Acylation. Part XXVII.[1] The Kinetics and Mechanism of the Spontaneous and Acid-catalysed Reactions of Dimethylketen with Water and Alcohols

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We report a kinetic study of the spontaneous and the carboxylic acid-catalysed additions of water and of a series of alcohols to dimethylketen in ether at 25°. The products are isobutyric acid or an isobutyryl ester. The addition of water is an autocatalytic process. The rate equations for the carboxylic acid-catalysed reactions, which do not proceed *via* a carboxylic anhydride intermediate, are respectively $-d[\text{Keten}]/dt = k_{cat}[H_2O][RCO_2H][\text{Keten}]$ and $-d[\text{Keten}]/dt = k_{cat}[R^1OH][R^2CO_2H][\text{Keten}]$. The catalytic effect of an acid is inversely related to its conventional strength and trichloroacetic acid is a very poor catalyst.

The spontaneous additions lead to rate equations which approximate closely to $-d[\text{Keten}]/dt = k_{\text{water dimer}}[(H_2O)_2][\text{Keten}]$ and $-d[\text{Keten}]/dt = k_{\text{alcohol trimer}}[(ROH)_3][\text{Keten}]$ for the water and alcohol reactions respectively. Water reacts more rapidly than the alcohols studied, although the alcohols are the more extensively associated in ether. Measurements of this association are reported; its extent is rather little dependent on the nature of R. The value of $k_{\text{alcohol trimer}}$ varies in a complex way with the nature of R; electron repulsion by, and the steric bulk of, R are two factors among others which affect the rate. The various results, including measurements of activation energy, considered in the light of our previous studies, constitute formidable evidence that both the spontaneous and the acid-catalysed addition of nucleophiles to ketens normally proceed *via* cyclic transition states.

KETENS add water and alcohols as in (1), leading to the respective carboxylic acid or ester. From the preparative viewpoint these reactions have appeared rather

$$R^1_2C{=}C{=}O + R^2OH \longrightarrow R^1_2CH{\cdot}CO_2R^2 \qquad (1)$$

slow compared with the addition of other reagents and acidic or basic catalysts have therefore often been employed.[2] However, few kinetic measurements are available. Recently work on the tertiary base-catalysed addition of alcohols to phenylketens has been reported.[3] We present here a kinetic study of the spontaneous and carboxylic acid-catalysed reactions of dimethylketen with water and with a series of alcohols in diethyl ether.

EXPERIMENTAL

Materials.—Dimethylketen, diethyl ether, and the carboxylic acids used as catalysts were prepared and purified as previously described.[1,4] Water was redistilled. 2-Chloroethanol was redistilled and a fraction, b.p. 129°, collected. The remaining alcohols were purified using an F and M 770 preparative scale gas–liquid chromatograph fitted with columns containing Carbowax 1500 on Celite. The alcohols were stored over a molecular sieve.

Kinetic Arrangements.—These were essentially those we have used and described before,[1,4] the loss of a 10-fold deficit of keten being followed spectrophotometrically at 384 mμ. Runs were normally conducted at 25°. Measurements at two other temperatures led to relevant Arrhenius parameters.

Acylation of Water.—The spontaneous reaction of water

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[1] Part XXVI, J. M. Briody, P. J. Lillford, and D. P. N. Satchell, preceding paper.

[2] R. N. Lacey, 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964.

[3] A. Tille and H. Pracejus, *Chem. Ber.*, 1967, **100**, 196.

[4] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 360.

exhibits autocatalytic behaviour, the acylation clearly being catalysed by the product, isobutyric acid. An estimate of k_{obs}, the pseudo-first-order rate constant for loss of keten, referring to the uncatalysed addition, can be obtained from the initial slope of the appropriate autocatalytic plot.

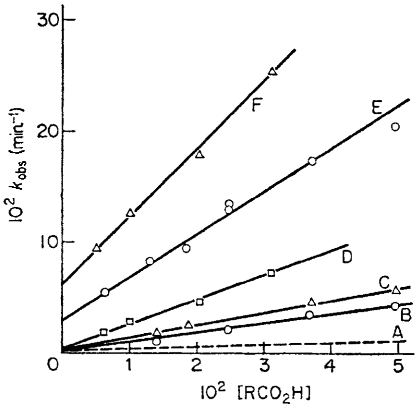

FIGURE 1 Orders in acid and water for the catalysed hydrolysis of dimethylketen in ether
$10^2[H_2O]_{stoich}$: A, 0·0; B, 2·6; C, 5·9; D, 11·7; E, 23·4; F, 35·1

A more convenient and accurate way to study the water reaction is deliberately to add a sufficient excess of isobutyric acid initially, so that that produced during the reaction is negligible compared with that already in solution. Under these conditions (*i.e.*, with initial acid and water concentrations both at least 10-fold greater than the initial keten concentration) the observed loss of keten is an accurately first-order process over more than three half-lives; k_{obs} for this catalysed addition is obtained from the slope of the first-order plot. Values of k_{obs} were reproducible to within ±5% with different batches of reagents.

TABLE 1

Hydrolysis of dimethylketen in the presence of added isobutyric acid at 25°

$[\text{Keten}]_{\text{initial}} = 10^{-3}$—$10^{-4}$M; for k_{obs} (min.$^{-1}$) see text; RCO_2H = isobutyric acid.

$10^2[H_2O]$	2·6	2·6	2·6	2·6
$10^2[RCO_2H]$ ...	1·23	2·47	3·68	4·92
10^2k_{obs}	1·01	2·07	3·48	4·33
$10^2[H_2O]$	5·9	5·9	5·9	5·9
$10^2[RCO_2H]$ ...	1·23	1·87	3·72	4·97
10^2k_{obs}	1·84	2·62	4·67	5·76
$10^2[H_2O]$	11·7	11·7	11·7	11·7
$10^2[RCO_2H]$ ...	0·62	1·00	2·03	3·10
10^2k_{obs}	1·91	2·84	4·60	7·32
$10^2[H_2O]$	23·4	23·4	23·4	23·4
$10^2[RCO_2H]$ ...	0·63	1·25	1·85	2·47
10^2k_{obs}	5·54	8·30	9·45	13·0
$10^2[H_2O]$	23·4	23·4	23·4	
$10^2[RCO_2H]$ ...	2·47	3·70	4·93	
10^2k_{obs}	13·4	17·3	20·6	
$10^2[H_2O]$	35·1	35·1	35·1	35·1
$10^2[RCO_2H]$ ...	0·50	1·00	2·03	3·10
10^2k_{obs}	9·45	12·6	18·0	25·4

By using a series of acid concentrations at a given, fixed water concentration, the value of k_{obs} for the spontaneous addition of water at that concentration can be obtained by extrapolation of the values of k_{obs} to zero acid concentration (Figure 1). This value can be compared with

$$-\frac{1}{[\text{Keten}]}\cdot\frac{d}{dt}[\text{Keten}] = k_{obs} = (k[H_2O]_{stoich}[RCO_2H]^y + k_{acid}[RCO_2H] \quad (2)$$

that found directly from the autocatalytic plot (Tables 1 and 2). Repetition of this process for a series of fixed water concentrations leads to the order in stoicheiometric water in the spontaneous reaction (see Discussion section). The orders in water and in acid in the catalysed reaction can, of course, also be calculated from the results so accumulated. Equation (2) applies to the catalysed system where the last term is the contribution to keten loss from its direct reaction with acid.[1] The order, y, in stoicheiometric acid is unity, as is evident from the rectilinearity of the plots in Figure 1. The order in stoicheiometric water is best obtained by plotting the slopes (S) of the lines in Figure 1 ($S = k[H_2O]^x_{stoich} + k_{acid}$) against $[H_2O]_{stoich}$. The result, Figure 2, shows that $x = 1$. The intercept in Figure 2, k_{acid}, should represent the second-order rate constant for the reaction of isobutyric acid with dimethylketen. Its value (0·26 l. mole.$^{-1}$ min.$^{-1}$) is in good agreement with that determined directly.[1] In these systems for studying the acylation of water the competing reaction with the carboxylic acid (product or catalyst), which leads to the anhydride, is of only minor importance (see Discussion section) and can be accurately allowed for, *e.g.*, by treating the results in the foregoing way.

TABLE 2

Rate of spontaneous reaction of water with dimethylketen at 25°

$[\text{Keten}]_{\text{initial}} \simeq 10^{-3}$M; for k_{obs} (min.$^{-1}$) see text.

(i) From intercepts of plots in Figure 1

$10^2[H_2O]$	2·6	5·9	11·7
10^2k_{obs}	0·0 ± 0·23	0·39 ± 0·30	0·75 ± 0·20
$10^2[H_2O]$	23·4	35·1	
10^2k_{obs}	3·26 ± 0·50	6·50 ± 0·40	

(ii) From initial slopes of autocatalytic plots

$10^2[H_2O]$	7·0	17·0	18·5
10^2k_{obs}	0·20 ± 0·20	0·84 ± 0·20	1·12 ± 0·20
$10^2[H_2O]$	24·0	32·0	
10^2k_{obs}	2·56 ± 0·30	5·84 ± 0·40	

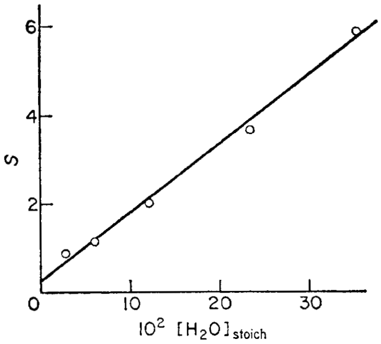

FIGURE 2 Plot of S ($= k[H_2O]^x_{stoich} + k_{acid}$) against $[H_2O]_{stoich}$

Acylation of Alcohols.—Autocatalysis does not, of course, complicate the spontaneous reactions of alcohols since the product is an ester. The observed loss of keten in the presence of a sufficient excess of an alcohol is always an accurately first-order process over more than three half-lives. Our values of the pseudo-first-order constant, k_{obs}, for a series of alcohols at various concentrations are in Table 3. The reactions are relatively very slow and it is necessary rigorously to exclude traces of oxygen and water which otherwise compete for the keten. Values of k_{obs} were nevertheless reproducible to within ±10%.

TABLE 3

Spontaneous reaction of alcohols with dimethylketen at 25°

$[\mathrm{Keten}]_{\mathrm{initial}} \simeq 10^{-2}$M; for k_{obs} (min.$^{-1}$) see text; ROH = alcohol.

(i) Methanol

10[ROH]	1·37	2·15	2·48	3·25	4·75	4·90
10^3k_{obs}	0·60	2·42	4·70	8·20	12·0	18·5

(ii) Ethanol

10[ROH]	1·00	2·00	2·50	2·98	3·47	3·98	4·30
10^3k_{obs}	0·46	3·16	4·66	6·42	8·87	12·5	16·7

(iii) Propanol

10[ROH]	1·50	2·27	2·93	3·50	3·90	4·72	5·13
10^3k_{obs}	0·80	2·73	3·64	8·30	10·4	17·8	21·3

(iv) n-Butanol

10[ROH]	1·03	1·72	3·10	4·10	4·90
10^3k_{obs}	0·32	1·50	5·95	14·3	25·0

(v) s-Butyl alcohol

10[ROH]	1·05	1·88	3·00	4·22	5·00
10^3k_{obs}	0·15	1·22	3·32	8·20	12·3

(vi) t-Butyl alcohol

10[ROH]	1·05	1·95	3·04	3·90	4·40	5·10
10^3k_{obs}	0·04	0·55	1·49	3·00	3·02	5·15

(vii) n-Octanol

10[ROH]	1·10	3·10	3·90	4·80
10^3k_{obs}	1·10	12·0	17·0	30·8

(viii) 2-Chloroethanol

10[ROH]	4·53
10^3k_{obs}	0·4

The catalysed addition of one alcohol, ethanol, was studied with a series of carboxylic acids as catalysts. The loss of keten remained accurately of the first order in all the catalysed runs regardless of the acid concentration, save for trichloroacetic acid. Our results for the catalysed processes are in Table 4. The reaction orders for the various alcohol systems are examined in the Discussion section.

Reaction Products and Stoicheiometry.—Reaction of water. Preparative-scale experiments, using concentration conditions similar to those of the kinetic runs, led to a high yield (>90%) of isobutyric acid as the only isolable product in both the spontaneous and the isobutyric acid-catalysed reactions of dimethylketen with water. I.r. examination of the product mixture from the catalysed reaction soon after its completion (*ca.* 10 half-lives), and without removal of solvent, indicated the existence of only a very small amount of isobutyric anhydride compared with that expected if all the keten had been converted into anhydride. I.r. measurements also showed that mixtures of isobutyric anhydride and acid in ether acylate water relatively very slowly compared with the rate of loss of keten in similar systems in which keten replaces the anhydride. It is clear therefore that the catalysed reaction of water with keten (and hence likewise the spontaneous reaction) does not proceed *via* the anhydride. The small amount of anhydride produced is due to a side reaction. The amount is compatible with the known rate constant for the spontaneous addition of isobutyric acid to the keten and indeed, as noted above, the kinetics lead to an indirect value of this rate constant in good agreement with previous data.[1]

TABLE 4

Acid-catalysed reaction of ethanol with dimethylketen at 25°

$[\mathrm{Keten}]_{\mathrm{initial}} \simeq 10^{-2}$M; k_{obs} (min.$^{-1}$) = rate constant for observed first-order loss of keten; k (min.$^{-1}$) = ($k_{obs} - k_{acid}[\mathrm{RCO_2H}]$).

(i) Isobutyric acid

10[EtOH]	0·72	0·72	0·72	1·59	1·59
$10^2[\mathrm{RCO_2H}]$	1·09	2·66	5·40	1·09	2·66
10^2k_{obs}	1·3	3·0	5·9	2·4	6·0
10[EtOH]	1·59	1·59	2·18	3·35	4·36
$10^2[\mathrm{RCO_2H}]$	4·30	4·55	2·66	2·66	0·60
10^2k_{obs}	8·6	9·5	6·9	9·9	4·4
10[EtOH]	4·36	4·36	4·36	4·36	
$10^2[\mathrm{RCO_2H}]$	1·10	2·66	4·25	5·30	
10^2k_{obs}	5·9	13·2	21·2	24·0	

(ii) Pivalic acid ([EtOH] = 0·17M)

$10^2[\mathrm{RCO_2H}]$	1·23	3·67
10^2k_{obs}	3·3	9·5
10^2k	2·8	8·2

(iii) Benzoic acid ([EtOH] = 0·17M)

$10^2[\mathrm{RCO_2H}]$	1·74	5·23
10^2k_{obs}	3·5	9·4
10^2k	2·9	7·4

(iv) 2-Chloropropionic acid ([EtOH] = 0·17M)

$10^2[\mathrm{RCO_2H}]$	1·59	4·65	4·78
10^2k_{obs}	2·0	5·1	5·2
10^2k	1·8	4·4	4·5

(v) Chloroacetic acid ([EtOH] = 0·17M)

$10^2[\mathrm{RCO_2H}]$	1·70	5·05
10^2k_{obs}	1·6	3·9
10^2k	1·4	3·6

(vi) Dichloroacetic acid ([EtOH] = 0·17M)

$10^2[\mathrm{RCO_2H}]$	1·20	3·60
10^2k_{obs}	1·1	2·3
10^2k	0·7	1·2

(vii) Trichloroacetic acid ([EtOH] = 0·17M)

$10^2[\mathrm{RCO_2H}]$	2·11	4·29
10^2k_{obs}	10·4	20·6
10^2k	0·3	—

Reaction of alcohols. The kinetic experiments suggested that the reaction of keten was quantitative. This was checked for methanol, ethanol, and t-butyl alcohol (one of the least reactive alcohols) by conducting preparative-scale experiments, which simulated as far as possible the concentration conditions of the kinetic runs, and analysing the products quantitatively with a Griffin and George D6 gas-balance chromatograph. A very high yield (>95%) of ester was found in each case. For these alcohols, and also for propanol, samples of the respective ester products were isolated from preparative reaction mixtures chromatographically and identified by comparison of their i.r. and n.m.r. spectra with those of authentic samples. No anomalous product was encountered and it is evident that ester formation proceeds cleanly, and in high yield, even for the more sluggish of the alcohols. The low yields reported by some other workers[2] doubtless arose owing to inadequate exclusion of atmospheric moisture and oxygen.

In the carboxylic acid-catalysed reactions of ethanol with the keten there exists always a competition between two processes, ester formation and anhydride formation. For most of the acids anhydride formation is relatively unimportant compared with the catalysed alcoholysis, and ethyl isobutyrate is formed in high yield (chromatographic analysis). For these acids i.r. examination of a reaction mixture shows that the ester (carbonyl stretch at 1740 cm.$^{-1}$) and (to a much smaller extent) the anhydride are both formed from the start of the reaction. However, trichloroacetic acid reacts much more rapidly with the keten than do any of the other catalysts. In its case i.r. examination shows that trichloroacetic isobutyric anhydride (carbonyl stretch 1844 cm.$^{-1}$) is effectively the only product initially formed, removing all (or an equivalent amount) of the keten, and that this anhydride subsequently, and relatively very slowly, acylates the ethanol. For trichloroacetic acid therefore the rate of removal of keten is dominated by the reaction with the acid. Hence when the acid is present in concentrations comparable with, or lower than, that of the keten, accurate first-order loss of keten over an extensive part of the reaction cannot be expected, nor is it found.

I.r. examination of mixtures of isobutyric anhydride, isobutyric acid, and ethanol also showed that the ethanol is acylated very slowly by this anhydride under concentration conditions for acid and ethanol similar to those obtaining in the keten reaction mixtures. The removal of ethanol in its acid-catalysed reactions with keten cannot, therefore, be due to acylation *via* the anhydride.

It follows that the small amount of isobutyric anhydride impurity[4] in our dimethylketen will not have affected our kinetic and other observations significantly.

Water and Alcohol Association in Ether Solution.—In benzene-like solvents the O–H stretching frequency of monomeric water and alcohols is found at *ca.* 3650—3700 cm.$^{-1}$. In ether solution alcohols are exclusively hydrogen-bonded to the solvent at low concentrations and the O–H frequency lies at 3500—3510 cm.$^{-1}$. For water a doublet is found with frequencies of 3513 and 3590 cm.$^{-1}$. At high concentrations in ether, alcohols (and water) tend to associate and new absorption at *ca.* 3300 cm.$^{-1}$ is expected on the basis of work in other solvents.[5] Unfortunately in ether this absorption is obscured by strong solvent bands. At the same time, however, the absorption representing the hydrogen-bonded monomer no longer obeys Beer's law with respect to stoicheiometric alcohol (because a significant amount is going to form associated species) and it is possible to assess the extent of association by determining the departure from Beer's law.[5] Experiments of this sort were conducted with water and with all the relevant alcohols. The concentration ranges studied spanned those used in the kinetic work (Table 5). All i.r. measurements were made on a Perkin-Elmer 457 double-beam instrument. The sample cell, fitted with silver or sodium chloride windows, had a path-length of 0·1 mm.

TABLE 5

I.r. measurements of alcohols in ether at 25° ± 2°

$D = \log(I_0/I)$ at stated wavelength; all wavelengths in cm.$^{-1}$.

(i) Methanol (3510)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·53	1·07	1·62	2·15	3·20	4·28	5·35
$10D$	0·58	1·10	1·68	2·21	3·13	4·08	5·00
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·53	1·06	1·58	2·08	2·97	3·89	4·75
(ii) Ethanol (3500)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·52	1·05	1·56	2·08	3·12	4·19	5·19
$10D$	0·54	1·06	1·55	2·02	2·92	3·78	4·58
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·52	1·05	1·53	1·98	2·85	3·70	4·50
(iii) Propanol (3505)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·50	1·00	1·49	1·99	3·00	3·98	5·00
$10D$	0·46	0·98	1·43	1·84	2·78	3·76	4·56
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·50	1·00	1·49	1·97	2·90	3·88	4·78
(iv) n-Butanol (3505)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·51	1·02	1·52	2·03	3·05	4·06	5·08
$10D$	0·49	0·98	1·45	1·95	2·86	3·80	4·50
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·51	1·02	1·52	2·03	2·97	3·96	4·69
(v) s-Butyl alcohol (3505)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·52	1·03	1·55	2·07	3·11	4·14	5·18
$10D$	0·42	0·91	1·32	1·75	2·59	3·47	4·13
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·52	1·03	1·55	2·07	3·06	4·04	4·78
(vi) t-Butyl alcohol (3500)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·50	0·99	1·49	2·00	2·98	3·98	5·00
$10D$	0·38	0·76	1·09	1·43	2·70	2·76	3·35
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·50	0·99	1·43	1·88	2·74	3·58	4·35
(vii) n-Octanol (3500)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·52	1·05	1·57	2·09	3·14	4·18	5·23
$10D$	0·57	1·18	1·70	2·20	3·16	4·08	5·05
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·52	1·05	1·57	2·00	2·90	3·71	4·57
(viii) 2-Chloroethanol (3460)							
$10[\mathrm{ROH}]_{\mathrm{stoich}}$ ...	0·48	0·98	1·45	1·93	2·93	3·90	4·88
$10D$	0·54	1·08	1·58	2·06	3·04	4·04	4·93
$10[\mathrm{ROH}]_{\mathrm{monomer}}$	0·48	0·98	1·45	1·88	2·76	3·70	4·50

RESULTS AND DISCUSSION

Since the observed loss of keten is everywhere a first-order process, one keten molecule will be involved in each of the various transition states we shall consider.

Spontaneous Reaction of Water.—The values of k_{obs} (Table 2) increase more quickly than does $[\mathrm{H_2O}]_{\mathrm{stoich}}$ and a plot (Figure 3) of $k_{\mathrm{obs}}/[\mathrm{H_2O}]_{\mathrm{stoich}}$ against $[\mathrm{H_2O}]_{\mathrm{stoich}}$ leads, at concentrations $\leqslant$ *ca.* 0·3 M-water, to a good straight line passing (within experimental error) through the origin. This indicates that over this concentration range the data obey equation (3) where $k_{\mathrm{water\ monomer}} =$

$$k_{\mathrm{obs}} = k_{\mathrm{water\ monomer}}\,[\mathrm{H_2O}]^2_{\mathrm{stoich}} \qquad (3)$$

0·47 l.^{2} mole^{-2} min.$^{-1}$. When $[\mathrm{H_2O}]_{\mathrm{stoich}} \geqslant$ *ca.* 0·3 k_{obs} is too large to fit equation (3). Significantly the i.r. experiments (Table 5) concerning the O–H stretching frequencies of water in ether show that the $[\mathrm{H_2O}]_{\mathrm{stoich}} < 0·3$ there is negligible deviation from a Beer's law relationship based on the assumption that $[\mathrm{H_2O}]_{\mathrm{stoich}} = [\mathrm{H_2O}]_{\mathrm{monomer}}$. Above 0·3M some slight deviation occurs, suggesting that now sufficient association is taking place just to disturb this assumption. Nevertheless water is clearly rather little associated in ether over the ranges we

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[5] R. G. Inskeep, F. E. Dickson, and J. M. Kelliker, *J. Mol. Spectroscopy*, 1960, **4**, 477; D. Papousch and L. Pago, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2666; W. Goody and S. C. Stanford, *J. Chem. Phys.*, 1941, **9**, 204; M. Saunders and J. B. Hine, *J. Chem. Phys.*, 1958, **29**, 1319; A. B. Littlewood and F. N. Willmott, *Trans. Faraday Soc.*, 1966, **62**, 3287; D. A. Ibbitson and L. F. Moore, *J. Chem. Soc.* (*B*), 1967, **76**; G. M. Barrow, *J. Phys. Chem.*, 1955, **59**, 1129; A. N. Fletcher and C. A. Heller, *J. Phys. Chem.*, 1967, **71**, 3742.

have studied, and below 0·3M the equilibrium (4), from which hydrogen-bonded solvent has been omitted for

$$2H_2O \overset{K_2}{\rightleftharpoons} (H_2O)_2 \qquad (4)$$

ease of representation, must lie well to the left. Since $[(H_2O)_2] = K_2[H_2O]^2$, therefore $[(H_2O)_2] = K_2[H_2O]_{stoich}{}^2$.

Equation (3) indicates that the reaction path at $[H_2O]_{stoich} \leqslant$ *ca.* 0·3M involves a transition state containing, besides the keten molecule, two molecules of water, the second molecule clearly acting as a catalyst. There is no detectable path involving only a single water molecule. It may be assumed therefore that either the keten reacts bimolecularly with dimeric water (present in very low concentration) or in a termolecular collision with two monomeric molecules. The latter process seems much the less likely. This view is supported by the curvature apparent in Figure 3 above 0·3M and the existence, above this concentration, of detectable association of water. Once a significant amount of dimer is formed it is probable for water (the phenomena for water and alcohols (see Experimental and Table 2) are likely to differ since water has two hydrogen atoms per molecule) that higher polymers also begin to appear and that these two contribute to the reaction, thus causing k_{obs} to exceed $k_{water\ monomer}$ $[H_2O]^2{}_{stoich}$ as found. If reaction *via* dimer is assumed at concentrations <0·3M then equation (5) follows.

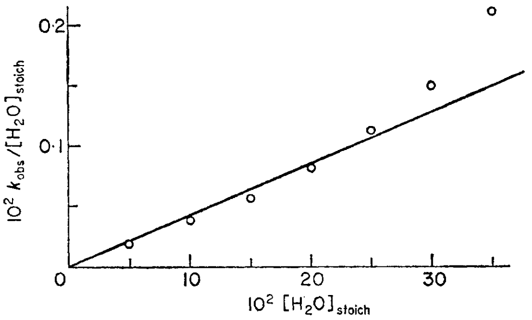

FIGURE 3 Spontaneous hydrolysis of dimethylketen in ether (Interpolated values at rounded molarities)

$$k_{obs} = k_{water\ monomer}[H_2O]^2{}_{stoich} = (k_{water\ monomer}/K_2)[(H_2O)_2] = k_{water\ dimer}[(H_2O)_2] \qquad (5)$$

The extent of association is so small that only an upper limit could be set on K_2. On this basis we find $k_{water\ dimer} \geqslant$ *ca.* 12 l. mole^{-1} min.$^{-1}$.

Reaction of Water Catalysed by Isobutyric Acid.—The observed reaction orders correspond to the rate equation (6) for this reaction which does not proceed *via* the anhydride. The direct, spontaneous reaction of isobutyric acid with the keten [1] is much slower than the catalysed addition of water by this acid, and the remaining possibility, the addition of isobutyric acid catalysed by water, appears negligible. The relatively slow addition of acid (and isobutyric acid is of the more reactive of paraffinic acids [1]) compared with that of water, in a system containing both, confounds previous conclusions.[2] It warns of the danger of founding mechanistic conclusions on reaction products only.

$$-d[\text{Keten}]/dt = k_{cat}[H_2O][RCO_2H][\text{Keten}] = k_{obs}[\text{Keten}] \qquad (6)$$

Equation (6) implies that the transition state for the catalysed addition of water involves one keten, one water, and one acid molecule. The value of $k_{cat} = 14{\cdot}8$ l.^{2} mole.$^{-2}$ min.$^{-1}$ compared with that of $k_{water\ monomer}$ shows that an acid molecule is considerably more effective than a second water molecule in aiding the addition. There is no detectable path involving acid and two water molecules.

Spontaneous Reaction of Alcohols.—Our kinetic results for the various alcohols are in Table 3 and measurements of their association are in Table 5. The range for $[ROH]_{stoich}$ was *ca.* 0·05—0·50M, wherein k_{obs} obeys equation (7) in which x varies between 3 and 2, the order tending to diminish as $[ROH]_{stoich}$ rises (Figure 4). There is no evidence for a term first-order in alcohol

$$-d[\text{Keten}]/dt = k_{ROH}[ROH]^x{}_{stoich}[\text{Keten}] = k_{obs}[\text{Keten}] \qquad (7)$$

(*i.e.*, with $x = 1$). The alcohol range covered by x depends upon the alcohol concerned.

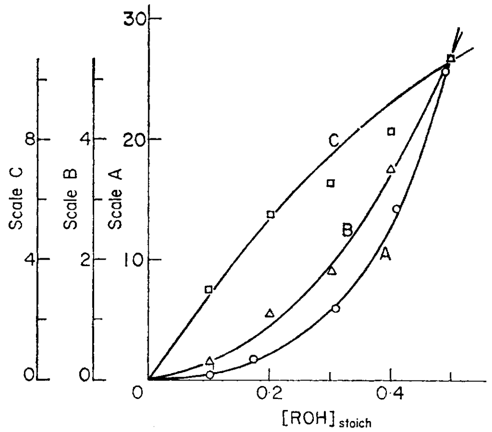

FIGURE 4 Spontaneous butanolysis of dimethylketen in ether. Scale A: 10^3k_{obs}; Scale B: $10^2k_{obs}/[ROH]_{stoich}$; Scale C: $10^2k_{obs}/[ROH]^2{}_{stoich}$

Table 5 shows that for all the alcohols a significant fraction of the stoicheiometric amount added exists in solution in an associated form, rather than as monomer. This is especially so at the higher values of $[ROH]_{stoich}$. By combining data in Tables 3 and 5 it is found that plots of k_{obs} against $[ROH]_{assoc}$ are reasonably rectilinear (Figure 5). This shows that the reaction is of the first-order in keten and also in associated alcohol and strongly suggests that the latter is effectively a single type of species over the concentration range involved (equation 8). The values of x in equation

$$-\mathrm{d}[\mathrm{Keten}]/\mathrm{d}t = k_{\mathrm{alcohol}\ y\text{-mer}}[\mathrm{Keten}][(\mathrm{ROH})_y] = k_{\mathrm{obs}}[\mathrm{Keten}] \quad (8)$$

(7) suggest that $y = 3$, and reasonably constant values of K_3, the equilibrium constant for trimer formation (9), can be calculated from the association data (Table 6). The net effect of substituents on the association is

$$3\mathrm{ROH} \overset{K_3}{\rightleftharpoons} (\mathrm{ROH})_3 \quad (9)$$

small and leads to a haphazard order for the magnitude of K_3. A similar effect is found fort he dimerisation of carboxylic acids.[6] Values of $k_{\mathrm{alcohol\ trimer}}$ calculated on the basis of (8) with $y = 3$ are in Table 6.

TABLE 6

Rate and equilibrium data for associated alcohols at 25°

For K_3 (l.^{2} mole^{-2}) and $k_{\mathrm{alcohol\ trimer}}$ (l. mole^{-1} min.$^{-1}$) see text.

		$k_{\mathrm{alcohol\ trimer}}$	
Alcohol	K_3	This work	From ref. 3 ($\times 10^3$)
Methanol	0·24	1·04	8·6
Ethanol	0·40	0·81	
Propanol	0·05	2·7	
n-Butanol	0·09	2·5	18·5
s-Butyl alcohol	0·07	1·7	
t-Butyl alcohol	0·33	0·23	
n-Octanol	0·40	1·13	
2-Chloroethanol	0·20	~0·04	

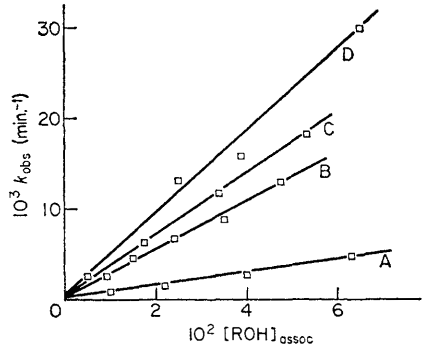

FIGURE 5 Dependence of alcoholysis on associated alcohol: A, t-butyl alcohol; B, ethanol; C, methanol; D, n-octanol

It is surprising that significant participation of dimeric alcohol is not implicated, for although cyclic, trimeric alcohol is often[5] thought to be prominent in weakly or non-hydrogen-bonding solvents (the true situation is still uncertain even in these solvents), appreciable dimer formation appears intuitively likely in such basic solvents as ether. In truth our various data (and especially our association data) are not sufficiently accurate rigorously to exclude participation by dimer, but the evidence points to a predominant reaction *via* the trimer.

Tille and Pracejus in their work[3] with phenylketens were mainly concerned with the tertiary amine-catalysed addition of alcohols, but they present a few measurements referring to the spontaneous addition. They worked with toluene solutions at relatively very low temperatures (−50°, −98°) and claim the acylations to be of the first order in $[\mathrm{ROH}]_{\mathrm{stoich}}$ at −98° and second-order at −50°. Although they calculated their rate constants for the lower temperature on the basis of $[\mathrm{ROH}]_{\mathrm{stoich}}$ it is only possible to understand their observed reaction order in terms of effectively complete conversion of added alcohol into a single type of polymer, say the trimer. Their data, recalculated on this assumption, are included in Table 6. Their result at −50° is very difficult to understand and their explanation of it unacceptable. As they appear aware, very appreciable association must still exist at −50° in toluene, and reaction cannot be due only to a route involving two monomer molecules: if polymers have to be invoked at −98° such species will certainly react at −50°. Moreover good second-order behaviour in $[\mathrm{ROH}]_{\mathrm{stoich}}$ cannot be expected over a range of alcohol concentrations if much of the alcohol is associated. Unfortunately Tille and Pracejus give few experimental details and no indication of the concentration ranges employed. It is very likely that alcohols, in fact, exhibit a variable order in $[\mathrm{ROH}]_{\mathrm{stoich}}$ in toluene at moderately low temperatures and concentrations, as found here for ether.

Data for the effect of temperature on the rate of reaction of ethanol with dimethylketen are in Table 7. Rather a small effect on k_{obs} is found, the apparent activation energy and entropy being $E_a = 3{\cdot}3$ kcal./mole and $\Delta S^{\ddagger} = -57$ e.u., respectively. This result is nicely in keeping with a mechanism *via* associated alcohol for although $k_{\mathrm{alcohol\ trimer}}$ in equation (8) will fall with fall in temperature this will be offset by an increase in K_3 and hence in $[(\mathrm{ROH})_3]$. The very highly negative entropy of activation certainly seems sensible.

TABLE 7

Effect of temperature on reaction of ethanol with dimethylketen

$[\mathrm{Keten}]_{\mathrm{initial}} \simeq 10^{-2}$M; for k_{obs} (min.$^{-1}$) see text; $[\mathrm{ROH}]_{\mathrm{stoich}} = 0{\cdot}301$M.

Temp.	$10^3 k_{\mathrm{obs}}$	
25°	6·55	$E_a = 3{\cdot}3 \pm 0{\cdot}2$ kcal. mole^{-1} $\Delta S^* = -57 \pm 5$ e.u.
15	4·60	
5	3·67	

Reaction of Ethanol Catalysed by Carboxylic Acids.—Our results are in Table 4. Catalysis by isobutyric acid was most thoroughly studied. The results for this acid are represented in Figure 6, where k_{obs} at various fixed values of $[\mathrm{EtOH}]_{\mathrm{stoich}}$ is plotted against $[\mathrm{RCO_2H}]$. The rectilinear plots, with intercepts which accord within experimental error with the values of k_{obs} expected for the spontaneous reaction of ethanol at the different concentrations, indicate that the order in acid is unity. A similar pattern of catalysis is found with the other acids (except trichloroacetic acid).

In these acid-catalysed systems k_{obs} is the sum of

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[6] D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 1965, **61**, 1199; G. Allen and E. F. Caldin, *Quart. Rev.*, 1953, **7**, 255.

three terms: that resulting from the spontaneous addition of ethanol to give ester, that from the direct reaction of the acid to give the corresponding anhydride, and that from the acid-catalysed addition of ethanol to give ester *via* a route which avoids the anhydride (see Experimental). This situation can, in view of our various earlier arguments and findings, be represented as in equation (10). As in the corresponding water re-

$$-\mathrm{d}[\text{Keten}]/\mathrm{d}t = \{k_{\text{alcohol trimer}}[(\text{ROH})_3] + k_{\text{acid}}[\text{RCO}_2\text{H}] + k_{\text{cat}}[\text{RCO}_2\text{H}][\text{ROH}]^2_{\text{stoich}}\}[\text{Keten}] = k_{\text{obs}}[\text{Keten}] \qquad (10)$$

action there is no evidence for significant contribution from an alcohol-catalysed addition of acid. The percentage contribution to k_{obs} made by the term $k_{\text{acid}}[\text{RCO}_2\text{H}]$ depends upon the acid; for most of the acids it is small (as for isobutyric acid, Figure 6) but for trichloroacetic acid, owing to the relatively very great spontaneous reactivity of this compound, it is virtually the only contribution.

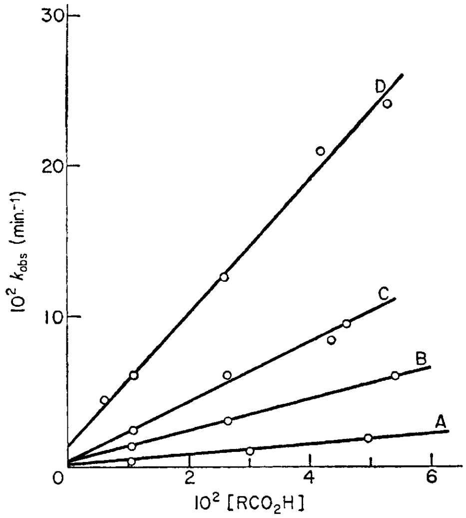


FIGURE 6 Isobutyric acid-catalysed ethanolysis of dimethylketen in ether

10[EtOH]: A, 0·0; B, 0·72; C, 1·59; D, 4·36

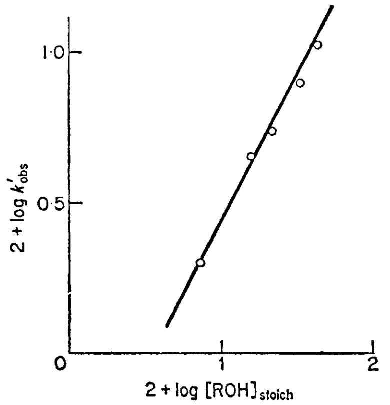


FIGURE 7 Order in alcohol in the isobutyric acid catalysed ethanolysis of dimethylketen

To obtain *z*, the order in alcohol in the acid-catalysed process, choice is made of a fixed acid concentration and, for a series of values of $[\text{ROH}]_{\text{stoich}}$, k_{obs} corrected for both $k_{\text{alcohol trimer}}[(\text{ROH})_3]$ and $k_{\text{acid}}[\text{RCO}_2\text{H}]$. The resulting constant $k'_{\text{obs}} = k_{\text{obs}} - (k_{\text{alcohol trimer}}[(\text{ROH}_3] + k_{\text{acid}}\ [\text{RCO}_2\text{H}]) = k_{\text{cat}}[\text{RCO}_2\text{H}][\text{ROH}]^2_{\text{stoich}}$. Hence a plot of log k'_{obs} against log $[\text{ROH}]_{\text{stoich}}$ leads to *z*. Figure 7 contains such a plot using the data for isobutyric acid catalysis at an acid concentration of $2{\cdot}66 \times 10^{-2}$M. A reasonably straight line with a slope close to unity (*i.e.*, $z \simeq 1$) is obtained. We can therefore write equations (11) for the catalysed ethanolysis. Our values of k_{cat} (Table 8) are calculated on this basis.

TABLE 8

Catalytic rate constants and carboxylic acid strength

For k_{acid} (l. mole^{-1}) and k_{cat} (l.^{2} mole^{-2} min.$^{-1}$) see text; pK_a = acid dissociation constant in aqueous solution at 25°.

Acid	k_{acid}	k_{cat}	pK_a
Pivalic	0·325	12·4	5·03
Isobutyric	0·225	11·3	4·90
Benzoic	0·201	8·6	4·20
2-Chloroproprionic......	0·16	5·5	4·10
Chloroacetic	0·048	4·2	2·85
Dichloroacetic............	≃0·03	⩽2·8	1·30
Trichloroacetic	5·2	<0·5	0·70

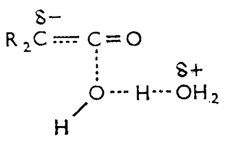
$$\begin{aligned} k_{\text{obs}} &= k_{\text{cat}}[\text{RCO}_2\text{H}][\text{ROH}]_{\text{stoich}} \\ &\simeq k_{\text{cat}}[\text{RCO}_2\text{H}][\text{ROH}] \end{aligned} \qquad (11)$$

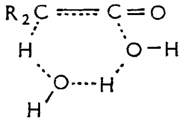
Equation (11) implies that the catalysed path has a transition state, containing besides the keten molecule, one acid and one alcohol molecule. The values of k_{cat} show that an inverse relationship exists between catalytic power and acid strength (pK_a). Indications of a similar effect were found[4] for the catalysed addition of *m*-chloroaniline to dimethylketen, when, however, only two acids were used. It is interesting that the ratio of the catalytic constants for these acids for the aniline addition, $(k_{\text{cat}})_{\text{isobutyric}} : (k_{\text{cat}})_{\text{chloroacetic}} = 2{\cdot}3$, is close to the value, 2·7, now obtained for the ethanolysis. Clearly the acid plays a similar role in both reactions. A significant feature is that trichloroacetic acid is a very feeble catalyst, whereas if ester formation normally took place *via* the anhydride it would be a relatively very good one.

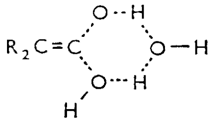
Reaction Mechanisms.—Spontaneous addition of water. The essential finding is that at least two water molecules are involved. Any path involving only one molecule is very much slower than the path (or paths) involving two. The second water molecule clearly acts as a catalyst. As deduced earlier the slow step probably incorporates dimeric water, the overall process being (12).

$$\begin{aligned} &2\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_2 && \text{Fast } (a) \\ &(\text{H}_2\text{O})_2 + \text{R}_2\text{C=C=O} \longrightarrow \text{R}_2\text{CH·CO}_2\text{H} + \text{H}_2\text{O} && \text{Slow } (b) \end{aligned} \qquad (12)$$

Since the addition of such weak nucleophiles as carboxylic acids involves what is essentially a nucleophilic attack by acid on the keten,[1] it follows that here, with water, we must have an assisted nucleophilic attack by oxygen in the slow step (12*b*). Considering the present information otherwise in isolation, we can represent the transition state for (12*b*) in three ways (I), (II), and (III). The route *via* the non-cyclic transition state (I) requires a final, rapid proton transfer between species H_3O^+ and (IV), and that *via* (III) a final, rapid prototropic rearrangement of (V). Transition state (II) leads directly to the products. Anticipating subsequent arguments we regard (II) as much the most likely. A telling point in favour of a cyclic scheme is that if the role of the catalytic molecule were simply to render the attacking molecule more nucleophilic by partially accepting a proton from it in the transition state, as in (I), there is no obvious reason why the solvent, to which water appears to be relatively so strongly hydrogen-bonded that no measureable dimer species exist, should not also be able to take such a role to some extent. But no term in monomeric water appears in the rate equation. In the cyclic schemes proton transfer, as well as proton acceptance, by the catalyst is involved.


(I)


(II)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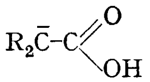
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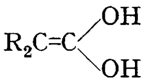
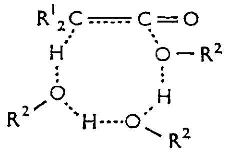
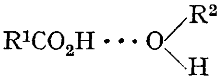

(V)

Spontaneous addition of alcohols. Here the reaction almost certainly involves only associated alcohol species, probably the trimer. The overall process approximates to (13). The reaction of monomeric alcohol (hydrogen-bonded to ether) is so slow as to be undetectable and, as for the water reaction, this alone suggests the involvement of a cyclic transition state for (13b). The anologue of (II) is (VI), containing a partially opened cyclic trimer. Table 6 shows that the rate constant for step (13*b*), $k_{\text{alcohol trimer}}$, varies in a complex way with alcohol structure. At least three factors must determine the rate; two can be identified. Clearly inductive electron-withdrawal by the chloro-substituent of 2-chloroethanol severely reduces the nucleophilicity of this alcohol, and an increase in electron-release to oxygen probably accounts for the greater reactivity of propan-1-ol and butan-1-ol than of ethanol. The importance of steric bulk (leading to interference with the keten methyl groups?) is evident from the fall in reactivity from butan-1-ol to t-butyl alcohol especially since t-butyl alcohol will possess the greatest electron-release. The reactivity sequence primary > secondary > tertiary has been found in purely preparative experiments.[2] To explain the complete straight-chain series H_2O (based on $k_{\text{water dimer}}$) $>$ MeOH $>$ EtOH $<$ Pr^nOH $>$ Bu^nOH $>$ n-$C_8H_{17}{\cdot}OH$ a further factor (or factors) must be invoked. Various alkane derivatives exhibit similar orders of reactivity in other contexts but speculation, rather than convincing explanation, is all that has been forthcoming so far. We shall not add to it. The data for $k_{\text{alcohol trimer}}$ are, as a whole, entirely compatible with a route dominated by nucleophilic attack on the carbonyl carbon atom of the keten, but with access to the β-carbon atom an energetically relevant feature, as in (VI).

$$3R^2OH \rightleftharpoons (R^2OH)_3 \qquad \text{Fast } (a)$$
$$(R^2OH)_3 + R^1{}_2C{=}C{=}O \longrightarrow R^1{}_2CH{\cdot}CO_2R^2 + 2R^2OH \qquad \text{Slow } (b) \qquad (13)$$

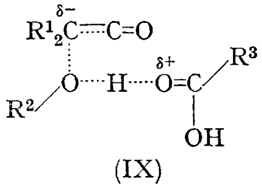

(VI)

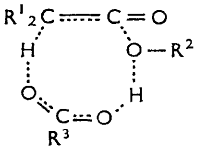
Carboxylic acid-catalysed addition of alcohols. The kinetic experiments show that, in this reaction, the transition state has the molecular composition keten, plus one acid molecule, plus one alcohol molecule, and does not lead to, or involve, the anhydride. The acid has thus taken over the catalytic functions of the second and third alcohol molecule in the spontaneous addition. Significantly, however, the efficiency of the acid in this respect is inversely related to its conventional strength, and as we have seen the same is true for the corresponding catalysed addition of anilines. It follows that protonation by the acid cannot be its dominant function. Schemes involving pre-equilibrium protonation of the keten must be discarded. Since complexes like (VII) or (VIII) can scarcely lead to catalysis of nucleophilic attack by oxygen (or nitrogen) and since the simple acceptance of protons from the substrate, as in (IX), can be much better effected by both the solvent and other alcohol molecules, it follows that the acid's role must be composite. This conclusion points almost inescapably to a cyclic transition state, *e.g.*, (X), in which the nucleophilic, bond-forming process by the alcoholic


(VII)

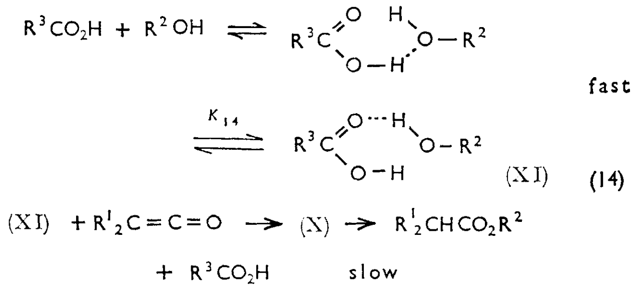
$R^1CO_2H \cdots NH_2{\cdot}C_6H_4R^2$

(VIII)


(IX)

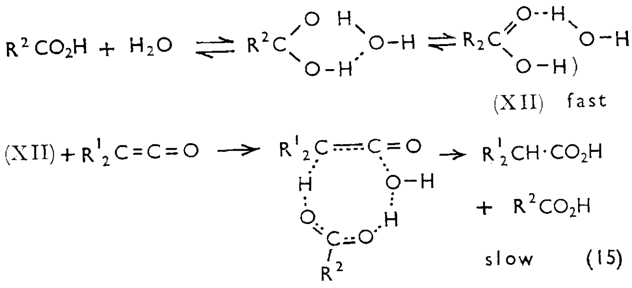

(X)

oxygen atom is energetically dominant, but the simultaneous proton transfer from the catalyst makes a significant contribution. In such a scheme the acid's nucleophilic role can be more important than its proton-donor power. An appropriate balance between these two properties is no doubt important in determining the overall activation energy. Carboxylic acids may also score over (say) other alcohol molecules as catalysts owing to readier ring formation (the $R^2{\cdot}CO_2$ system is held planar) and reduced steric interference with the R groups of the keten. The complete reaction can conveniently be visualised as (**14**), with the basic function of the acid making itself felt in K_{14}.



(14)

Isobutyric acid-catalysed addition of water. In this system the presence of acid reduces the order in water to unity. By the arguments given above the overall the reaction can be visualised as (15). The various



(15)

transition states may also (or alternatively) involve the keten's carbonyl oxygen atom, with a rapid prototropy following on, but however this may be, the evidence for cyclic species is formidable.[7]

[8/167 *Received, February 5th,* 1968]

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[7] See also P. J. Lillford and D. P. N. Satchell, *Chem. and Ind.*, 1967, 1750.