A Comparison of the Mechanisms of Hydrolysis of Diphenylketene and Dimethylketene in Diethyl Ether Solution

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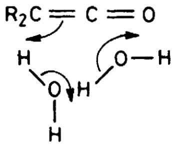
The spontaneous hydrolysis of diphenylketene in diethyl ether solution at 25 °C is first order in the ketene concentration and third order in the stoicheiometric water concentration; unlike the hydrolysis of dimethylketene, it is not auto-catalytic and hydrolysis is negligibly catalysed by added carboxylic acids. Added boron trifluoride strongly inhibits the hydrolysis of diphenylketene in ether but powerfully catalyses that of dimethylketene; the formation of the strong Brønsted acid H_2OBF_3 (association constant K = 120 ± 20 l mol^{-1} at 25 °C) underlies these effects. A pK_a value of *ca.* 0.5 is deduced for this acid and the results as a whole point to the marked inability of diphenylketene, compared with dimethylketene, to accept protons from Brønsted acids. Predominantly nucleophilic attack on the ketene is, however, easier for the diphenyl-derivative whose spontaneous hydrolysis varies between *ca.* 5- and *ca.* 40-fold faster over the range of stoicheiometric water concentrations used.

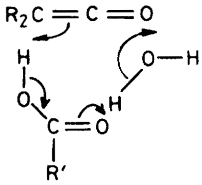
There have been three previous kinetic studies of the addition of water to ketenes [equation (1)]: the reaction has been

$$R_2C{=}C{=}O + H_2O \longrightarrow R_2CHCO_2H \qquad (1)$$

examined using substituted phenylketenes in aqueous solution,[1] using dimethylketene in ether solution,[2] and using ketene itself in the gas phase.[3] The combined evidence[4] strongly suggests that monomeric water does not add to ketenes and that the addition (under homogeneous conditions) involves a cyclic transition state, such as (I) or (II), in which a second species assists in the proton transfer. For ketene[3] and dimethylketene[2] added carboxylic acids provide catalysis; in keeping with this, for dimethylketene in ether solution, mild auto-catalysis is observed as the concentration of product acid builds-up.[2] We now report on the kinetic behaviour of diphenylketene in this reaction in ether solution at 25 °C. We have also measured the primary hydrogen isotope effects on the rates of hydrolysis of both diphenyl- and dimethyl-ketene and examined the effects of added boron trifluoride on these rates.



(I)



(II)

Experimental

The methods of preparation and purification of materials, the equilibrium measurements, and the kinetic procedures, all followed closely our previous practice in work with these ketenes[2,5] and with other materials.[6] Deuterium oxide (99.8%) was the Goss product. The reproducibility of $k_{obs.}$, the observed first-order rate constant for loss of ketene, was within ±8% for all the reactions studied, except for the spontaneous hydrolysis of dimethylketene where the reproducibility was within ±10% and where $k_{obs.}$ values were obtained from the initial slopes of the auto-catalytic plots. Our results are collected in the Tables and Figures, which also include the relevant concentration conditions.

Preparative-scale experiments, conducted under concentration conditions as similar as possible to those of the kinetic runs, showed that in all cases the only product was the corresponding acid [equation (1)]. Spectroscopic measurements were made using a Unicam SP1750 instrument fitted with SP1802 and SP1805 accessories (u.v.–visible), a Perkin-Elmer 297 instrument (i.r.), and a JEOL JNM-PMX60S1 high-resolution spectrometer (n.m.r.)

Table 1. Reaction of diphenylketene with water in diethyl ether solution at 25.0 °C

$[\text{Ketene}]_{\text{initial}} \simeq 2.0 \times 10^{-3}$M; $k_{obs.}$ = observed first-order rate constant for loss of ketene.

(a) Spontaneous reaction

$[H_2O]$/M	0.016	0.066	0.083	0.104	0.142	0.166
$10^3k_{obs.}$/s^{-1}	0.013	0.44	0.87	1.64	4.36	6.50
$[H_2O]$/M	0.176	0.222	0.233	0.247		
$10^3k_{obs.}$/s^{-1}	7.73	14.9	18.5	21.8		

(b) Reaction in the presence of acetic acid ($[H_2O]$ = 0.222M)

$[MeCO_2H]$/M	0.00	0.010	0.032	0.060	0.093
$10^3k_{obs.}$/s^{-1}	14.9	15.3	16.0	14.8	14.4

Results and Discussion

The Spontaneous Hydrolysis.—A surprising finding was that, whereas the spontaneous hydrolysis of dimethylketene in ether at 25 °C is an auto-catalytic process,[2] there was no detectable auto-catalysis in our runs with diphenylketene: good first-order behaviour for loss of ketene was observed over 3—4 half-lives. Our results are in Table 1. The $k_{obs.}$ values vary from *ca.* 5- to *ca.* 40-times larger than the corresponding values for dimethylketene in the same range of stoicheiometric water concentrations. The greater reactivity of the diphenyl-derivative towards water is in agreement with previous qualitative conclusions.[4]

For diphenylketene a plot of $k_{obs.}/[H_2O]^2_{stoich.}$ *versus* $[H_2O]_{stoich.}$ is rectilinear and passes close to the origin (Figure 1). The hydrolysis is therefore third order in the stoicheio-

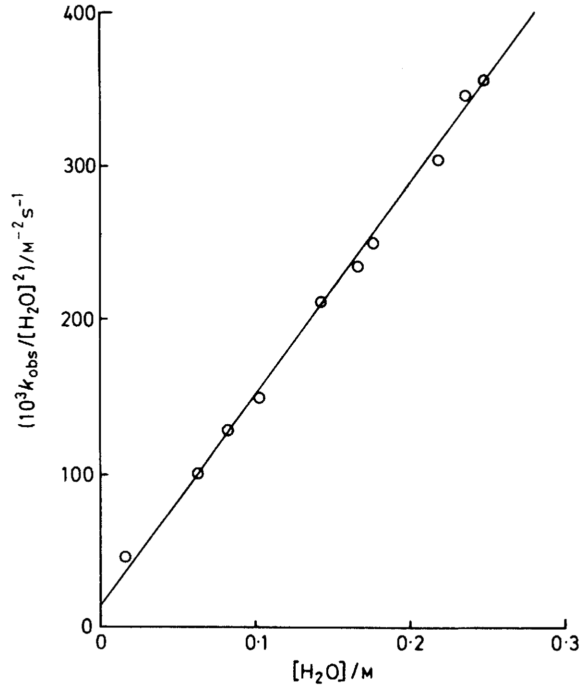


Figure 1. Graph of $k_{obs.}/[H_2O]^2$ *versus* $[H_2O]$ for hydrolysis of diphenylketene

metric water concentration. This represents another difference between the the kinetic behaviours of dimethyl- and diphenylketenes: with the former the spontaneous hydrolysis is second order in the water concentration.[2]

Water is negligibly polymerised in ether at 25 °C in the concentration range concerned [2] and our results with diphenylketene therefore suggest that its hydrolysis proceeds either *via* the direct reaction of a low concentration of trimeric water, as shown in equations (2)—(3), or *via* one or more of a set of schemes involving prior addition to the ketene

$$3H_2O \underset{}{\overset{K_3}{\rightleftharpoons}} (H_2O)_3 \quad \text{fast} \qquad (2)$$

$$\mathrm{Ph_2C{=}C{=}O} + (H_2O)_3 \xrightarrow[k_{trimer}]{} \mathrm{Ph_2CHCO_2H} + (H_2O)_2 \quad \text{slow} \qquad (3)$$

carbonyl group, such as that shown in equations (4)—(6). Both schemes, (2)—(3) and (4)—(6), lead [equations (7) and (8), respectively] to the observed reaction orders. Whichever scheme is chosen, a cyclic proton transfer in the slow step seems likely, and also a transition state which is of effectively

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

$$\mathrm{Ph_2C{=}C{=}O} + (H_2O)_2 \overset{K_5}{\rightleftharpoons} \mathrm{Ph_2C{=}C}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix} + H_2O \quad \text{fast} \qquad (5)$$

$$\text{(III)}$$

$$\text{(III)} + (H_2O)_2 \xrightarrow{k_6} \mathrm{Ph_2CHCO_2H} + (H_2O)_2 \quad \text{slow} \qquad (6)$$

$$-\mathrm{d[ketene]/d}t = k_{trimer}[(H_2O)_3][\text{ketene}] = k_{trimer}K_3[H_2O]^3[\text{ketene}] = k_{obs.}[\text{ketene}] \qquad (7)$$

$$-\mathrm{d[ketene]/d}t = k_6[\text{(III)}][(H_2O)_2] = k_6K_5K_2{}^2[H_2O]^3[\text{ketene}] = k_{obs.}[\text{ketene}] \qquad (8)$$

Table 2. Isotope effects on the spontaneous hydrolysis in diethyl ether solution at 25.0 °C

$k_{obs.}$ = observed first-order rate constant for loss of ketene.

(a) Diphenylketene ($[\text{ketene}]_{initial} \simeq 2 \times 10^{-3}$M)

$[D_2O]$/M	0.066		0.166	
$[H_2O]$/M		0.066		0.166
$10^3k_{obs.}/s^{-1}$	0.27	0.44	4.18	6.50
	k_{H_2O}/k_{D_2O} = 1.67		k_{H_2O}/k_{D_2O} = 1.55	
	(average = 1.61)			

(b) Dimethylketene ($[\text{ketene}]_{initial} \simeq 3 \times 10^{-3}$M)

$[D_2O]$/M	0.166		
$[H_2O]$/M		0.166	
$10^3k_{obs.}/s^{-1}$	0.090	0.224	k_{H_2O}/k_{D_2O} = 2.47

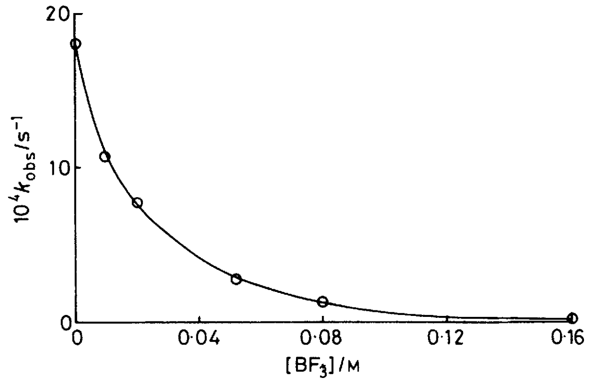


Figure 2. Effect of boron trifluoride on the hydrolysis of diphenylketene; $[H_2O]_{stoich.}$ = 0.105M; for $k_{obs.}$ see text

the same size in each case (three water molecules will be in it). For reasons given in our previous work with ketenes, and that of others recently reviewed,[4] we prefer scheme (2)—(3). Why diphenylketene should require a larger cyclic transition state than dimethylketene is not obvious, but it is interesting that the spontaneous hydrolysis of *p*-chlorophenyl isocyanate in ether, a reaction that involves rather similar considerations, is also reported [7] to occur *via* the addition of trimeric water.

The Effects of Carboxylic Acids.—The absence of detectable auto-catalysis with diphenylketene suggests that an added carboxylic acid will not be such an effective catalyst for the hydrolysis as with the dimethylketene.[2] This is confirmed by the results shown in Table 1. Under the conditions used, negligible catalysis was found. [The rate of removal of the ketene by direct reaction with the acid to give the (mixed) anhydride is small at the acid concentrations involved.[8]] These results show that a carboxylic acid is not so successful at providing an alternative hydrolysis transition state for diphenylketene as with dimethylketene; the presence of electron-withdrawing substituents on the β-carbon atom of diphenylketene suggests that this fact is connected with a greater difficulty in transferring a proton to diphenylketene and that the energetics of the nucleophilic attack at the carbonyl-carbon atom are relatively more important than with the dimethyl-derivative. Results compatible with this conclusion are the hydrogen-isotope effects for the spontaneous hydrolysis of the two compounds (Table 2): the use of deuterium oxide has a relatively small effect for diphenylketene. The interpretation of the isotope effects is not, however, simple

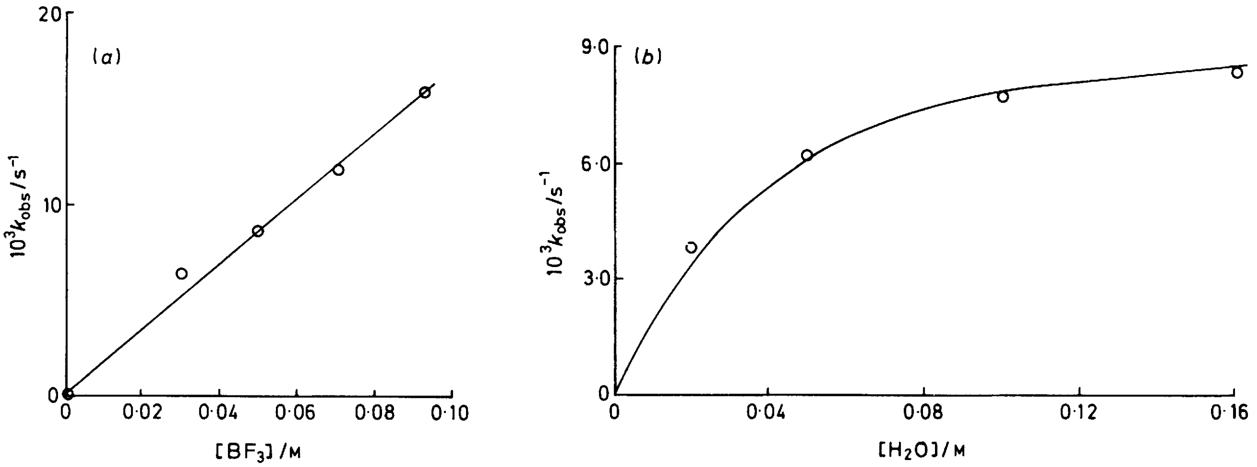


Figure 3. Effect of boron trifluoride on the hydrolysis of dimethylketene; for $k_{obs.}$ see text. (*a*) $[H_2O]_{stoich.}$ = 0.166M; (*b*) $[BF_3]_{stoich.}$ = 0.051M

since several effects, including those on the water association equilibria, will be present.

The Effects of Boron Trifluoride.—Measurements (at 3 500 cm^{-1}) of the i.r. absorption of (monomeric) water (0.10M) in ether solution in the presence of various concentrations (0.04—0.13M) of boron trifluoride, reveal the existence of a rapidly established equilibrium (9) with an association constant

$$H_2O + BF_3 \rightleftharpoons H_2O{:}BF_3 \qquad (9)$$

K = 120 ± 20 l mol^{-1} at 25 ± 1 °C. Analogous experiments in which the effects of boron trifluoride on the two ketenes were studied revealed no interaction between dimethylketene and boron fluoride and a very weak interaction with diphenylketene, such that negligible diphenylketene was associated with boron trifluoride in the experiments described below.

Results that confirm the reluctance of diphenylketene to react with Brønsted acids are those obtained for hydrolysis of the ketenes in the presence of added boron trifluoride. For diphenylketene the addition of boron trifluoride leads to marked inhibition of hydrolysis (Figure 2) and it is clear that $H_2O{:}BF_3$, which is progressively formed as $[BF_3]_{stoich.}$ is increased, is relatively very unreactive compared with free water. For dimethylketene, however, the presence of boron trifluoride leads to a greatly increased rate of hydrolysis (Figure 3) and the adduct $H_2O{:}BF_3$ is clearly much more reactive than free water. So much so that the boron trifluoride-catalysed route dominates the hydrolysis and good first-order kinetics for loss of ketene are observed, instead of the auto-catalysis usual for the spontaneous hydrolysis.

For dimethylketene the observed variations in $k_{obs.}$ for different stoicheiometric water and boron trifluoride concentrations, together with the known association of these reagents, suggests the outline mechanism of equations (10)—(11) for which the rate equation is (12).

$$H_2O + BF_3 \overset{K}{\rightleftharpoons} H_2O{:}BF_3 \qquad (10)$$

$$H_2O{:}BF_3 + Me_2C{=}C{=}O \xrightarrow{k_2} Me_2CHCO_2H + BF_3 \quad \text{slow} \qquad (11)$$

$$-d[\text{ketene}]/dt = k_2[H_2O{:}BF_3][\text{ketene}] = k_{obs.}[\text{ketene}] \qquad (12)$$

The continuous lines in Figure 3 were computed with the values k_2 = 0.18 l mol^{-1} s^{-1} and K = 150 l mol^{-1}. This value of K is in reasonable agreement with that determined directly (see above). The value of k_2 is approximately twice that found for the addition of trichloroacetic acid to dimethylketene.[5] This result suggests [5] that the pK_a for $H_2O{:}BF_3$ is *ca.* 0.5 and that the details of step (11) may approximate to those shown in equation (13).

$$Me_2C{=}C{=}O + H_2O{:}BF_3 \xrightarrow{\text{slow}} [Me_2CHCO]^+[HOBF_3]^- \xrightarrow{\text{fast}} Me_2CHCO_2H + BF_3 \qquad (13)$$

Compared with dimethylketene, it is evident that diphenylketene reacts relatively very slowly with the strong Brønsted acid H_2OBF_3. In the past all comparisons [4] of the reactivities of aryl- and alkyl-ketenes have shown the former to be the more reactive in additions to substrates HX. However, all previous comparisons have involved attack on the ketene by relatively nucleophilic substrates (water, alcohols, and amines).

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