96. *Acid-catalysed Hydration of Acraldehyde. Kinetics of the Reaction and Isolation of β-Hydroxypropaldehyde.*

By R. H. Hall and E. S. Stern.

A kinetic study of the acid-catalysed hydration of acraldehyde to β-hydroxypropaldehyde (hydracraldehyde; 3-hydroxypropan-1-al) in aqueous sulphuric acid confirms that the reaction is of the first order with respect to acraldehyde. The rate constants are independent of initial acraldehyde concentration, increase with increasing acid concentration, and are strictly proportional to Hammett's acidity function. β-Hydroxypropaldehyde, isolated (in poor yield) from the hydration media and characterised as the 2 : 4-dinitrophenylhydrazone, dimerises spontaneously to 4-hydroxy-2-2′-hydroxyethyl-1 : 3-dioxan, the unsymmetrical structure of which is proved by acetylation and hydrolysis. Representative kinetic experiments on the dehydration of β-hydroxypropaldehyde, using the dimer as starting material, demonstrate the ready reversibility of both the dimerisation of this aldehyde and the hydration of acraldehyde. A reversible mechanism proposed for the hydration of acraldehyde involves, as rate-determining step, the addition of a water molecule to the oxonium ion $CH_2{:}CH{\cdot}CH{:}OH^+$ and the simultaneous redistribution of the charge to give the oxonium ion $^+H_2O{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OH$ which is the conjugate acid of the enol of β-hydroxypropaldehyde.

With the ready availability of acraldehyde on a commercial scale (see, *inter alia*, B.P. 569,625, 573,507, 600,454, 625,330; B.P. Appl. 22,712/39; Watson, *Chem. Eng.*, 1947, **54**, No. 12, 107), the preparation of β-hydroxypropaldehyde, an intermediate of great potential value in the solvent or the plasticiser field, has recently received considerable attention.

Although β-hydroxypropaldehyde may be prepared in several ways (cf. Nef, *Annalen*, 1904, **335**, 219; Glattfield and Sander, *J. Amer. Chem. Soc.*, 1921, **43**, 2675; Wohl and Schweitzer, *Ber.*, 1908, **41**, 3603; Stepanow and Schtschukin, *Chem. Zentr.*, 1927, I, 1167), most of the recent work has been concerned with the acid-catalysed hydration of acraldehyde (U.S.P. 2,434,110; German microfilmed reports PB 70,309, Frames 8214—8220; 73,508, Frames 7528—7537; and 19,417; G.P. Appl. D 89,752 IVd, Class o, 1943).

For the catalytic hydration processes described in the literature, conditions seem to be chosen rather arbitrarily and little systematic work appears to have been published in this connection. The kinetic data on the hydration of acraldehyde (Pressman and Lucas, *J. Amer. Chem. Soc.*, 1942, **64**, 1953), which are rather incomplete, are based on experiments with perchloric acid as catalyst and very dilute (about 0·03M.) solutions of acraldehyde, and are not, therefore, directly applicable to preparative work. A detailed kinetic study of the acid-catalysed hydration of acraldehyde was undertaken to provide fuller data, capable of such application, and an insight into the mechanism of the reaction, which has not hitherto been fully elucidated (cf. Hammett, "Physical Organic Chemistry," McGraw-Hill, 1940, p. 293).

In the present work the catalyst used for the hydration of acraldehyde between 20° and 50° was sulphuric acid in the concentration range 0·2—3·8N. The aldehyde concentration range studied was 0·138—2·76M. (*i.e.*, 1—20% v/v). In view of the possible polymerisation of acraldehyde in acid solution, it was decided to follow not only the rate of disappearance of the ethenoid unsaturation (by the bromine absorption method) but also the variations in the concentration of the carbonyl function (by an oximation procedure).

The presence of the acid catalyst, however, introduced large blank values into the analytical determinations of the carbonyl function and accurate values were difficult to obtain. Nevertheless, it was established that during the kinetic runs the aldehyde content of the media remained sensibly constant until after the equilibrium point of the hydration reaction had been reached. Prolonged reaction beyond this point, however, caused a diminution in the aldehyde concentration and it was concluded that a slow polymerisation was then occurring. It was also found that the rate of disappearance of aldehyde during this stage increased with increasing initial acid and acraldehyde concentrations. The fate of the aldehyde group during the polymerisation was not further investigated but it has been stated by Helberger (PB 19,417; FD 4806/47) that 3-formyl-Δ^3-dihydropyran is formed as hydration product. His claim that this is the sole volatile reaction product, however, is invalidated by the isolation of β-hydroxypropaldehyde from hydration media in the course of the present work (see below).

The kinetic data for the hydration of acraldehyde are collected in Tables I and II; the equilibrium concentration of acraldehyde was determined in each case and all kinetic runs were performed in duplicate. The equilibrium position was found to vary with temperature (cf. Pressman and Lucas, *loc. cit.*) and with the aldehyde concentration (Table II), higher conversions being achieved at lower temperatures and higher initial acraldehyde concentration; acid concentration was found to have no appreciable effect on the equilibrium position. The equilibrium constant K was calculated from the equation

$$K = \frac{\text{equilibrium concentration of } \beta\text{-hydroxypropaldehyde}}{\text{equilibrium concentration of acraldehyde}}$$

and the relationship $K = k_1/k_{-1}$ gave the ratio of the first-order rate constants of the forward and the backward reaction.

$$H_2O + CH_2{:}CH{\cdot}CHO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HO{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$$

The sum of these rate constants corresponds to the overall rate constant k determined experimentally and defined (Hammett, *op. cit.*, p. 102) by

$$k = k_1 + k_{-1} = (2{\cdot}3/t) \log x_e/(x_e - x)$$

where x_e is the β-hydroxypropaldehyde concentration at equilibrium and x is that at time t.

TABLE I.

Effect of acid concentration and of temperature.

Initial acraldehyde concn. = 0·690M. throughout; k_1 = first-order rate constant of hydration; k_{-1} = first-order rate constant of dehydration; c_A = acid concentration; $K = k_1/k_{-1}$; H_0 = acidity function (values of Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721).

Temp.	H_2SO_4 concn. (N.).	$10^4(k_1 + k_{-1})$ (min.$^{-1}$).	10^4k_1 (min.$^{-1}$).	10^4k_{-1} (min.$^{-1}$).	Conversion at equilibrium (%).	K.	H_0.	log $10^4(k_1 + k_{-1})$ $+H_0$.	$\frac{10^4(k_1 + k_{-1})}{c_A}$.
20·0°	0·20	4·25	4·06	0·19	95·5	21·2	+1·26	1·88	21·3
20·0	1·00	22·5	21·5	1·0			+0·52	1·87	22·5
20·0	2·00	54·6	52·1	2·5			+0·12	1·86	27·3
20·0	3·80	152	145	7·0			−0·52	1·66	40
30·0	0·20	10·9	10·3	0·62	94·3	16·5	+1·26	2·30	54·5
30·0	1·00	57·8	54·5	3·3			+0·52	2·24	57·8
30·0	2·00	135	127	7·7			+0·12	2·25	67·5
30·0	3·80	350	330	20			−0·52	2·02	92·1
40·0	0·20	24·7	22·7	2·0	92·0	11·5	+1·26	2·65	124
40·0	1·00	133	122	11			+0·52	2·64	133
40·0	2·00	312	287	25			+0·12	2·61	156
40·0	3·80	855	787	68			−0·52	2·41	225
50·0	0·20	60·5	53·9	6·6	89·0	8·1	+1·26	3·04	303
50·0	1·00	305	272	33			+0·52	3·00	305
50·0	1·50	470	418	52			+0·32	2·99	313
50·0	2·00	665	592	73			+0·12	2·94	333

TABLE II.

Effect of acraldehyde concentration.

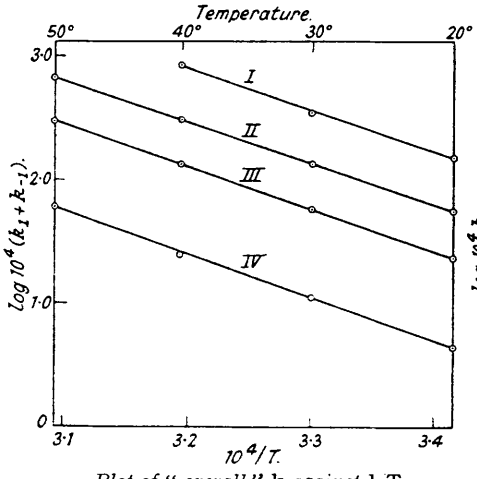
H_2SO_4 concn. is 1·00N. throughout.

Temp.	Initial acraldehyde concn. (M.).	$10^4(k_1 + k_{-1})$ (min.$^{-1}$).	10^4k_1 (min.$^{-1}$).	10^4k_{-1} (min.$^{-1}$).	Conversion at equilibrium (%).	K.
20·0°	0·138	22·9	21·3	1·6	92·9	13·1
20·0	0·690	22·5	21·5	1·0	95·5	21·2
20·0	1·38	22·7	21·9	0·8	96·5	27·6
20·0	2·76	20·6	20·0	0·6	96·9	31·3
50·0	0·138	303	255	48	84·0	5·25
50·0	0·690	305	272	33	89·0	8·1
50·0	1·38	297	271	26	91·1	10·2
50·0	2·76	269	250	19	93·1	13·5

It was found that the rate constants k and k_1 were independent of the initial acraldehyde concentration within the range 0·138—1·38M.; for 2·76M-acraldehyde solutions, however, the rate constants were lower by about 10% (Table II). This reduction is attributed to the changes in solvating and proton-donating properties of the reaction medium caused by the relatively high concentration of acraldehyde (~6 mol.-%), by analogy with the effect (cf. Braude *et al.*, *J.*, 1944, 443; 1948, 1982) of increasing concentrations of oxygenated organic substances in the reaction medium on the reaction rate and acidity function.

FIG. 1.

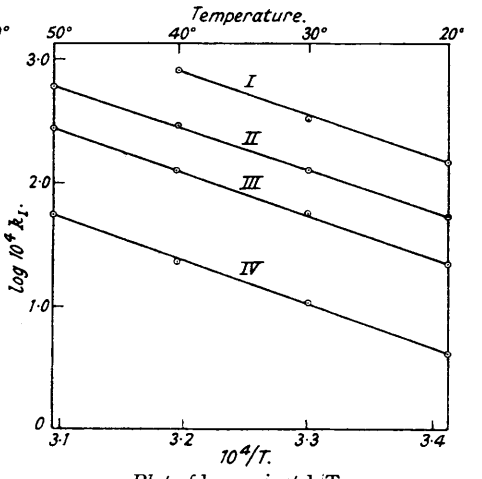
Arrhenius energy of activation.



Plot of " overall " k against 1/T.

FIG. 2.

Arrhenius energy of activation (hydration).



Plot of k_1 *against* 1/T.

Acid concns.: I, 3·8N.; II, 2·0N.; III, 1·0N.; IV, 0·2N.

The rate constants k increased with increasing acid concentration (Table I), but were not directly proportional to the stoicheiometric concentration of sulphuric acid, a relationship found by Pressman and Lucas (*loc. cit.*) to hold for 0·25N- and 0·5N-perchloric acid. Thus the ratio of k to c_A (Table I) increased greatly with acid concentration. The relation between k and acidity was accurately expressed for sulphuric acid concentrations between 0·20 and 2·00N. by Hammett and Deyrup's acidity function equation (*J. Amer. Chem. Soc.*, 1932, **54**, 2721), *viz.*, $H_0 + \log k =$ constant, where H_0 is the acidity function, a measure of the tendency of the medium to donate a proton to a neutral base. For 3·8N-sulphuric acid the value of $H_0 + \log k$ was somewhat low.

Measurements at different temperatures showed that the rate constants k, k_1, and k_{-1} accurately obeyed the Arrhenius equation, the linearity of the log k–$1/T$ plots (Figs. 1, 2, and 3) being very marked.

The difference between the Arrhenius energies of activation (Tables III and IV) of the backward and the forward reaction (ΔE), *i.e.*, the heat of reaction, when 0·20—2·00N-sulphuric acid was used, was found to be 6·0 ± 0·2 kcals. per mol. This agreed closely with the value found by Pressman and Lucas (*loc. cit.*), *viz.*, 5·8 kcals. per mol., for ΔE under very different reaction conditions.

TABLE III.

Arrhenius energies of activation (in kcals./mol.).

Calculated from Table I. Initial acraldehyde concn. = 0·690M. throughout. Temp. range: 20·0—50·0°. $E = 2{\cdot}303 \times 1{\cdot}986 \times \frac{T_a T_b}{T_b - T_a} \times \log (k_b/k_a)$.

H_2SO_4 concn. (N.).	$E_{(k_1+k_{-1})}$.	$E_{(k_1)}$.	$E_{(k_{-1})}$.	$\Delta E = [E_{(k_{-1})} - E_{(k_1)}]$.
0·20	16·5	16·1	22·2	6·1
1·00	16·3	15·8	21·9	6·1
2·00	15·6	15·1	21·0	5·9
3·80	15·7	15·4	20·8	5·4

TABLE IV.

Arrhenius energies of activation (in kcals./mol.).

Calculated from Table II; H_2SO_4 concn. = 1·00N. throughout.

Initial acraldehyde concn. (M.).	$E_{(k_1+k_{-1})}$.	$E_{(k_1)}$).	$E_{(k_{-1})}$.	ΔE.
0·138	16·2	15·5	21·3	5·8
0·690	16·3	15·9	21·9	6·0
1·38	16·1	15·8	21·8	6·0
2·76	16·1	15·8	21·7	5·9

TABLE V.

Effect of mercuric sulphate.

Temp. = 50·0°; H_2SO_4 concn. = 1·00N.; initial acraldehyde concn. = 0·690M. throughout.

$HgSO_4$ concn. (% w/v)	nil	1	5	10
$10^4(k_1 + k_{-1})$ (min.$^{-1}$)	305	358	384	407

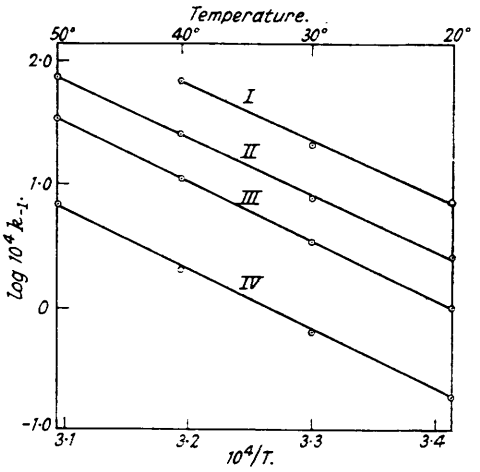
Addition of mercuric sulphate to the hydration mixture resulted in a considerable increase in the overall rate constant k (Table V); the rate of polymerisation of the aldehyde also appeared to be increased greatly, and solid deposits were observed in two runs before equilibrium had been attained.

Although the rate constants k and k_1 were independent of the initial acraldehyde concentration (see above) the rate constants k_{-1}, which were calculated by difference (Table II) and were much less accurate than the other rate constants, appeared to be appreciably affected by the initial acraldehyde concentration; in this connection it is noteworthy that the initial acraldehyde concentration also affected the equilibrium constants K, and these effects are probably related to the rapid reversible dimerisation of β-hydroxypropaldehyde which is discussed later.

The reversibility both of the dimerisation of the hydroxy-aldehyde and of the hydration of acraldehyde was proved in the course of kinetic experiments on the dehydration of the former. In view of its rapid dimerisation (see below) its dimer was used as the starting material for these experiments; in acid solution, under conditions exactly analogous to those under which the hydration had been studied, it was found that olefinic unsaturation appeared (*i.e.*, dehydration occurred) at an overall rate in satisfactory agreement with that of the hydration reaction; similar agreement was found for the equilibrium constants and for the energies of activation of the forward and the reverse reaction (cf. Experimental). The wide limits of error deemed "satisfactory agreement" are due to the inaccuracies inherent in the study of a reaction which reaches equilibrium at a conversion of less than 15%.

FIG. 3.

Arrhenius energy of activation (dehydration).



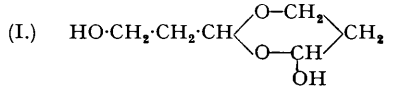
Plot of k_{-1} *against* 1/T.

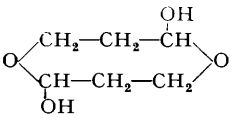
Acid concns.: I, 3·8N.; II, 2·0N.; III, 1·0N.; IV, 0·2N.

The isolation of pure β-hydroxypropaldehyde from the product of the acid-catalysed hydration had not previously been reported, and was thought by Helberger (PB 19,417) to be impracticable. In the present investigation it was found that after hydration at 50° for a time just sufficient to establish equilibrium and after careful neutralisation (pH 6—7) of the acid catalyst with solid calcium carbonate, 93% of acraldehyde had been converted and 96% of the initial aldehyde function remained in solution; the concentrate, obtained by passing the neutralised solution three times through a falling-film evaporator, contained about 10—20% water, and about 80—85% of the initial aldehyde function (by oxime determination). This concentrate was slowly distilled under oil-pump pressure at the lowest practicable bath temperature (cf. Glattfield and Sander, *J. Amer. Chem. Soc.*, 1921, **43**, 2675); in spite of these precautions, much resinification took place and the yield of pure β-hydroxypropaldehyde of b. p. 38°/0·2 mm. was low, amounting to a maximum of 20% of the theoretical weight.

The distillate, a comparatively mobile oil, was observed to become warm spontaneously within a few minutes of distillation, giving a viscous oil of n_D^{20} 1·4783, presumably the so-called " β-hydroxypropionaldehyde lactol " of Bergmann, Miekeley, and Lippmann (*Ber.*, 1929, **62**, 1467). By analogy (cf. Späth and Schmid, *Ber.*, 1941, **74**, 859) with acetaldol (which in our hands dimerised more slowly than β-hydroxypropaldehyde) this substance is now assigned the formula of the hemiacetal (I), and not the symmetrical formula (II) proposed by Bergmann *et al.* (*loc. cit.*).

The unsymmetrical structure (I) was shown to be correct by acetylation of the dimer by the method of Bergmann *et al.* (*loc. cit.*), and by hydrolysis of the diacetate with 0·05N-aqueous hydrochloric acid at 70° (cf. Späth and Schmid, *loc. cit.*), whereby it was found that the two

(I.) 



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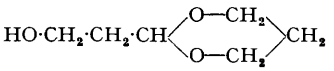
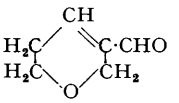
(III.) 



(IV.)

acetyl groups were removed at different rates (Table VI). This, in conjunction with the hydrogenolysis of the diacetate to 2-2′-hydroxyethyl-1 : 3-dioxan (III), reported by Bergmann *et al.* (*loc. cit.*), may be accepted as conclusive proof of the unsymmetrical structure of dimeric β-hydroxypropaldehyde in accordance with the predictions of Späth and Schmid (*loc. cit.*) and of Owen (*Ann. Reports*, 1944, **41**, 139).

Reaction of the dimer of β-hydroxypropaldehyde with 2 : 4-dinitrophenylhydrazine in anhydrous methanol containing a little concentrated sulphuric acid rather surprisingly gave a high-melting derivative (m. p. 228°, decomp.), the ultra-violet light absorption of which was in agreement with that of an αβ-unsaturated aldehyde (cf. Braude and Jones, *J.*, 1945, 498). This compound was thought to be the 2 : 4-*dinitrophenylhydrazone* of 3-formyl-Δ^3-dihydropyran (IV), a postulate supported by the elementary analysis. In view of the work reported by Helberger (PB 19,417), this material was not examined further but it is hoped that its identity may be established with certainty when details of Helberger's work become available.

In aqueous hydrochloric acid solution, dimeric β-hydroxypropaldehyde reacted with 2 : 4-dinitrophenylhydrazine giving a mixture of its own 2 : 4-*dinitrophenylhydrazone*, together with that of acraldehyde and a little of the 2 : 4-dinitrophenylhydrazone, m. p. 228° (decomp.), obtained before.

This is a further confirmation of the fact that dimeric and monomeric β-hydroxypropaldehyde are in equilibrium in the solutions used, as is the case with the homologue, acetaldol (Späth, Lorenz, and Freund, *Ber.*, 1942, **75**, 1029); a further equilibrium is set up in acid solution between β-hydroxypropaldehyde and acraldehyde. The formation of the 3-formyl-Δ^3-dihydropyran may thus be explained by assuming a union of the two aldehydes, or a self-condensation of the former, and subsequent loss of water.

Experimental.

Materials.—Acraldehyde was fractionated before use through a 2-ft. glass column packed with single-turn glass helices; it had b. p. 51—52° and was stabilised by the addition of 0·2% (w/v) of quinol. Analysis both by oximation and by bromine absorption showed 92% purity; the remaining 8% was water.

Pure acraldehyde (100·3% by oximation; 99·4% by bromine absorption) was used in some runs which, however, gave kinetic results in close agreement with those obtained with 92% acraldehyde.

Kinetic Measurements.—The kinetic runs were carried out in 100 ml. of reaction medium in two-necked Pyrex flasks; one neck carried a double-surface condenser connected to a vent line. Samples were withdrawn through the other neck by means of calibrated, narrow-stem, rapid-delivery 1-ml. or 2-ml. or of calibrated bulb 5- or 10-ml. pipettes connected to a suction line. The reaction vessels were kept in a water tank, thermostatically controlled to within ±0·05° by a mercury–toluene bulb thermoregulator. All runs were carried out in duplicate.

To start a run the solution of the acid was rapidly added to the acraldehyde solution, both solutions having been pre-heated to the required temperature. The flask was vigorously shaken and a sample was taken from the homogeneous medium; the whole operation took less than 12 seconds. Four or five further samples and two equilibrium samples were analysed in the course of each run by the bromine absorption method, and two or three samples per run by the oximation method for aldehyde content.

The bromine absorption method (see below) of analysis gave very consistent results and the rate constants of any one run were generally within ±3%. Three runs in which the variation of rate constants exceeded ±5% were rejected and repeated. Duplicate runs then agreed to within ±3%. Average values of the duplicate runs are recorded in Tables I and II. Three typical runs are given below, titres being in ml. of 0·1N-sodium thiosulphate :

(*a*) 2·00N-H_2SO_4; 0·690M-acraldehyde; 20·0°.

Time (mins.)	0	30	60	91	122	155	620	900
Bromine absorption titre of 1·00 ml.	13·75	11·78	10·13	8·46	7·28	6·14	0·55	0·55
10^4k (min.$^{-1}$)	—	53·9	53·3	56·2	55·1	55·4	—	—

Concn. of acraldehyde at equilibrium : 4·0% of initial concn. 10^4k (average) : 54·8 min.$^{-1}$.

(*b*) 2·00N-H_2SO_4; 0·690M-acraldehyde; 50·0°.

Time (mins.)	0	3	7	11	15	19	60	80
Bromine absorption titre of 1·00 ml.	12·46	10·49	8·48	6·70	5·46	4·40	1·35	1·37
10^4k (min.$^{-1}$)	—	648	637	668	662	680	—	—

Concn. of acraldehyde at equilibrium : 11·0% of initial concn. 10^4k (average) : 659 min.$^{-1}$.

(*c*) 1·00N-H_2SO_4; 0·138M-acraldehyde; 20·0°.

Time (mins.)	0	60	121	180	301	1200	1520
Bromine absorption titre of 5·00 ml.	13·78	12·10	10·66	9·35	7·22	1·00	0·99
10^4k (min.$^{-1}$)	—	23·4	23·0	23·5	23·8	—	—

Concn. of acraldehyde at equilibrium : 7·2% of initial concn. 10^4k (average) : 23·4 min.$^{-1}$.

The experimental conditions of the dehydration, carried out with dimeric β-hydroxypropaldehyde as starting material, were in every way analogous to those described above. In view of the low accuracy to be expected from these experiments, the following two runs only were performed (in duplicate), both with 1·00N-sulphuric acid and 0·065M-dimeric aldehyde (*i.e.*, 0·130M-β-hydroxypropaldehyde), titres being recorded as above :

(*a*) At 20·0°.

Time (mins.)	(i)	120	180	240	340	1440
Bromine absorption titre of 10·0 ml.		0·36	0·55	0·64	0·82	1·33
10^4k (min.$^{-1}$)		26·3	29·6	27·3	28·2	—
Time (mins.)	(ii)	125	180	240	334	1440
Bromine absorption titre of 10·0 ml.		0·37	0·54	0·66	0·79	1·33
10^4k (min.$^{-1}$)		26·1	28·9	28·5	27·1	—

Concn. of acraldehyde at equilibrium (% of initial aldehyde function) : 5·2.
10^4k (average) : (i) 27·9 min.$^{-1}$; (ii) 27·7 min.$^{-1}$.
$K = 18·2$; $k_1 = 26·4$ min.$^{-1}$; $k_{-1} = 1·4$ min.$^{-1}$.

(*b*) At 50·0°.

Time (mins.)	(i)	6	9	12	15	18	21	180
Bromine absorption titre of 10·0 ml.		0·47	0·75	0·93	1·09	1·29	1·38	3·19
10^4k (min.$^{-1}$)		265	298	287	278	288	270	—
Time (mins.)	(ii)	3	6	9	12	15	20	150
Bromine absorption titre of 10·0 ml.		0·24	0·45	0·71	0·91	1·13	1·28	3·19
10^4k (min.$^{-1}$)		261	253	279	280	291	256	—

Concn. of acraldehyde at equilibrium (% of initial aldehyde function) : 12·4.
10^4k (average) : (i) 281 min.$^{-1}$; (ii) 270 min.$^{-1}$.
$K = 7·0$; $k_1 = 241$ min.$^{-1}$; $k_{-1} = 34·4$ min.$^{-1}$.

Calculated Arrhenius energies of activation (in kcals./mol.) :

$E_{(k_1+k_{-1})}$ 14·4, $E_{(k_1)}$ 13·9, $E_{(k_{-1})}$ 20·1. $\Delta E = E_{(k_{-1})} - E_{(k_1)} = 6·2$ kcals. per mol.

Analytical Procedures.—(A) *Bromine absorption.* The sample was run into 20·0 ml. of standard (0·1N.) bromide–bromate reagent at 0°; after acidification with an excess of diluted (1 : 1) " AnalaR " hydrochloric acid, the mixture was kept at 0° for 30 seconds, treated with cold 20% w/v

aqueous potassium iodide solution, diluted with 100 ml. of distilled water, and titrated with standard 0·1N-thiosulphate solution without indicator. Blank determinations were performed on the bromide–bromate reagent to permit calculation of unsaturation. Under the above conditions β-hydroxypropaldehyde was not brominated.

(B) *Oximation.* The sample was run into 50 ml. of neutral hydroxylamine hydrochloride reagent (20 g. of hydroxylamine hydrochloride per litre of approx. 90% ethanol, containing 25 ml. of 0·2% w/v alcoholic bromophenol-blue). After being heated (under reflux) on the steam-bath for 20 minutes, the solution was titrated at room temperature with 0·1N-sodium hydroxide solution. Blank determinations, performed under conditions identical but for the absence of hydroxylamine hydrochloride from the reagent solution, gave corrections for the acidity of the hydration mixture. Cf. Maltby and Primavesi, *Analyst*, 1949, **74**, 498.

Preparation of β-Hydroxypropaldehyde.—A mixture of acraldehyde (75 ml.; purity 92%; 1 mol.), 3N-sulphuric acid (100 ml.), and water (325 ml.) was kept at 50° for 2·5 hours. The solution, the volume of which had decreased to 475 ml. (at room temp.), was rapidly cooled to 0°, and a sample was analysed; the acraldehyde conversion, determined by bromine absorption, was 93%, and the loss of aldehyde less than 1% (by oximation). Solid calcium carbonate was slowly added to the stirred solution until it was neutral (pH 6·8) to methyl-red (external indicator). After filtration under suction and thorough washing of the residue with distilled water, the solution (about 550—600 ml.) contained 96% of the initial amount of aldehyde function (by oximation).

The neutralised hydration medium was passed through a falling-film evaporator kept under vacuum (12 mm.); the evaporation surfaces were steam-heated, and the contact time was less than 20 seconds. The volume of liquid was reduced by about 40—50% per pass and generally three passes sufficed to remove about 85—95% of the water. The total loss of aldehyde function in these operations varied from 12 to 18%, 7%, presumably, being accounted for as unreacted acraldehyde.

The crude β-hydroxypropaldehyde (70—80 g.), containing about 15—25% of its weight of water and some polymeric material, was then distilled at the oil-pump under about 0·1—0·5 mm. The pure aldehyde (12—15 g.) distilled very slowly at 38—45°/0·2—0·5 mm. (Glattfield and Sander, *loc. cit.*, give b. p. 80—86°/14 mm.), and extensive resinification of the flask contents took place.

Dimeric β-Hydroxypropaldehyde (*4-Hydroxy-2-2′-hydroxyethyl-1 : 3-dioxan*).—The distillate from the above preparation became warm spontaneously and thickened to a viscous oil, n_D^{20} 1·4783, which was redistilled. Again, distillation proceeded slowly and some non-volatile, resinous material (2·5 g.) remained in the still. The distillate (10—12 g.), b. p. 40°/0·2 mm., n_D^{20} 1·4418, became warm spontaneously and gave the viscous dimer, n_D^{20} 1·4783 [Found: C, 48·95; H, 8·05; *M* (cryoscopic in dioxan), 152, 146. Calc. for $C_6H_{12}O_4$: C, 48·65; H, 8·15%; *M*, 148]. Oximation of the dimer by the procedure outlined above showed the presence of 1·99 potential carbonyl groups per mol., *i.e.*, the dimer behaved analytically as monomeric β-hydroxypropaldehyde.

2 : 4-*Dinitrophenylhydrazones.* (i) In anhydrous methanol. The dimeric aldehyde (1 g.) was dissolved in methanol (10 ml.) containing concentrated sulphuric acid (1 g.) and 2 : 4-dinitrophenylhydrazine (1·5 g.). After two days a solid (1·2 g.), probably *3-formyl-Δ³-dihydropyran* 2 : 4-*dinitrophenylhydrazone*, m. p. 214° (decomp.), had separated. After crystallisation from benzene containing 10% of ethyl acetate and chromatography on alumina (Peter Spence, type H) from benzene solution, it had m. p. 228° (decomp.) (Found: C, 49·35; H, 4·5. $C_{12}H_{12}O_5N_4$ requires C, 49·3; H, 4·15%), and light absorption maximum (in EtOH) at 3770 A., ε = 30,000.

(ii) In water. Dissolution of the dimeric aldehyde (1·5 g.) in a 2N-hydrochloric acid solution of 2 : 4-dinitrophenylhydrazine (2·5 g.) gave, within 5 minutes, a yellow precipitate (2 g.), m. p. 95—100°, which resolidified and then melted at 155—160° (decomp.). Chromatography of this material from benzene solution on alumina separated three substances: the most readily eluted was acraldehyde 2 : 4-dinitrophenylhydrazone (about 80 mg.), m. p. 161—162° (mixed m. p. with authentic material of m. p. 164° was 162—163°), light absorption maximum (in EtOH) at 3690 A., ε = 25,000 (Braude and Jones, *J.*, 1945, 498, give $\lambda_{max.}$ 3660 A., ε = 25,500). The intermediate benzene eluates contained slightly impure (?) 3-formyl-Δ³-dihydropyran 2 : 4-dinitrophenylhydrazone (about 150 mg.), m. p. 217—219° (decomp.), light absorption maximum (in EtOH) at 3770 A., ε = 31,000. The most strongly adsorbed material was eluted with benzene–ethyl acetate (5 : 1) and consisted of *β-hydroxypropaldehyde* 2 : 4-*dinitrophenylhydrazone* (about 1 g.), m. p. 110°. This was once more chromatographed and then recrystallised from benzene. It finally had m. p. 132·5—133° (Found: C, 42·85; H, 4·25; N, 21·8. $C_9H_{10}O_5N_4$ requires C, 42·55; H, 3·95; N, 22·05%) and light absorption maximum (in EtOH) at 3600 A., ε = 24,000.

Structure of Dimeric β-Hydroxypropaldehyde.—The dimeric aldehyde (5 g.) was acetylated by the method of Bergmann *et al.* (*Ber.*, 1929, **62**, 1467) by being kept with acetic anhydride (10 ml.) and pyridine (10 ml.) at room temperature for 24 hours. Ether (150 ml.) was then added and the solution was washed with N-aqueous sodium hydroxide, N-aqueous hydrochloric acid, and, finally, water. The ethereal layer was dried and evaporated at 12 mm., leaving an oil (2·8 g.) which was fractionated. The product (2·1 g.), 4-acetoxy-2-2′-acetoxyethyl-1 : 3-dioxan, had b. p. 96°/0·1 mm., n_D^{20} 1·4489 (Found: C, 51·65; H, 7·4. Calc. for $C_{10}H_{16}O_6$: C, 51·7; H, 6·95%). Bergmann *et al.* (*loc. cit.*) give b. p. 122—123°/0·5 mm., n_D^{20}

TABLE VI.

Hydrolysis of 4-acetoxy-2-2′-acetoxyethyl-1 : 3-dioxan by 0·05N-HCl at 70·0°.

Time (mins.).	Titre (ml. 0·01N-NaOH).	Diff. from blank (ml.).	Acetyl groups hydrolysed.	Time (mins.).	Titre (ml. 0·01N-NaOH).	Diff. from blank (ml.).	Acetyl groups hydrolysed.
Blank	24·20	—	—	70	28·40	4·2	1·7(5)
0	26·05	1·85	0·7(5)	90	28·70	4·5	1·9
5	26·70	2·5	1·0(5)	110	28·85	4·65	1·9(5)
10	26·90	2·7	1·1(5)	120	29·0	4·8	2·0
20	27·20	3·0	1·2(5)	130	29·1	4·9	2·0(5)

1·4490. This diacetate was hydrolysed by the method used by Späth and Schmid (*Ber.*, 1941, **74**, 859) for the hydrolysis of acetaldol dimer diacetate: it (0·1114 g.), n_D^{20} 1·4489, was added to approximately 0·05N-aqueous hydrochloric acid (100 ml.) at 70·0° ± 0·3°. Samples (5 ml.) of the homogeneous solution were titrated against freshly prepared 0·01N-sodium hydroxide solution (phenolphthalein indicator). Boiled-out distilled water was used for the hydrolysis and titration. Results are given in Table VI.

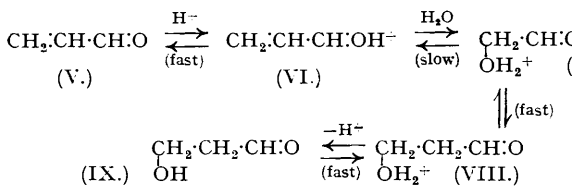
Discussion.

Previous discussions of the mechanism of hydration reactions based on kinetic work have dealt largely with the hydration of reactive olefins (Lucas *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 460, 2138; cf. Hammett, *op. cit.*, p. 292) and it has been postulated that an intermediate carbonium ion is formed by interaction of the olefin with a solvated hydrogen ion. Evidence adduced in favour of this mechanism included the fact that the rate of hydration is of the first order with respect to both the hydrocarbon and the catalyst concentration, the proportionality of the reaction rate to acid concentration in mixtures at constant ionic strength, and the similarity of the effects of different strong acids.

The hydration of αβ-unsaturated carbonyl compounds was investigated by Lucas *et al.* (*J. Amer. Chem. Soc.*, 1937, **59**, 1461; 1942, **64**, 1122, 1953; 1944, **66**, 1818), and interpreted in the case of mesityl oxide, of acraldehyde, and of 3-methylbut-2-en-1-al in terms of two simultaneous reactions, a hydroxonium-ion-catalysed hydration of "uncomplexed," and to a less extent of "complexed" starting material, *i.e.*, hydration *via* a carbonium ion and an oxonium ion, respectively. Evidence put forward for this dual mechanism is the observed increase in the ratio of rate constant to acid concentration with increasing acid concentration (from 0·2 to 2·0N.); Lucas *et al.* appear to interpret this as an increased contribution of the oxonium-ion mechanism at higher acidities, although it is probably better ascribed to effects of the medium as represented by Hammett's acidity function.

The salient experimental facts emerging from the present work are: the hydration is an equilibrium reaction (the equilibrium being approachable from both sides) of the first order with respect to acraldehyde, the rate constants being independent of initial acraldehyde concentration within the range studied. The dependence of the rate constants (between 20° and 50°) on the acid concentration is accurately expressed by Hammett's acidity function (data for the temperature dependence of which are not available in the literature). This is a criterion for specific hydrogen-ion catalysis, in view of the non-proportionality of rate constants to stoicheiometric acid concentration (cf. Hammett *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 830; 1936, **58**, 2182; 1939, **61**, 2791). The Arrhenius energies of activation of the hydration and dehydration reactions determined experimentally are 15·7 ± 0·4 and 21·6 ± 0·6 kcals. per mol., respectively, over the wide range of conditions examined: the rate-determining step of the dehydration is therefore unlikely to involve the normal ionic or covalent fission of a carbon–oxygen bond, as the energy requirements for these would be higher. Moreover, the comparatively small difference (6·0 ± 0·2 kcals. per mol.) in these energies of activation (which is equal to the heat of reaction) makes it appear probable that both the hydration and the dehydration proceed through the same rate-determining step.

The following mechanism is in accord with the facts observed and the deductions listed above. The first step of the hydration reaction is the reversible, fast (cf. Braude, *J.*, 1944, 447; Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686), acid-induced transfer of a hydrogen ion from its solvate to the carbonyl group of acraldehyde (V) to give the oxonium ion (VI); during the next



step, the rate-determining nucleophilic addition of a water molecule, the charge on the ion is redistributed, and the conjugate acid of an enol (VII) is produced which reverts to the carbonyl compound, the conjugate acid (VIII) of β-hydroxypropaldehyde; this tautomerisation would be expected to be fast (cf. Remick, "Electronic Interpretation of Organic Chemistry," J. Wiley and Sons, Inc., 1943, p. 376) and is therefore unlikely to constitute the rate-determining step. Fast reversible loss of a hydrogen ion from the conjugate acid finally affords β-hydroxypropaldehyde.

In the dehydration of this aldehyde the same steps are followed in the reverse order. The first is the fast acid-catalysed transfer of a hydrogen ion from the solvate to the aldehyde (IX); this will take place at the oxygen atom of the alcohol and not at that of the carbonyl group, as a carbonyl compound has stronger proton-donating (and thus weaker proton-accepting) properties than has an alcohol (cf. Braude *et al.*, *J.*, 1948, 1971, 1982). The oxonium ion (VIII) formed undergoes acid-catalysed enolisation (cf. Hammett, *op. cit.*, p. 231), generally a slow reaction (cf. Remick, *op. cit.*, p. 375) which in the case of the halogenation of carbonyl compounds constitutes the rate-determining step (Lapworth, *J.*, 1904, **85**, 30; Bell, " Acid-Base Catalysis," Oxford, Clarendon Press, 1941, pp. 52, 69, 137); the rate of enolisation of acetone thus determined is, however, still about ten times as great as that of the dehydration of β-hydroxypropaldehyde under consideration here. Moreover, in the present case the charge on the oxonium ion (VIII) may be expected to facilitate tautomerisation, and it is thus most unlikely that the enolisation step is rate-determining in the dehydration of β-hydroxypropaldehyde. This makes it seem more likely that the rate-determining step is the loss of water from the enol (VII) which proceeds with a simultaneous redistribution of the charge to give the oxonium ion (VI), which on loss of a hydrogen ion affords acraldehyde (V).

The essential rôle of the acid catalyst is thus to permit the formation of the oxonium ions (VI and VII), interconversion of which involves the addition or loss of a neutral water molecule. This step will require less energy than the addition of one ion to, or its separation from, another. The formation of the enolic ion (VII) from the conjugate acid (VIII) of β-hyroxypropaldehyde in the dehydration reaction is presumably necessary as the olefinic link of the enol (VII) provides a ready means of charge distribution during the loss of the water molecule, and thus of forming the conjugated system of the ion (VI).

Several effects observed in the present work are not readily predictable on the basis of the mechanism proposed, although they are not excluded by it. They include the variation of the equilibrium constant K with temperature, and the effect of acraldehyde concentration on the equilibrium constant and on the rate constant k_{-1} (cf. Table II). Whilst the former variation may be explained thermochemically, the latter effects are probably due to the dimerisation of β-hydroxypropaldehyde, which is, however, readily reversible and does not prevent an approach to the equilibrium from the β-hydroxypropaldehyde side.

No difficulty was experienced owing to the polymerisation or cyclic condensation of the aldehydes in solution, and the constancy of the equilibrium values (taken after 6 and 8 half-times of reaction) provides good evidence that these undesirable side reactions are very much slower than the hydration of acraldehyde under the conditions here examined.

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