222. *Kinetics of the Hydration of Mesityl Oxide and Crotonaldehyde.*

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The velocity of hydration of mesityl oxide and crotonaldehyde in solutions of strong acids increases more rapidly than the acid concentration, but less rapidly than the acidity function, h_0. Solutions of sulphuric and phosphoric acid give abnormally high velocities, indicative of general acid catalysis. The hydration of mesityl oxide in deuterium oxide is slower by a factor of 3—4 than it is in water. These findings are consistent with the mechanism proposed by Noyce and Reed, in which the rate-determining step is the same as in an enol–keto-transformation, involving the slow transfer of a proton from the catalyst to a carbon atom.

Kinetic measurements on the reversible hydration of olefins [1,2,3] have shown that in aqueous solutions of strong acids the reaction velocity is closely proportional to the acidity function h_0 up to a concentration of 4M, but the exact interpretation of this fact is still a matter of debate.[3,4] Similar measurements on the hydration of crotonaldehyde [5] and ββ-dimethylacraldehyde [6] show a closer proportionality between velocity and acid concentration, though the range of acid concentrations studied extended only up to 1·9M and 1M, respectively. Noyce and Reed [7] studied the dehydration of compounds of the type p-X·C_6H_4·CH(OH)·CH_2·CO·CH_3 up to high concentrations of mineral acid. They found that when X = OMe the rate is closely proportional to h_0, suggesting that the mechanism is the same as with the olefins. However, when X = H or NO_2 the rate increases much less rapidly than h_0: this fact, together with a consideration of the effect of substituents upon the velocity, led Noyce and Reed to propose for these systems a different mechanism, which will be discussed later in this paper. The object of the present work was to study the hydration of mesityl oxide and crotonaldehyde under a wider range of conditions, including the effect of deuterium substitution.

Experimental

" AnalaR " mesityl oxide and crotonaldehyde were redistilled, and had b. p. 128—129° and 102·0—102·4°, respectively. Concentrated solutions of acids were standardized by weight, and weighed amounts of these were diluted to give solutions for the kinetic experiments. Deuterium oxide (99·5% D_2O) was supplied by the Stuart Oxygen Company.

All kinetic measurements were made at 25°, both dilatometric and spectrophotometric methods being used. The former employed conventional dilatometers of 25—50-ml. capacity having capillaries 0·5—1 mm. in diameter. A comparison of the observed volume changes with the densities of mesityl oxide, diacetone alcohol, crotonaldehyde, and acetaldol indicates that the hydration goes almost to completion with mesityl oxide, but only about half-way with crotonaldehyde; the latter conclusion is less certain because of uncertainty as to the density of pure acetaldol. More accurate information about the position of equilibrium can be obtained from spectrophotometry, as described below.

The dilatometric measurements were carried out with 2—3% solutions of mesityl oxide or crotonaldehyde, giving a total movement of about 20 cm. in the capillary. Three methods were used to derive first-order velocity constants. For the fastest reactions an infinity reading R_∞ could be observed directly, and the velocity constant obtained by plotting log $(R_\infty - R)$ against the time. For reactions of intermediate speed the graphical method of Guggenheim [8]

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[1] Ciapetta and Kilpatrick, *J. Amer. Chem. Soc.*, 1948, **70**, 639.

[2] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372.

[3] Boyd, Taft, Wolf, and Christman, *J. Amer. Chem. Soc.*, 1960, **82**, 4729.

[4] Taft, Deno, and Skell, *Ann. Rev. Phys. Chem.*, 1958, **9**, 303.

[5] Winstein and Lucas, *J. Amer. Chem. Soc.*, 1937, **59**, 1461.

[6] Lucas, Stewart, and Pressman, *J. Amer. Chem. Soc.*, 1944, **66**, 1818.

[7] Noyce and Reed, *J. Amer. Chem. Soc.*, 1958, **80**, 5539.

[8] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

was employed, and for the slowest reactions R_∞ was calculated by using the amount of substance taken and results from the faster reactions. The three methods gave concordant results when applied to the same set of observations.

Spectrophotometric measurements with mesityl oxide employed the absorption peak at 243 mμ for which we found $\varepsilon = 1{\cdot}11 \times 10^4$, in good agreement with previous values.[9] Kinetic measurements were made with $\sim 7 \times 10^{-5}$M-solutions in 1 cm. silica cells, a Unicam SP 500 spectrophotometer being used. For solutions of hydrochloric acid in protium oxide the optical density after about 10 half-lives remained constant at 7% of its initial value. In sulphuric acid solutions the final optical density was higher and less reproducible, and in some cases increased again after several days. It seems probable that some slow subsequent reaction takes place in sulphuric acid solutions, and the velocity constants were therefore calculated for both acids by plotting log $(D_t - 0{\cdot}07D_0)$ against t, where D_t and D_0 are the optical densities at times t and zero. This procedure gave linear plots over at least 90% of the reaction for hydrochloric acid solutions, and over more than 50% of the reaction for sulphuric acid; the velocity constants thus obtained agree within a few per cent with those obtained by dilatometry.

In deuterium oxide solutions the equilibrium proportion of mesityl oxide was about 10% in hydrochloric acid, and somewhat higher in sulphuric acid. Velocity constants were calculated by plotting log $(D_t - 0{\cdot}1D_0)$ against t: this gave straight lines for about 65% of the reaction, after which the slope decreased. This decrease is probably due to the gradual replacement of hydrogen by deuterium on the =CH– group of mesityl oxide, owing to the reversibility of the hydration.

TABLE 1.

Hydration of mesityl oxide at 25°.

Dilatometric method, except constants marked *, which were determined spectrophotometrically.
c = acid concn. (moles/l.); k = first-order velocity constant (sec.$^{-1}$).

Hydrochloric acid

c	0·36	0·40	0·59	0·75	0·88	0·90	1·06	1·26	1·55	1·67	1·69	2·07	2·11	2·61	2·84
$-H_0$...	−0·38	−0·34	−0·11	0·03	0·12	0·14	0·23	0·34	0·49	0·55	0·56	0·72	0·73	0·92	0·98
10^6k ...	30	34 *	48	62	81 *	76	104*	122 *	146	160	164	213	220	300	340

Perchloric acid

c	0·31	0·50	0·71	0·91	1·36	1·75	1·90	2·01	2·28	2·66
$-H_0$...	−0·45	−0·20	0·00	0·13	0·44	0·67	0·73	0·79	0·92	1·07
10^6k ...	24	38	53	72	107	143	167	175	202	245

Nitric acid

c	0·37	0·50	0·61	0·81	1·07	1·62	2·14	2·32	2·66	2·99
$-H_0$...	−0·38	−0·21	−0·10	0·05	0·22	0·51	0·72	0·78	0·90	1·02
10^6k ...	28	40	51	61	80	131	176	192	225	268

Sulphuric acid

c	0·27	0·50	0·78	0·82	0·88	1·12	1·50	1·53	1·81	1·92	2·28
$-H_0$...	−0·42	−0·13	0·09	0·12	0·17	0·33	0·56	0·58	0·73	0·82	0·99
10^6k ...	36	68	109	111	139 *	177	253	286 *	345	380	512

Phosphoric acid

c	0·96	1·86	2·80	3·72	4·75
$-H_0$...	−0·65	−0·29	0·03	0·28	0·61
10^6k ...	32	77	139	205	311

Hydrochloric acid in deuterium oxide

c	1·02	2·36	3·27
$-H_0$ ...	0·21	0·82	1·15
10^6k ...	27·5 *	80 *	126 *

Sulphuric acid in deuterium oxide

c	0·64	0·74	1·26	2·80
$-H_0$...	−0·02	0·06	0·41	1·28
10^6k ...	25 *	28·5 *	58 *	197 *

Crotonaldehyde has a strong absorption band at about 200 mμ, and a much weaker one at 304 mμ: the latter is more convenient for measurement with the Unicam spectrophotometer. For freshly prepared aqueous solutions $\varepsilon = 37{\cdot}3$, and the final value corresponded to 43% hydration. Spectrophotometry was also used to discover whether the carbonyl compounds are appreciably protonated at the acidities used in the kinetic experiments. The addition of hydrochloric acid (up to 2·6M for mesityl oxide and 4·0M for crotonaldehyde) caused no

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[9] Nagakura, Minegiski, and Stanfield, *J. Amer. Chem. Soc.*, 1957, **79**, 1033.

detectable instantaneous change in extinction coefficient, and it may be concluded that protonation is insignificant.

The first-order velocity constants obtained by both dilatometric and spectrophotometric methods represent the sum of the constants for the forward and the reverse reactions. However, since the equilibrium position does not depend detectably upon the acidity, and is little affected by the change from water to deuterium oxide, the observed constants may be used directly for considering the effect of acidity or deuterium substitution.

The results obtained are given in Tables 1 and 2. The values of h_0 are taken from Long and Paul's compilation[10] or from the measurements by Bascombe and Bell,[11] and Högfeldt and Bigeleisen.[12]

TABLE 2.

Hydration of crotonaldehyde at 25°.

c = acid concentration (moles/litre); k = first-order velocity constant (sec.$^{-1}$).

Hydrochloric acid

c	0·44	1·15	2·64	3·02	3·96	5·20
$-H_0$	−0·29	0·29	0·93	1·06	1·38	1·78
10^6k	38	108	283	327	503	642

Nitric acid

c	1·82	2·57	3·61
$-H_0$	0·60	0·87	1·20
10^6k	161	215	382

Sulphuric acid

c	0·59	1·70	2·84
$-H_0$	−0·06	0·67	1·28
10^6k	95	355	777

DISCUSSION

The results with mesityl oxide are the more extensive and will be discussed first. For a given acid the reaction velocity increases more rapidly than the concentration and less rapidly than the acidity function h_0. This is illustrated by Fig. 1, in which log k for hydrochloric acid is plotted against H_0 and log c: the broken line is of unit slope. This behaviour falls between the two extreme possibilities, and the direct proportionality between reaction velocity and concentration suggested by the measurements of Winstein and Lucas[5] is not borne out by our results over a larger range of concentrations. Moreover, the different acids studied show individual behaviour, as shown by Fig. 2, which contains plots of log k against H_0 for all the acids. The curves for hydrochloric, perchloric, and nitric acid lie fairly close together, but solutions of sulphuric and phosphoric acid give higher velocities. If the velocity is plotted against acid concentration rather than acidity function, hydrochloric, perchloric, and nitric acid again show similar behaviour, and sulphuric acid again has a higher catalytic effect. When plotted on this basis the curve for phosphoric acid lies below those for the other acids; however, this acid is far from completely dissociated at the relevant concentrations, and any reasonable estimate of the degree of dissociation shows that it also has a greater catalytic power than solutions of the strong acids of equal hydrogen-ion concentration. It may be noted that the results with sulphuric acid cannot be explained in terms of the second dissociation of sulphuric acid, since this occurs only to a small extent at these concentrations.

The less extensive results for the hydration of crotonaldehyde reveal similar behaviour, as shown in Fig. 3. The velocity again increases less rapidly than h_0, but more rapidly than c: hydrochloric and nitric acid give similar velocities, but sulphuric acid is a more efficient catalyst.

Similarly, it was observed by Noyce and Reed[7] that in the dehydration of $Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$ and p-$NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$ sulphuric acid is about twice as effective a catalyst as perchloric acid of the same concentration or acidity.

These results with sulphuric and phosphoric acid suggest strongly that the reversible dehydration of β-hydroxy-aldehydes and -ketones is subject to general acid catalysis, so that the observed velocities contain terms involving $[HSO_4^-]$ and $[H_3PO_4]$, as well as

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[10] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

[11] Bascombe and Bell, *J.*, 1959, 1096.

[12] Högfeldt and Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15.

$[H^+]$. This behaviour contrasts with the specific hydrogen-ion catalysis observed with olefins,[1] and implies that the mechanism involves a slow proton-transfer, probably also when the only catalyst present is the hydrogen ion. This view is supported by the large hydrogen isotope effect which we have observed ($k_h/k_d = 3{\cdot}5$ for hydrochloric acid and 4·0 for sulphuric acid), again contrasting with the very small effect found for the hydration of olefins.[13]

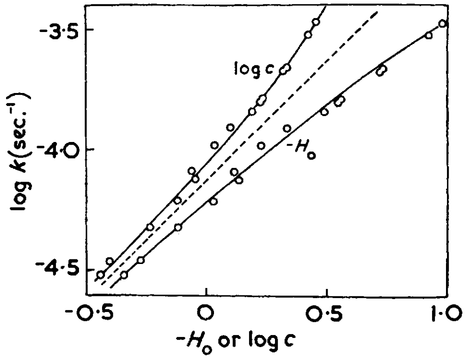

FIG. 1. Hydration of mesityl oxide in hydrochloric acid solution. (The broken line is of unit slope.)

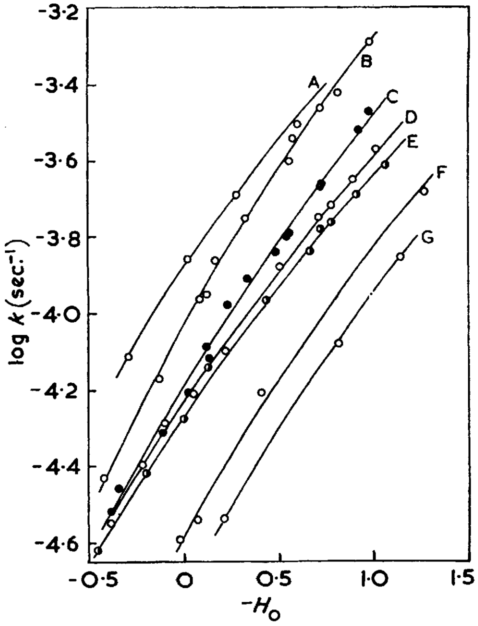

FIG. 2. Hydration of mesityl oxide in acid solutions. A, H_3PO_4; B, H_2SO_4; C, HCl; D, HNO_3; E, $HClO_4$; F, D_2SO_4; G, DCl.

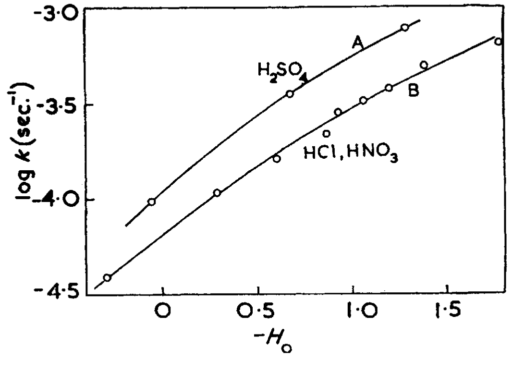

FIG. 3. Hydration of crotonaldehyde in acid solutions. A, H_2SO_4; B, HCl or HNO_3.

All these facts are in agreement with the mechanism proposed by Noyce and Reed, which for mesityl oxide can be generalized as:

$$\mathrm{Me_2C{:}CH{\cdot}COMe + H_2O \rightleftharpoons HO{\cdot}CMe_2{\cdot}CH{:}CMe{\cdot}OH} \quad \text{(Fast)}$$
$$\mathrm{HO{\cdot}CMe_2{\cdot}CH{:}CMe{\cdot}OH + Acid \rightleftharpoons HO{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe{:}OH^+ + Base} \quad \text{(Slow)}$$
$$\mathrm{HO{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe{:}OH^+ + Base \rightleftharpoons HO{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe + Acid} \quad \text{(Fast)}$$

The separate stages of the initial reversible stage have been omitted: it involves acid catalysis, and the equilibrium will lie far to the left, since the addition of water destroys

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[13] Purlee and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5807.

the conjugated system. The remainder of the reaction scheme constitutes an acid-catalysed keto–enol transformation, which is well known to involve general acid catalysis and to show a large deuterium isotope effect.

It is not clear what type of acidity dependence would be expected in reactions involving a rate-determining proton transfer from hydrogen ions in solutions of strong acids. Long and Paul[14] have suggested that in such cases the velocity should follow the acidity function, and this is approximately so for isotope exchange in trimethoxybenzene[15] and nitro-azulene,[16] though the position is complicated because the extent of protonation of these compounds does not always follow the acidity function as usually defined. As shown above, the velocity of the reactions studied here increases less rapidly than h_0, but more rapidly than the hydrogen-ion concentration.

The contrast between the catalytic behaviour and hydrogen isotope effect in the hydration of olefins on the one hand and of unsaturated aldehydes and ketones on the other can be attributed to the presence in the latter of the carbonyl group, which makes possible a different reaction mechanism. However, it is likely that under some conditions general acid catalysis and a large solvent isotope effect will occur in the addition of water to simple double or triple bonds, as has already been observed by Drenth and Hogeveen[17] in the hydration of acetylenic thio-ethers. The mechanism would then involve the rate-determining transfer of a proton from the catalyst to the multiple bond, analogous to the isotope exchange of trimethoxybenzene[18] and azulene,[19] for which general acid catalysis has been established.

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[14] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.
[15] Kresge and Chiang, *J. Amer. Chem. Soc.*, 1959, **81**, 5509.
[16] Long and Schulze, *J. Amer. Chem. Soc.*, 1961, **83**, 3340.
[17] Drenth and Hogeveen, *Rec. Trav. chim.*, 1960, **79** 1002.
[18] Kresge and Chiang, *Proc. Chem. Soc.*, 1961, 81; *J. Amer. Chem. Soc.*, 1961, **83**, 2877.
[19] Colapietro and Long, *Chem. and Ind.*, 1960, 1056.