cf. Bell, *Proc. Roy. Soc.*, *A*, 1934, **143**, 389).

There is an approximate correlation between the values of A at each temperature and the value of K_d. If a relation of the type

$$A = GK_d^{\,x} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

TABLE VI.

Catalytic power of acids in anisole.

Acid.	K_d.	*A*.		
		146·2°.	100·5°.	50°.
Trichloroacetic	0·80	29·0	1·4	0·015
Dichloroacetic	0·050	0·675	0·034	0·00053
Monochloroacetic	0·0016	0·0275	0·0011	—

is obeyed, the most probable value for the exponent x is 1·1—1·2. A similar consideration of the second-order part of the reaction for trichloroacetic and dichloroacetic acids in benzene leads to a probable value of 1·3—1·4 for x.

Equation (3) is well established as a general relation between acid strength and catalytic power, though hitherto values less than unity have always been observed and predicted for the exponent. It may therefore be pointed out that an exponent greater than unity is possible if the reaction involves more than one acid molecule. Thus in the present case if we consider only the mechanism involving two acid molecules, the reaction may be represented by the following scheme (P = paraldehyde, HA = acid) :

$$\mathrm{P} + \mathrm{HA} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{PH^+{\cdot}A^-}$$

$$\mathrm{PH^+{\cdot}A^-} + \mathrm{HA} \xrightarrow{k_3} \mathrm{PH_2{}^{++}{\cdot}A_2{}^{--}} \xrightarrow{k_4} 3\mathrm{CH_3{\cdot}CHO} + 2\mathrm{HA}$$

where $k_2 \gg k_1$ and $k_3 \ll k_4$ and k_2. The first stage will then be an equilibrium with the equilibrium constant $K = k_1/k_2$, and the velocity of the net reaction is given by

$$v = k_3[\mathrm{PH^+ . A^-}][\mathrm{HA}] = k_3K[\mathrm{P}][\mathrm{HA}]^2$$

The equilibrium constant K refers to a protolytic reaction, and will hence be approximately directly proportional to K_d, the dissociation constant of the acid in water (cf. Bell, *Ann. Reports*, 1934, **31**, 79). The rate-determining velocity constant k_3 refers to the same type of reaction, and will be related to K_d by an equation of the type $k_3 = G'K_d{}^y$, where G' is a constant and $y < 1$ (cf. Bell, *Proc. Roy. Soc.*, *A*, 1936, **154**, 414). This gives finally for the second-order constant

$$A = v/[\mathrm{P}][\mathrm{HA}]^2 = GK_d{}^{1+y}$$

i.e., an equation of the Brönsted type with an exponent greater than unity.

The Effect of the Solvent upon Catalytic Power.—The magnitude of this effect is illustrated by the velocity constants for trichloroacetic acid at 20° given in Table VII.

TABLE VII.

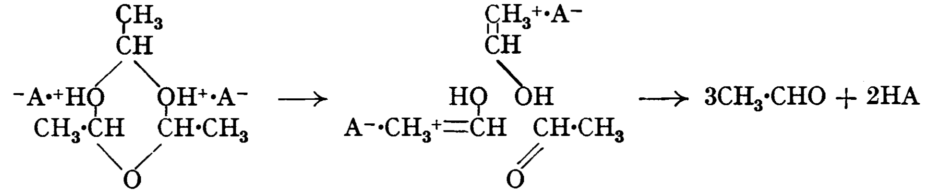
The effect of the solvent on catalytic power.

Solvent	Nitrobenzene	Benzene	Anisole	Amyl acetate
c	0·129	0·126	0·134	0·2
$k \times 10^4$	328	11·5	0·35	$<$0·01

This wide range of values contrasts with the small variations found for trichloroacetic acid in eight different solvents in the rearrangement of *N*-bromoacetanilide (Bell, *Proc. Roy. Soc.*, *A*, 1934, **143**, 377). In the latter case, however, all the solvents were of the hydrocarbon type, while here the chemical type of the solvent has been varied. The low velocity in anisole and amyl acetate is no doubt due to combination of the acid with the basic oxygen atoms of these solvents. Weissberger and Högen (*Z. physikal. Chem.*, 1931, **156**, 321) and Weissberger and Fasold (*ibid.*, 1931, **157**, 65) have shown that the reactivity of hexane solutions of trichloroacetic acid towards indicators and diazoacetic ester is lowered greatly by adding compounds containing ether or carbonyl groups, while Hantzsch has produced much evidence that solvents containing oxygen atoms reduce the reactivity of acids in general. The inhibiting effect of water in the present reaction is a parallel phenomenon. The same type of solvation is responsible for the fact that carboxylic acids exist as double molecules in hydrocarbon solvents, but as single molecules in ethers, esters and ketones.

On the other hand, although the oxygen atoms in the nitro-group show little tendency to combine with acids, carboxylic acids exist partly as single molecules in this solvent (Brown and Bury, *J. Physical Chem.*, 1926, **30**, 694). The high reaction velocity (compared with benzene) observed in nitrobenzene may thus be due to the presence of unsolvated single acid molecules.

Reaction Mechanism.—In view of the fact that the reaction is catalysed by acids in general, the first step is no doubt the transfer of a proton to one or more of the oxygen atoms in the paraldehyde molecule. Since decomposition can take place at a higher temperature in the absence of catalysts, the effect of this transfer may be merely to weaken the carbon–oxygen bonds and thus to allow the same mechanism to operate at a lower temperature. On the other hand, it is possible to formulate a prototropic mechanism involving the production of the enolic form of acetaldehyde : thus the reaction involving two acid molecules would take place as follows :



This resembles the mechanism usually assumed for an acid-catalysed prototropic change, except that the removal of the proton does not depend on the presence of a new basic species, *e.g.*, a solvent molecule. This modification of Lowry's scheme is necessary for any prototropic change exhibiting acid or basic catalysis in a solvent possessing neither acidic nor basic properties.

SUMMARY.

(1) Two methods are described for following the kinetics of the depolymerisation of paraldehyde, one dilatometric and the other analytical.

(2) Data are given for the catalysed depolymerisation in benzene, nitrobenzene, anisole, and amyl acetate solutions at temperatures between 0° and 150°, the catalysts used being hydrogen chloride, and tri-, di-, and mono-chloroacetic acids.

(3) The reaction is unimolecular with respect to paraldehyde, while the apparent order with respect to acid varies between 1·5 and 2·5. The data are best accounted for by assuming a composite mechanism involving all three oxygen atoms in the paraldehyde molecule.

(4) Approximate constants for the second-order part of the reaction can be used to compare the catalytic power of the acids used. These constants are in the same order as the acid strengths, and vary somewhat more rapidly than the dissociation constants in water.

(5) The effect of the solvent on the reaction velocity is very great. This is due partly to chemical interaction between acid and solvent, and partly to varying association of the carboxylic acids.

(6) A possible prototropic reaction mechanism is suggested.

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