Kinetics and Mechanisms of the Reactions of Ketenes with Water and Alcohols in Dioxane Solutions

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The spontaneous addition of water to diphenyl- and to dimethyl-ketene in dioxane–H_2O and dioxane–D_2O mixtures is third order in the stoicheiometric water concentration, $[H_2O]_s$, when $[H_2O]_s \lesssim 1.5$M. At higher water concentrations (up to 19M) the observed order falls, and the patterns of the results for the two ketenes are similar, but differ in detail. The isotope effect $k_{H_2O}/k_{D_2O} = 1.7$—2.3 for all the systems studied. The addition of ethanol to diphenylketene in dioxane–ethanol mixtures has a kinetic pattern very similar to that for addition of water to this ketene, except that the change to a lower order occurs when $[EtOH]_s \simeq 5$M. The variation of the activation parameters with medium composition is also very similar for all these spontaneous additions: at low water or ethanol concentrations $E_a = 1 \pm 1$ kcal mol^{-1}, and $\Delta S^‡ = -60 \pm 8$ cal K^{-1} mol^{-1}; at higher concentrations E_a rises somewhat, and $\Delta S^‡$ becomes less negative. The results are considered in the light of previous work. It is concluded that water and alcohol add to ketenes by a common mechanism in non-hydroxylic solvents of low dielectric constant, and that this involves a cyclic, hydrogen-bonded transition state such as (**1**). Hydroxide ions (*ca.* 5×10^{-3}M) have no effect on the rate of water addition in dioxane, but hydrogen ions have powerful effects: the addition to diphenylketene is inhibited, that to dimethylketene is catalysed. These observations are explained. The isotope effect $k_{H_3O^+}/k_{D_3O^+} \simeq 1.9$ for the catalysis. We propose a catalytic mechanism with a cyclic transition state (**3**) involving a dominant slow proton transfer to the ketene β-carbon atom.

The mechanisms of the spontaneous and catalysed additions of water and alcohols to ketenes have been studied by a number of workers, mainly by kinetic methods.[1–13] Most workers have used ketoketenes [reactions (1) and (2)], these being more stable

$$R'_2C{=}C{=}O + H_2O \longrightarrow R'_2CHC{\lessgtr}^{O}_{OH} \qquad (1)$$

$$R'_2C{=}C{=}O + R'OH \longrightarrow R'_2CHC{\lessgtr}^{O}_{OR'} \qquad (2)$$

than aldoketenes towards polymerisation and oxidation. Different kinetic patterns have been found in different circumstances, and a number of reaction mechanisms have been suggested. We now present a kinetic study of the addition of water to dimethylketene and to diphenylketene using a series of dioxane–H_2O and dioxane–D_2O mixtures containing up to 19.5M-water. We report too on the addition of ethanol to diphenylketene in a series of dioxane–ethanol mixtures containing up to 10M-ethanol. We have also examined the effects of temperature and of added acid and base. No previous kinetic work with ketenes has involved dioxane solutions, and no similar range of solvent compositions has been examined. We critically consider possible mechanisms of addition in the light of the data now available.

Experimental

Materials.—Most materials were prepared and/or purified as in earlier work with ketenes in this laboratory.[3,6,12] 1,4-Dioxane was purified by distillation from sodium. Deuterium oxide (99.7%) was the Goss product.

Kinetic Arrangements.—These followed previous lines[3,6,12] for reaction mixtures containing $\lesssim$1.0M-water or 2.0M-ethanol. At higher concentrations the additions are too fast at 25 °C to follow by conventional u.v. spectroscopy, and the stopped-flow method was used (modified[14] Durrum–Gibson instrument). Because the ketene must be injected as a solution in pure dioxane, the maximum water or alcohol concentration theoretically obtainable using the stopped-flow apparatus was 50% v/v. The initial ketene concentration was always 2—5 × 10^{-3}M. As found for diethyl ether solutions,[3,12] the reaction of water with dimethylketene in dioxane is auto-catalytic at low ($\lesssim$0.5M) water concentrations. For these conditions k_{obs} (the observed first-order rate constant for loss of ketene) was calculated from the initial slopes of the first-order plots. At higher water concentrations the auto-catalytic effect of the product becomes negligible compared with the rate of the spontaneous reaction, and first-order plots were accurately rectilinear. For diphenylketene no auto-catalysis is detectable even at very low water concentrations. Values of k_{obs} were more reproducible than in diethyl ether solution. Repeat determinations were always reproducible to within ±7%, as were those rate constants that could be obtained by both the conventional and stopped-flow methods.

Reaction Products.—Preparative-scale reactions, using concentration conditions similar to those of the the kinetic runs, showed that reactions (1) and (2) proceed in high yield in dioxane.

Results

Typical results, including relevant concentrations and other conditions, are in Figures 1—5 and Tables 1—2. They show the following features.

(i) At low concentrations of water or ethanol, their spontaneous additions to ketenes in dioxane are third order in the stoicheiometric water ($[H_2O]_s$) or ethanol ($[EtOH]_s$) concentration. For diphenylketene this order changes rather sharply when $[H_2O]_s$ or $[D_2O]_s$ reaches *ca.* 1.5M, and when $[EtOH]_s$ reaches *ca.* 5.0M, and thereafter continues to fall slowly throughout the range of water and alcohol concentrations studied. For dimethylketene the change to a lower order is less sharp and occurs when $[H_2O]_s$ *ca.* 2.0M (Figures 1—4).

(ii) Diphenylketene is *ca.* 25-fold more reactive than is

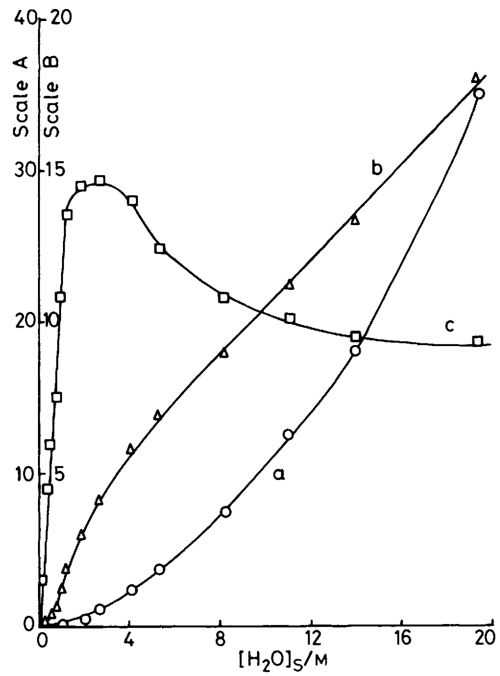


Figure 1. Spontaneous addition of water to diphenylketene in dioxane at 25 °C: a, k_{obs}/s^{-1} against $[H_2O]_s$ (Scale A); b, 10 $k_{obs}/[H_2O]_s$/l mol^{-1} s^{-1} against $[H_2O]_s$ (Scale B); c, $10^2k_{obs}/[H_2O]_s^2$/l^2 mol^{-2} s^{-1} against $[H_2O]_s$ (Scale B)

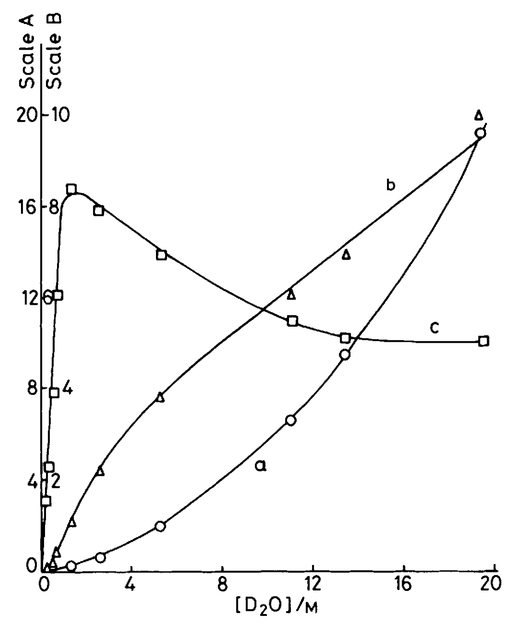


Figure 2. Spontaneous addition of deuterium oxide to diphenylketene in dioxane at 25 °C: a, k_{obs}/s^{-1} against $[D_2O]_s$ (Scale A); b, 10 $k_{obs}/[D_2O]_s$/l mol^{-1} s^{-1} against $[D_2O]_s$ (Scale B); c, $10^2k_{obs}/[D_2O]_s^2$/l^2 mol^{-2} s^{-1} against $[D_2O]_s$ (Scale B)

dimethylketene towards the spontaneous addition of water at low values of $[H_2O]_s$ (Figures 1 and 3).

(iii) Diphenylketene reacts spontaneously *ca.* 16-fold faster with water than with ethanol at low solute concentrations (Figures 1 and 4).

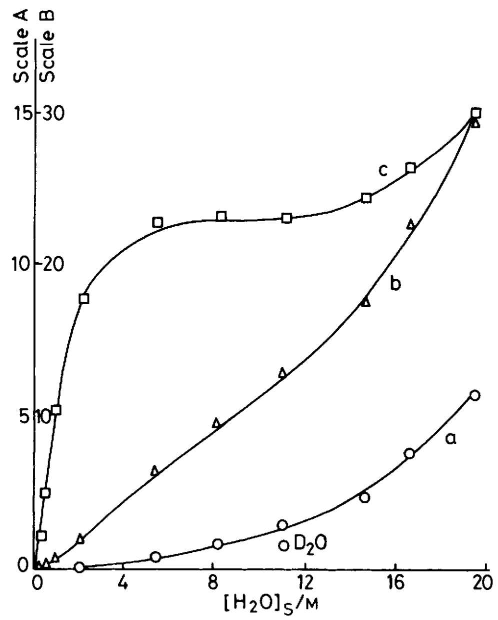


Figure 3. Spontaneous addition of water to dimethylketene in dioxane at 25 °C: a, k_{obs}/s^{-1} against $[H_2O]_s$ (Scale A); b, 10^2 $k_{obs}/[H_2O]_s$ against $[H_2O]_s$ (Scale B); c, $10^3k_{obs}/[H_2O]_s^2$ against $[H_2O]$ (Scale A)

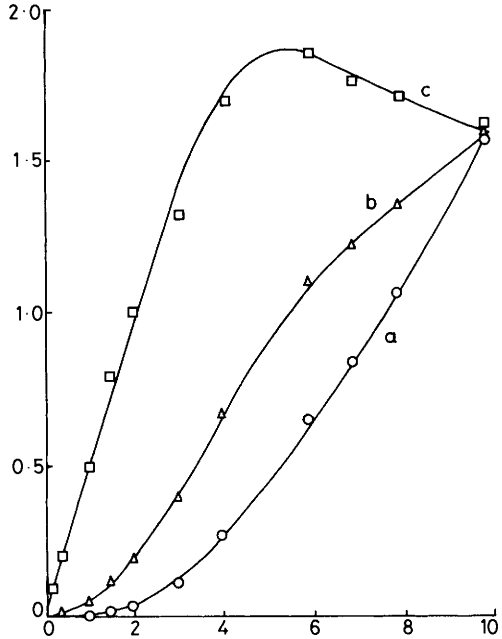


Figure 4. Spontaneous addition of ethanol to diphenylketene in dioxane at 25 °C: a, k_{obs}/s^{-1} against $[EtOH]_s$; b, 10 $k_{obs}/[EtOH]_s$/l mol^{-1} s^{-1} against $[EtOH]_s$; c, $10^2k_{obs}/[EtOH]_s^2$/l^2 mol^{-2} s^{-1} against $[EtOH]_s$

(iv) Under the same conditions, the reactions in dioxane are *ca.* 6-fold slower than in diethyl ether solutions.

(v) The effects of added hydrogen ions on the rate of addition of water in dioxane are very different for diphenyl- and dimethylketene (Figure 5). Powerful catalysis is found for dimethylketene, but powerful inhibition for the diphenyl derivative.

(vi) Added hydroxide ions have little effect on k_{obs} for water addition at low values of $[OH^-]$ (Figure 5).

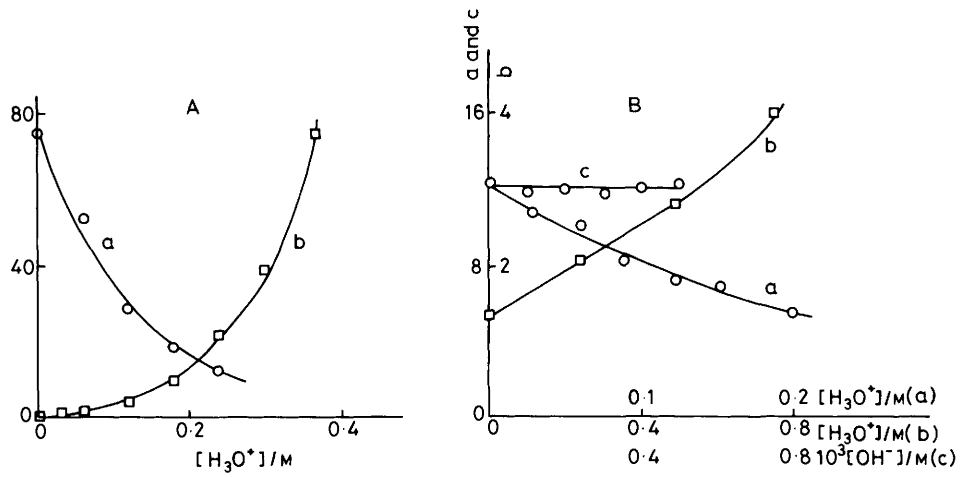


Figure 5. A, Effect of hydrogen ions on the addition of water ($[H_2O]_s$ = 2.22M) at 25 °C: a, $10^2k_{obs}/s^{-1}$ for diphenylketene; b, k_{obs}/s^{-1} for dimethylketene. B, Effects of hydrogen and hydroxide ions on the addition of water ($[H_2O]_s$ 11.1M) at 25 °C: a, c, k_{obs}/s^{-1} for diphenylketene; b, k_{obs}/s^{-1} for dimethylketene

Table 1. Hydrogen isotope effects on the spontaneous and hydrogen ion-catalysed addition of water to ketenes in dioxane at 25 °C. k_{H_2O} and k_{D_2O} are the observed first-order rate constants for spontaneous addition of H_2O and D_2O, respectively; $k_{H_3O^+}$ and $k_{D_3O^+}$ are the corresponding catalytic constants obtained for solutions containing perchloric acid; L_2O represents H_2O or D_2O

(a) Spontaneous addition						
(i) Diphenylketene						
$[L_2O]_s$/M	0.13	0.55	1.38	2.77	5.50	11.1
k_{H_2O}/k_{D_2O}	2.0	1.9	1.7	1.9	1.8	1.9
$[L_2O]_s$/M	13.8	19.4				
k_{H_2O}/k_{D_2O}	1.9	1.8				
(ii) Dimethylketene						
$[L_2O]_s$/M	2.20	11.1				
k_{H_2O}/k_{D_2O}	2.3	1.8				
(b) Catalysed addition to dimethylketene						
$[L_2O]_s$/M	2.20	11.1				
$[HClO_4]_s$/M	0.061	0.12				
$k_{H_3O^+}/k_{D_3O^+}$	1.7	2.2				

Table 2. Effect of temperature on the spontaneous additions of water and ethanol to ketenes in dioxane solution. k_{obs} = observed first-order rate constant; $[\text{ketene}]_{\text{initial}} \simeq 4 \times 10^{-3}$M; units of E_a kcal mol^{-1}, of $\Delta S^\ddagger$ cal K^{-1} mol^{-1}

Addition of water				
(a) Diphenylketene				
(i) $[H_2O]_s$ = 0.55M				
t_p/°C	25.0	53.5	73.0	$E_a \simeq 0$
$10^2\ k_{obs}/s^{-1}$	1.81	1.99	1.89	$\Delta S^\ddagger$ -52 ± 3
(ii) $[H_2O]_s$ = 11.1M				
t_p/°C	25.0	48.8	66.8	$E_a = 3.8 \pm 0.5$
k_{obs}/s^{-1}	11.7	22.9	33.5	$\Delta S^\ddagger = -42 \pm 2$
(b) Dimethylketene				
(i) $[H_2O]_s$ = 1.11M				
t_p/°C	25.0	42.0	61.0	$E_a = 1.8 \pm 0.5$
$10^3\ k_{obs}/s^{-1}$	6.15	7.68	9.20	$\Delta S^\ddagger = -64 \pm 3$
(ii) $[H_2O]$ = 11.1M				
t_p/°C	25.0	40.0	63.0	$E_a = 5.8 \pm 2$
k_{obs}/s^{-1}	1.48	2.48	4.57	$\Delta S^\ddagger = -40 \pm 2$
Addition of ethanol to diphenylketene				
(i) $[EtOH]_s$ = 0.99M				
t_p/°C	25.0	42.0	59.5	$E_a = 1.0 \pm 1$
$10^3\ k_{obs}/s^{-1}$	6.29	7.54	7.68	$\Delta S^\ddagger = -67 \pm 5$
(ii) $[EtOH]$ = 7.88M				
t_p/°C	25.0	39.5	59.5	$E_a = 1.7 \pm 0.5$
k_{obs}/s^{-1}	0.98	1.18	1.71	$\Delta S^\ddagger = -33 \pm 2$

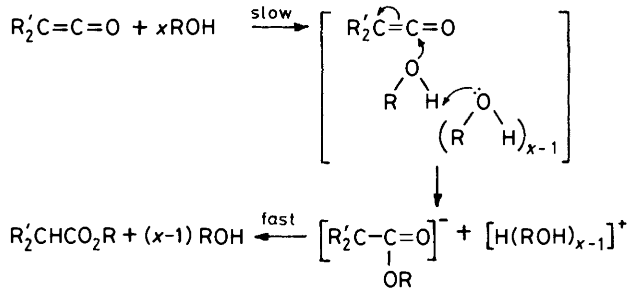
(vii) Replacement of H_2O by D_2O has a very similar effect on k_{obs} for all reactions and conditions studied: k_{H_2O}/k_{D_2O} always lies in the range 1.7—2.3 (Table 1, Figures 1 and 2).

(viii) The dependence of the activation parameters on solvent composition has a similar pattern for both dimethyl- and diphenyl-ketene, and this pattern is the same for the addition of either water or ethanol. At low values of $[H_2O]_s$ or $[EtOH]_s$, E_a is small (0—3 kcal mol^{-1}), while $\Delta S^\ddagger$ is large and negative (-50 to -70 cal K^{-1} mol^{-1}); at higher values of $[H_2O]_s$, or $[EtOH]_s$, E_a rises somewhat, and $\Delta S^\ddagger$ becomes notably less negative (Table 2).

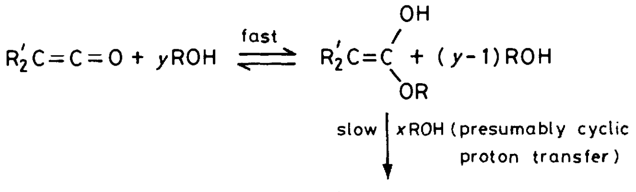
Discussion

(a) *Spontaneous Additions.*—The pattern of the present results, considered in conjunction with the more limited information available for diethyl ether solutions,[3,6,12] makes it very probable indeed that, although there may exist differences in fine detail, water and ethanol add spontaneously to ketenes in ethereal solvents by the same type of mechanism. This conclusion is contrary to recent suggestions of Seikaly and Tidwell.[15] It seems reasonable to assume that similar mechanisms of spontaneous addition will also apply for water and alcohols in other non-hydroxylic media of low dielectric constant, although no direct comparison is yet available.

Most of the work that throws light on the mechanism of the spontaneous additions refers to ethereal and other non-hydroxylic solvents. When considering it there should be kept in mind the large body of information[16—20] that refers to the reactions of water and alcohols in such solvents with other



Scheme 1.



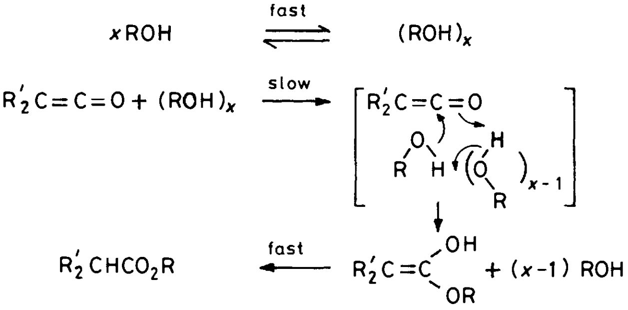
Scheme 2.

acylating agents, and with carbonyl groups in aldehydes or ketones. For many such systems orders >1 in ROH (where ROH represents water or alcohol) are found. It is widely agreed that mechanisms involving cyclic, hydrogen-bonded transition states, involving more than one ROH molecule, are probable. Such transition states could, in principle, be formed from ROH monomers or polymers. Systems for which the amount of self-associated ROH have been measured[3,21,22] and considerations of the relative reactivity of solvent-free and solvent-associated polymers,[22] suggest that the reactants may be the polymers. The existence, and possible involvement, of polymers must therefore be taken into account when discussing additions to ketenes. In particular, the extent of association in any system controls the free monomer concentration $[(\mathrm{ROH})_1]$ and will affect the observed reaction order in $[\mathrm{ROH}]_\mathrm{s}$. Thus if the equilibria such as (3) lie well to the left, then $[(\mathrm{ROH})_1] \simeq [\mathrm{ROH}]_\mathrm{s}$, and

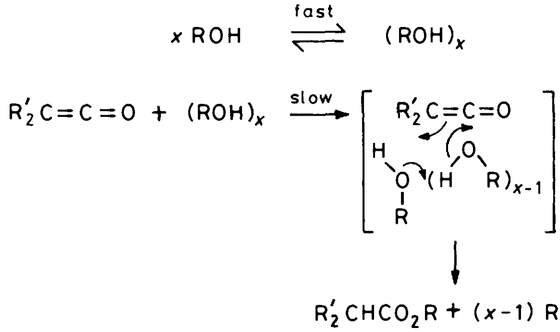
$$n\,\mathrm{ROH} \rightleftharpoons (\mathrm{ROH})_n \qquad (3)$$

$[(\mathrm{ROH})_n] \propto [\mathrm{ROH}]_\mathrm{s}^n$. This situation can lead to integral and constant reaction orders in $[\mathrm{ROH}]_\mathrm{s}$. However, if a significant fraction of ROH is associated, then these relationships will not be obeyed, rather complex relationships will normally exist, and the observed reaction order in $[\mathrm{ROH}]_\mathrm{s}$ will be expected to fall progressively as $[\mathrm{ROH}]_\mathrm{s}$ is increased. That simple, apparently constant, reaction orders are sometimes found under such circumstances[16,18] must arise fortuitously. Unfortunately, quantitative study of ROH association is difficult: the gross extent of association can be measured, but differentiation between possible polymers is uncertain. It is, however, known[3,22,23] that at 25 °C in ethereal solvents, $\gtrsim 15\%$ of the water or alcohol is polymerised when $[\mathrm{ROH}]_\mathrm{s} \gtrsim 0.5$—1M. For hydrocarbons it is clear[21,24,25] that far higher concentrations of polymers exist: at 20—30 °C when $[\mathrm{ROH}]_\mathrm{s} \simeq 1.0\mathrm{M}$, 20—70% of the solute may be associated. At low temperatures the proportion will be greater.

Mechanism.—In all, four mechanisms have been considered for the spontaneous addition of species ROH to ketenes.[1,3,5] Their essentials are shown in Schemes 1—4. Additions to the carbonyl group will occur in the molecular plane, those to the carbon–carbon double bond perpendicular to this plane.[17,23]



Scheme 3.



(1)

Scheme 4.

The mechanism that obtains in media of high dielectric constant, such as water or water-rich mixed solvents, may differ from that occurring in ethereal or hydrocarbon solvents; we are here concerned primarily with the latter solvents. Apart from the observed reaction orders and activation parameters, any satisfactory scheme must be able to account for the general findings[15,17,26] (i) that electron-withdrawing substituents in the ketene mildly accelerate the addition of ROH (evident again in the present work), and (ii) that important steric hindrance is sometimes evident.

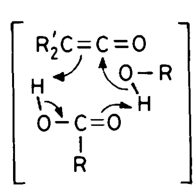
Scheme 1 seems likely to involve significant charge separation in its transition state; this would be energetically unfavourable in any medium of low dielectric constant. The finding of very low E_a values both in the present work, and for hydrocarbon solvents,[5] therefore argues strongly against this Scheme, as does the fact that *bona fide* ionisation mechanisms appear to require[16,20] *ca.* 5 ROH molecules to stabilise their transition states, whereas for ketene additions $x \leqslant 3$. Scheme 1 also involves general base catalysis. Since ethers and alcohols are of similar basicity,[27] it would be expected that ethereal solvents could replace the second, or at least the third, ROH molecule. Examples, such as the present work, where $x = 3$, and no lower-order terms in ROH are detectable at low ROH concentrations, would seem unlikely if Scheme 1 obtains. We conclude therefore that although Scheme 1 might be viable in a medium of high dielectric constant, such as a highly aqueous system, it is unattractive for the present systems, especially when $[\mathrm{ROH}]_\mathrm{s} \gtrsim 1\mathrm{M}$. Theoretical studies[20] suggest that, for carbonyl additions, a dipolar general base mechanism is a possible alternative in pure water to a mechanism like Scheme 3, but not in dilute ethereal solutions.

In Scheme 2 the rapidly formed intermediate is a ketene hydrate (or hemiacetal). In reactions of ketenes with water or alcohols no intermediates are detected; if Scheme 2 obtains, its pre-equilibrium must therefore lie well to the left. The minimum reaction order in ROH will thus be two. Systems[1,4] which lead to orders of unity cannot therefore be explained by Scheme 2, whatever the state of association of the alcohol or water. A further difficulty with this scheme concerns its slow step. Work on the hydrolysis of ketene acetals[28] suggests that proton transfer to the β-carbon atom of the intermediate in Scheme 2 will be much slower for the diphenyl- than for the dimethyl-derivative. For diphenylketene to be more reactive than dimethylketene, as now found, it would be necessary for the pre-equilibrium to lie much further to the right for the former ketene. There is no direct evidence on this point, but knowledge of acetal formation by aromatic and aliphatic aldehydes suggests the opposite may be the case.

Other problems concern the particular suggestion[5] that Scheme 2 applies for the addition of 2-phenylethanol (0.2—1.3M) to ketenes in toluene solution at 18—80 °C. A mainly second-order dependence on alcohol concentration was found, and Scheme 2 was proposed with $x = y = 1$ as a means of avoiding mechanisms involving alcohol dimer. Although the authors concede that substantial amounts of the alcohol are associated under their conditions, they appear to assume that the active reactant is the monomer, and that its concentration is proportional to $[\mathrm{ROH}]_s$. The dimer is dismissed as a possible reactant since it is believed to comprise $<5\%$ of $[\mathrm{ROH}]_s$, higher polymers predominating. The author's conclusions seem doubly suspect. First, in this system $[(\mathrm{ROH})_1]$ is unknown, but is unlikely to parallel $[\mathrm{ROH}]_s$ over the range of concentrations used; the observed second-order dependence on $[\mathrm{ROH}]_s$ can therefore hardly reflect the involvement of monomer in the slow step of Scheme 2. Secondly, just because a species exists in low concentrations, that does not preclude it from being a principal reactant. In an earlier publication on the stereoselective addition of 2-phenylethanol to phenylmethylketene Jähme and Rüchardt[29] conclude that the proton transfer from the alcohol to the ketene β-carbon atom is the stereoselective process, and that both this proton, and the alcohol residue in the product ester, arise from the same alcohol molecule. This conclusion presumably underlies their emphasis on monomers. However, Scheme 2 is not compatible with this conclusion even were the monomer to participate in it. The results[29] for stereoselective addition show that the greatest stereoselectivity actually occurs at high alcohol concentrations (*i.e.* when polymeric alcohol is prominent). Jähme and Rüchardt also conclude[5] incorrectly[20] that mechanisms such as Schemes 3 and 4 cannot account for values of E_a close to zero.

The principal problem with Scheme 3 is that it is identical with that most favoured (certainly in predominantly non-hydroxylic solvents) for additions of water and alcohols to aldehydes and ketones.[19,20] Such additions are catalysed by acids, the acids participating in the hydrogen-bonded cycle, or at least helping in some way to transfer the proton to the carbonyl oxygen atom. If Scheme 3 applies to ketenes it would be expected that acids would play a similar role. The absence of detectable acid catalysis (reported now and previously[12]) for diphenylketene, compared with the powerful catalysis found for dimethylketene, seems to rule out this Scheme: such a dramatic difference in proton transferability, while expected at the ketene β-carbon atom, is not anticipated at the carbonyl oxygen atom.

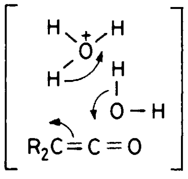
Scheme 4 can probably account for all the known facts concerning additions of ROH species to ketenes, including those now found. If the nucleophilic attack on the carbonyl carbon atom is the dominant feature of the slow step, but the proton transfer to the β-carbon atom contributes significantly, the somewhat greater reactivity of diphenylketene, compared with dimethylketene, in the spontaneous additions can be understood. So too can the greater susceptibility of the latter compound to carboxylic acid catalysis *via* transition state (**2**), in which the proton transfer must play an energetically more important role than in transition state (**1**) for the spontaneous reaction, in which the assistance to nucleophilic attack will be greater. The present results for dilute solutions of water or ethanol in dioxane show that $x = 3$ in the spontaneous additions, but other values could apply in other circumstances; for example with bulky ROH species[4,5] or in hydrocarbon solvents[1,4,5] where (i) all ROH species are largely solvent-free, and potentially highly reactive, so that cyclic ($x \geqslant 3$) polymers (which are the only solvent-free polymers in ethers) are not required, and (ii) the ketene may exist in solution in association with one, or more, ROH molecules, so that even $x = 1$ in Scheme 4 would correspond to two, or more, ROH molecules in the transition state. (In ether solution the ketene is unlikely to compete successfully for ROH.) It has been argued[30] that the most favourable hydrogen-bonded cycles involve eight atoms [*e.g.*, cycles such as those in (**1**) and (**2**)], and theoretical calculations[20] show that mechanisms like Scheme 4 can have activation parameters similar to those found experimentally.



(2)

As argued on p. 1488, the observed order in $[\mathrm{ROH}]_s$ will only be expected to remain at x provided that the pre-equilibrium in Scheme 4 lies well to the left; if the temperature is sufficiently reduced, or if $[\mathrm{ROH}]_s$ is made sufficiently large, the order should fall owing to substantial association of ROH. A fall in order is evident in the present systems (Figures 1—4). It is interesting to compare our results with those obtained for other hydrolyses studied using a wide range of mixed aqueous, or mixed alcoholic solvent compositions. Various studies of this type exist.[16–21] They mostly involve acylations or additions. Some show a pattern of results similar to those for the present systems, and this extends also to the variation in activation parameters. The authors of these previous studies are generally agreed that observed changes in order, and in activation parameters, can be attributed to changes in solution structure, *i.e.* to changes in the nature of the ROH species as $[\mathrm{ROH}]_s$ rises. Thus if less (new) association of ROH is required to construct the transition state, then E_a will be greater, but $\Delta S^\ddagger$ will be less negative, as found (Table 2). Changes in initial state solvation of the ketene may also become important when $[\mathrm{ROH}]_s$ is large. These considerations, and our results (Table 1) for the dependence of the isotope effect on solvent composition, lead us to suggest that there may occur little change in the transition state structure over the range of compositions we have studied. The fact that the detailed dependence of the reaction order on solvent composition is different for dimethyl- and diphenylketene (Figures 1 and 3) suggests that the mechanisms of addition to these two compounds are not identical.

(b) *Catalysed Addition.*—Our results (Figure 5) for diphenylketene in dioxane containing 11.1M-water show that the addition of water is not detectably catalysed by low concentrations of hydroxide ions. This result agrees with those found[10,11] for ketene and for di-t-butylketene. The effects of added hydrogen ions (as perchloric acid) are, however, striking (Figure 5). The effects are especially large in mixtures containing only 2.2M-H_2O. Constant ionic strength was not maintained in these experiments, and the curvature of the plots in Figure 5A probably arises from secondary effects of the added acid in a medium of such low dielectric constant. The results in Figure 5B for mixtures containing 11.1M-H_2O show greater rectilinearity. We interpret our results as indicating that hydrogen ions catalyse the addition of water to diphenylketene feebly (or not at all), but that added $HClO_4$ reduces the spontaneous rate of addition by engaging water molecules, and altering their state of



(3)

aggregation (ClO_4^- ions are known[31] to have powerful structure-breaking effects in dioxane–water mixtures). Our results suggest that the addition of 0.20M-perchloric acid to mixtures containing 11.1 and 2.2M-water reduces the effective water molarity for spontaneous addition to *ca.* 10 and *ca.* 1M, respectively. The insensitivity of diphenylketene towards catalysis by hydrogen ions is concordant with our previous results for the behaviour of this ketene towards electrophilic reagents.[6,12] The effects of added boron fluoride in diethyl ether are similar to those now found for perchloric acid.

The results for dimethylketene do indicate catalysis by hydrogen ions. The catalysis is probably first order in $[H_3O^+]$. Making a small allowance for the effect of added perchloric acid on the effective water molarity for the spontaneous addition, but ignoring any electrolyte effects on the catalysis itself, we calculate for the mixture containing 11.1M-water that the catalytic rate constant, $k_{H_3O^+} \simeq 12\ l\ mol^{-1}\ s^{-1}$ at 25 °C. At 2.2M-water an approximate value, $k_{H_3O^+} \simeq 20\ l\ mol^{-1}\ s^{-1}$, can be calculated from the straight portion of the plot (Figure 5A). It seems that when the dielectric constant is low, and when there is less water available to stabilise the hydrogen ions, this ion is more effective in catalysing the addition. Our values of $k_{H_3O^+}$ can be compared with the value of *ca.* 4 l mol^{-1} s^{-1} found[11] with di-t-butylketene in 50% (v/v) acetonitrile–water at 25 °C. This medium is richer in water, and has a higher dielectric constant than ours, and therefore would be expected to lead to a smaller value of $k_{H_3O^+}$, as found. However, the substituents in di-t-butylketene are more electron-donating than those in dimethylketene, and a value of $k_{H_3O^+}$ somewhat greater than 4 l mol^{-1} s^{-1} might have been expected. Perhaps some element of steric hindrance is present for the di-t-butyl derivative.

In the light of our discussion of the spontaneous hydrolysis, the mechanism of catalysis presumable involves a slow proton transfer to the ketene β-carbon atom during which charge is dispersed. The similarity of our isotope effects for the spontaneous and catalysed additions (Table 1) leads us to suggest some cyclic process [*e.g. via* transition state (**3**)] for the catalytic path, rather than the simple proton transfer proposed by Tidwell.[11]

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