Kinetics and Mechanism of the Addition of Alcohols to Ketenes in Diethyl Ether Solution in the Presence of Boron Trifluoride

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The kinetics are reported of the boron trifluoride-catalysed additions of seven alcohols to dimethylketene in diethyl ether solution at 25 °C. All the reactions involve the rapid initial formation of a 1 : 1 alcohol–boron trifluoride adduct (formation constant *K*) which transfers a proton to the ketene in the slow step of the addition. For t-butyl alcohol, ethanol, methanol, phenylmethanol, and 2-chloroethanol the *K* values are $\gtrsim 1\,000$, 320 ± 50, 300 ± 50, 80 ± 20, and 65 ± 15 l mol^{-1}, respectively. The more acidic an alcohol the faster is the reaction of its 1 : 1 boron trifluoride adduct with the ketene. For t-butyl alcohol the relatively slow reaction of its adduct is catalysed by a further molecule of the adduct and by free boron trifluoride.

At 25 °C the spontaneous addition of ethanol to diphenylketene in ether (like that to dimethylketene) is first order in the ketene and third order in the ethanol concentration. In this reaction diphenylketene is *ca.* 10-fold more reactive than the dimethyl derivative in the concentration range studied. Whereas the addition of boron trifluoride to the solution catalyses the addition of ethanol (and the other alcohols) to dimethylketene to such an extent that the spontaneous addition makes a negligible contribution to the overall rate, with diphenylketene the alcohol–boron trifluoride adduct is relatively so unreactive that added boron trifluoride strongly inhibits the spontaneous addition. The ethanol–boron trifluoride adduct is $>10^4$-fold less reactive towards diphenylketene than towards dimethylketene. These results support our previous conclusions concerning additions of acidic species to ketenes.

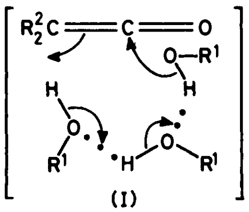
The spontaneous addition (1) of unhindered alcohols to dimethylketene in dilute solution in diethyl ether is kinetically first order in the ketene and third order in the alcohol;[1] the transition state (I) of the addition step probably involves an

$$Me_2C{=}C{=}O + ROH \longrightarrow Me_2CHCO_2R \qquad (1)$$

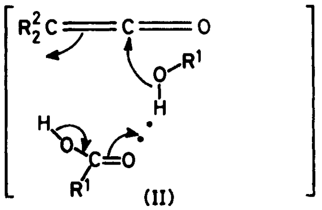
hydrogen-bonded alcohol polymer.[1,2] The addition of alcohols to ketenes in aprotic solvents has been shown[2,3] to be catalysed by carboxylic acids, by amides, and by tertiary amines; all the catalysed additions are kinetically first order in the catalyst, the alcohol, and the ketene; in these catalysed reactions the transition state of the addition step probably involves an hydrogen-bonded 1 : 1 adduct formed from a catalyst and an alcohol molecule[2,3] [*e.g.* (II)]. We report now on the alcoholysis of (principally) dimethylketene in diethyl ether solution in the presence of boron trifluoride. Previous attempts[4] to catalyse ketene alcoholysis with covalent halides appear to have failed.

Experimental

Our methods were those used previously in this laboratory in studies with alcohols,[1] ketenes,[2] and covalent halides.[5] In kinetic work the ketene was always in deficit and the observed first-order rate constant for its loss, k_{obs}, was reproducible to within ±10%. Good agreement (±12%) was obtained with previous kinetic data for the spontaneous alcoholysis of dimethylketene.[1] Typical results, together with the concentration and other relevant conditions, are in the Tables and Figures. Direct interaction between boron trifluoride and the ketenes in diethyl ether solution is negligible under the conditions used here. Preparative experiments using mixtures of boron trifluoride, ketene, and alcohol in ether at concentrations similar to those of the kinetic runs lead to effectively quantitative yields of the relevant ester.



(I)



(II)

Results and Discussion

(i) *Dimethylketene.*—The kinetics of addition of seven alcohols were studied. Three different patterns of results were obtained (Figures 1 and 2). t-Butyl alcohol gave the results labelled A and was the only alcohol to show this pattern. The results labelled B correspond to ethanol; methanol, phenylmethanol, and 2-chloroethanol also exhibit results of this general type (Table 1). The results labelled C are those for 2,2,2-trifluoroethanol and diphenylmethanol behaves in a similar way (Table 1). For all the alcohols, catalysis by boron trifluoride is evident and the contribution of the spontaneous hydrolysis to k_{obs} was always negligible under the concentration conditions used.

(a) *Ethanol, methanol, phenylmethanol, and* 2-*chloroethanol.* For these alcohols it is found that when the stoicheiometric boron trifluoride concentration, $[BF_3]_s$, is held constant and $[ROH]_s$ is varied, then when enough alcohol has been added to provide a modest excess over the boron trifluoride, k_{obs} reaches a limiting, constant value (*e.g.* Figure 1B). A similar effect is observed when $[ROH]_s$ is held constant and $[BF_3]_s$ is varied (*e.g.* Figure 2B). The results suggest, and are in every case compatible with, the rapid formation of a 1 : 1 adduct between the alcohol and boron trifluoride which subsequently reacts with the ketene [equations (2) and (3)]. The data give no indication of the formation of $1BF_3$–$2ROH$ adducts in these ether solutions. The formation of 1 : 1 and 1 : 2 BF_3–

Table 1. Alcoholysis of dimethylketene in diethyl ether solution at 25.0 °C

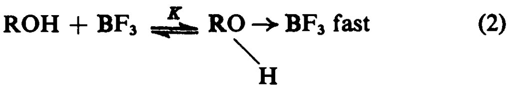
k_{obs} = observed first-order rate constant (see text); $[\ ]_s$ represents the stoicheiometric (total) concentration used; $[\text{Ketene}]_{init} \simeq 10^{-3}$M

(i) t-Butyl alcohol. See Figures 1A and 2A								
(ii) Ethanol. See Figures 1B and 2B								
(iii) Methanol								
(a) $10^2[BF_3]_s$ = 5.10M								
$10^2[MeOH]_s$/M	1.20	1.60	2.90	4.11	5.76	8.23	16.4	
$10^2k_{obs}/s^{-1}$	2.5	3.4	5.0	7.1	9.3	9.9	10.4	
(b) $10^2[MeOH]_s$ = 4.11M								
$10^2[BF_3]_s$/M	1.03	2.06	3.10	4.12	5.10	8.20		
$10^2k_{obs}/s^{-1}$	1.4	3.4	5.0	6.4	7.1	8.1		
(iv) 2-Chloroethanol								
$10^3[BF_3]_s$ = 5.00M								
$10^2[CH_2ClCH_2OH]$/M	1.44	2.48	4.90	6.46	7.45	12.4	15.0	
$10^2k_{obs}/s^{-1}$	2.9	4.0	6.6	7.0	7.0	7.3	7.4	
(v) Phenylmethanol								
(a) $10^2[BF_3]_s$ = 1.00M								
$10^2[PhCH_2OH]_s$/M	1.00	1.50	3.20	4.80	6.40	7.90	10.5	14.9
$10^2k_{obs}/s^{-1}$	3.0	4.1	5.2	5.4	6.0	6.4	7.1	7.4
(b) $10^2[PhCH_2OH]_s$ = 6.40M								
$10^3[BF_3]_s$/M	4.10	6.00	8.20	10.0	13.0			
$10^2k_{obs}/s^{-1}$	2.5	3.8	5.2	6.1	8.1			
(vi) Diphenylmethanol								
(a) $10^2[BF_3]$ = 0.90M								
$10^2[Ph_2CHOH]_s$/M	3.30	6.60	9.60	12.4				
$10^2k_{obs}/s^{-1}$	1.2	2.2	3.2	4.6				
(b) $10^2[Ph_2CHOH]_s$ = 6.60M								
$10^2[BF_3]_s$/M	1.00	1.50	2.00	3.00	5.00			
$10^2k_{obs}/s^{-1}$	2.5	3.8	5.0	7.7	13			
(vii) 2,2,2-Trifluoroethanol. See Figures 1C and 2C								

Table 2. Values of k_2 and K for the boron trifluoride-catalysed alcoholysis of dimethylketene. For k_2 and K see text; temperature = 25.0 °C

ROH	k_2/l mol^{-1} s^{-1}	K/l mol^{-1}	k_2K/l^2 mol^{-2} s^{-1}
Bu^{t}OH	0.18	≲1 000	
EtOH	1.2	320(±50)	380
MeOH	2.0	300(±50)	600
PhCH$_2$OH	8.0	80(±20)	640
ClCH$_2$CH$_2$OH	15	65(±15)	965
Ph$_2$CHOH			41
CF$_3$CH$_2$OH			18

ROH adducts is suggested by other work[6] but, in keeping with the present results, the evidence for 1 : 2 adducts refers to media with dielectric constants appreciably larger than that of diethyl ether. Alcohols are predominantly monomeric in ether at the concentrations involved in the present work[1] and our results confirm a previous study of the boron trifluoride–ethanol equilibrium in ether solution using an i.r. technique.[7]



$$\text{ROH} + \text{BF}_3 \overset{K}{\rightleftharpoons} \underset{\text{H}}{\text{RO}} \rightarrow \text{BF}_3 \text{ fast} \qquad (2)$$

(III)

$$\text{(III)} + \text{Me}_2\text{C=C=O} \xrightarrow{k_2} \text{Me}_2\text{CHCO}_2\text{R} + \text{BF}_3 \text{ slow} \qquad (3)$$

The rate equation for the outline mechanism of equations (2) and (3) is (4).

$$-\text{d[ketene]}/\text{d}t = k_2[\text{(III)}][\text{ketene}] = k_{obs}[\text{ketene}] \qquad (4)$$

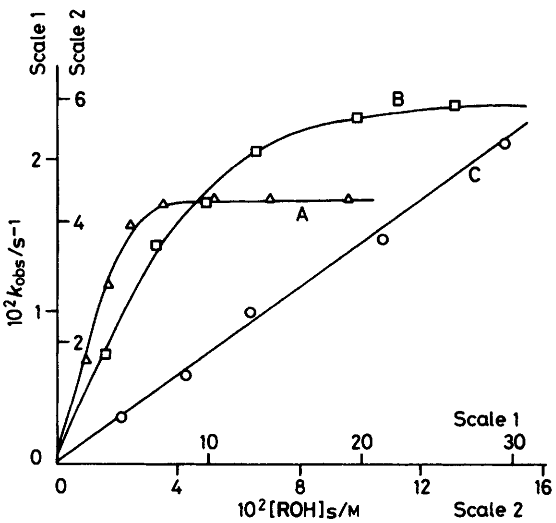


Figure 1. Effects of alcohol concentration at fixed boron trifluoride concentration with dimethylketene: A, t-butyl alcohol ($10^2[BF_3]_s$ = 4.19M); B, ethanol ($10^2[BF_3]_s$ = 5.10M); C, 2,2,2-trifluoroethanol ($10^2[BF_3]_s$ = 1.00M). Scale 1 for A; scale 2 for B and C

The continuous lines in Figures 1B and 2B are computed with K = [(III)]/[BF$_3$][ROH] = 320 l mol^{-1} and k_2 = 1.2 l mol^{-1} s^{-1}. As can be seen, both sets of data are reasonably fitted by these values of K and k_2. Similar self-consistency was observed in experiments with methanol, phenylmethanol, and 2-chloroethanol. For these alcohols our derived values of K and k_2 are in Table 2. The variations in K show, as expected, that K falls when the alcohol contains electron-withdrawing

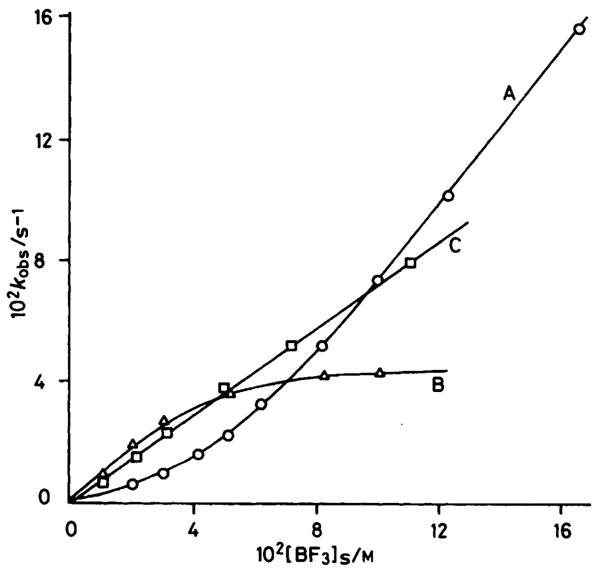


Figure 2. Effects of boron trifluoride concentration at fixed alcohol concentration with dimethylketene: A, t-butyl alcohol ($10^2[ROH]_s = 5.30$M); B, ethanol ($10^2[ROH]_s = 3.30$M); C, 2,2,2-trifluoroethanol ($10^2[ROH]_s = 4.30$M)

substituents and is therefore of lower basicity, whereas the changes in k_2 show that the more acidic (or less basic) the alcohol the faster does its boron trifluoride adduct react with dimethylketene.

(b) 2,2,2-*Trifluoroethanol and diphenylmethanol.* The structures of these alcohols suggest that they are probably much less basic towards boron trifluoride than the others studied. If their K values are relatively small the pre-equilibrium (2) will lie well to the left under the concentration conditions used. In such circumstances we have equation (5). In agreement with

$$k_{obs} = k_2[(III)] = k_2K[BF_3]_s[ROH]_s \qquad (5)$$

equation (5) the k_{obs} values for these alcohols (*e.g.* Figures 1C and 2C) show no tendency to reach a limiting value in the concentration range examined: k_2 continues to increase proportionately as either $[BF_3]_s$ or $[ROH]_s$ is increased. For these cases only the product k_2K can be obtained (Table 2). Although k_2 is likely to be large for these alcohols, the unfavourable position of their pre-equilibria with boron trifluoride renders them less reactive, under comparable concentration conditions, than the other alcohols in the boron trifluoride-catalysed addition to dimethylketene. The opposing effects of substituents on K and k_2 make 2-chloroethanol the most reactive of the alcohols studied.

(c) *t-Butyl alcohol.*—Figures 1A and 2A show the results for this alcohol. With $[BF_3]_s$ fixed, increases in $[ROH]_s$ lead to behaviour (Figure 1A) suggestive of a relatively large value of K ($\gtrsim 1\,000$). The plot (Figure 2A) with $[ROH]_s$ fixed and $[BF_3]_s$ increasing indicates a greater than first-order dependence on $[BF_3]_s$ when $[BF_3]_s < [ROH]_s$ and an approximately rectilinear dependence on $[BF_3]_s$ when $[BF_3]_s \gtrsim [ROH]_s$. Since, as Figure 1A shows, 1 : 1 adduct formation between the alcohol and boron trifluoride is virtually quantitative in the concentration range involved, it appears for t-butyl alcohol that the reaction of the adduct with the ketene is catalysed by the free boron trifluoride when $[BF_3]_s > [ROH]_s$ and by a second molecule of the adduct when $[BF_3]_s < [ROH]_s$. We therefore suggest equations (6)—(9) as a possible outline mechanism. The corresponding rate equation is (10), where $[BF_3]$ represents the free boron trifluoride concentration (*i.e.* $[Et_2O \rightarrow BF_3]$).

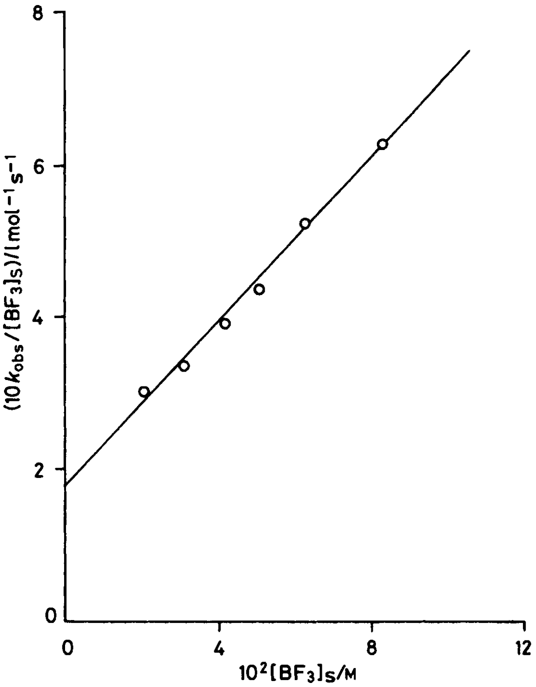
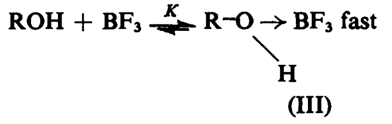


Figure 3. Plot of $k_{obs}/[BF_3]_s$ against $[BF_3]_s$ for t-butyl alcohol. $10^2[Bu^tOH] = 5.30$M



$$ROH + BF_3 \overset{K}{\rightleftharpoons} \underset{\substack{\diagdown \\ H}}{R{-}O} \rightarrow BF_3 \text{ fast} \qquad (6)$$

(III)

$$Me_2C{=}C{=}O + (III) \xrightarrow{k_2} Me_2CHCO_2R + BF_3 \text{ slow} \qquad (7)$$

$$Me_2C{=}C{=}O + 2(III) \xrightarrow{k_2^1} Me_2CHCO_2R + BF_3 + (III) \text{ slow} \qquad (8)$$

$$Me_2C{=}C{=}O + (III) + BF_3 \xrightarrow{k_2^{11}} Me_2CHCO_2R + 2BF_3 \text{ slow} \qquad (9)$$

$$-d[\text{ketene}]/dt = \{k_2[(III)] + k_2^1[(III)]^2 + k_2^{11}[(III)][BF_3]\}[\text{ketene}] = k_{obs}[\text{ketene}] \qquad (10)$$

For the data of Figure 2A, $[(III)] \simeq [BF_3]_s$ and $[BF_3] \simeq 0$ when $[BF_3]_s < [ROH]_s$. Also $[(III)] \longrightarrow [ROH]_s$ (=constant) and $[BF_3] \simeq ([BF_3]_s - [ROH]_s)$ when $[BF_3]_s > [ROH]_s$. For such circumstances equation (10) predicts a region at low values of $[BF_3]_s$ where k_{obs} will show some dependence on $[BF_3]_s^2$, followed by a region at high values of $[BF_3]_s$ where k_{obs} will increase rectilinearly with $[BF_3]_s$, as found. A plot of $k_{obs}/[BF_3]_s$ against $[BF_3]_s$ at low values of $[BF_3]_s$ should lead to a straight line with intercept k_2 and slope k_2^1 (Figure 3). We find $k_2 = 0.18$ l mol^{-1} s^{-1} and $k_2^1 = 5.5$ l^2 mol^{-2} s^{-1}. These values, together with the values of k_{obs} at high boron trifluoride concentrations, show that $k_2^{11} \simeq 30$ l^2 mol^{-2} s^{-1}. If our suggestions are correct these values show that free boron

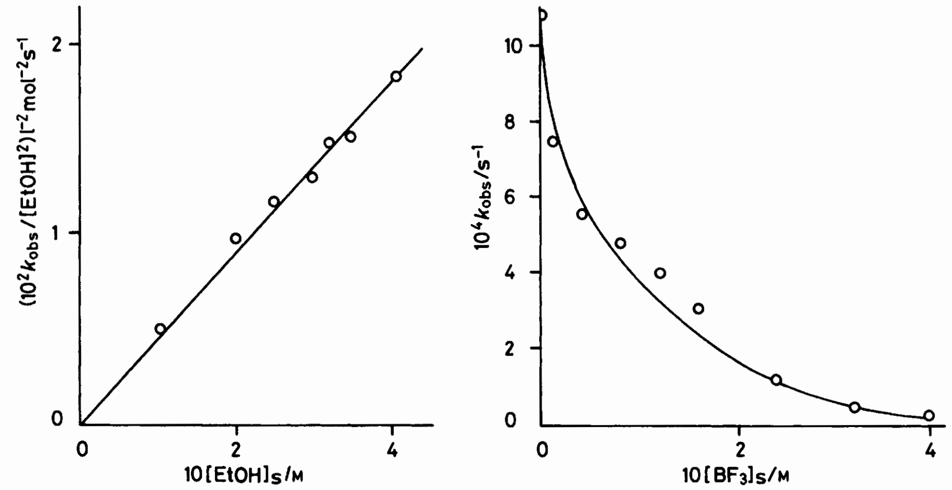
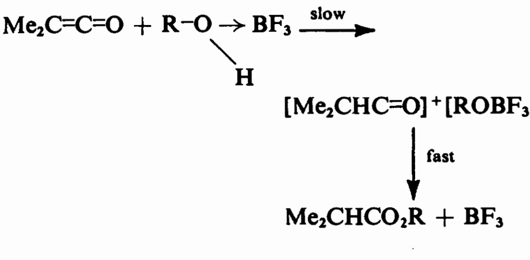


Figure 4. A, Spontaneous addition of ethanol to diphenylketene: $10^3[\text{ketene}]_{\text{init}} \simeq 2.0\text{M}$. B, Effect of boron trifluoride on the addition of ethanol to diphenylketene: $10^3[\text{ketene}]_{\text{init}} \simeq 2.0\text{M}$; $[\text{EtOH}]_s = 0.29\text{M}$

trifluoride is a more powerful catalyst for reaction (7) than is (III) itself.

The self-catalysis by (III) and the catalysis by free boron trifluoride are not immediately obvious from Figure 1A. Examination of the rapidly increasing portion of the graph shows, however, that k_{obs} is indeed increasing faster than would be expected from simple proportionality to the amount of 1 : 1 adduct formed and, moreover, that the steady limiting value (1.74×10^{-2} s^{-1}) of k_{obs} {which corresponds to the complete conversion of $[BF_3]_s$ into (III)} is in good agreement with that expected (1.73×10^{-2} s^{-1}) from equation (10) using the values deduced above for k_2 and k_2^1.

(d) *Detailed mechanism.* We suggest, in keeping with our earlier conclusions about additions to ketenes,[8] that in the present reactions where the alcohol being added forms, at least initially, part of a strong Brønsted acid, the slow step constitutes a proton transfer to the β-carbon atom of the ketene to give an ion-pair which then rapidly leads to the final product. We visualise steps (3) and (7) therefore in more detail as equation (11). Of all the k_2 values (Table 2) that for t-butyl alcohol is much the smallest. This may reflect the relatively low acid strength of $\mathrm{Bu^t\underset{H}{O}\rightarrow BF_3}$ and/or a steric difficulty in transferring the proton with this adduct. We presume that the role of the acid catalyst in steps (8) and (9) is the stabilisation of the incipient anion, perhaps *via* bonding to one of the fluorine atoms. Steps (8) and (9) are unlikely to be termolecular reactions; probably they involve species such as $\mathrm{R{-}\underset{H}{O}\rightarrow \overset{F}{\underset{F}{B}}F\cdots H{-}\underset{R}{O}\rightarrow BF_3}$ and $\mathrm{R{-}\underset{H}{O}\rightarrow \overset{F}{\underset{F}{B}}F\rightarrow BF_3}$ formed in low concentration. Evidence for similar species is known.[6,9]



$$\mathrm{Me_2C{=}C{=}O + R{-}\underset{H}{O}\rightarrow BF_3 \xrightarrow{slow} [Me_2CHC{=}O]^+[ROBF_3]^- \xrightarrow{fast} Me_2CHCO_2R + BF_3} \quad (11)$$

(ii) *Diphenylketene.*—We have shown recently[10,11] that, compared with dimethylketene, diphenylketene is relatively very unreactive towards the addition of strongly electrophilic species HX, although towards the addition of species HX for which nucleophilic attack on the ketene is kinetically dominant, diphenylketene is more reactive than is dimethylketene. Thus the spontaneous addition of water is faster to diphenyl- than to dimethyl-ketene, whereas trichloroacetic acid adds more rapidly to the latter.

Results of experiments on the addition of ethanol to diphenylketene in diethyl ether solution in the presence and in the absence of boron trifluoride, are shown in Figure 4. The spontaneous addition (Figure 4A), like that to dimethylketene,[1] is third order in the ethanol concentration and doubtless has a similar mechanism.[1,2]. The reaction is *ca.* 10 times faster at a given value of $[EtOH]_s$ with diphenyl- than with dimethyl-ketene. However, in contrast to the behaviour found with dimethylketene described in (i)(a) above, the presence of boron trifluoride does not catalyse the addition to diphenylketene; it inhibits it (Figure 4B). It is clear that the $\mathrm{Et\underset{H}{O}\rightarrow BF_3}$ adduct, which is progressively formed as $[BF_3]_s$ is increased, is relatively very unreactive towards diphenylketene compared with the free ethanol. The k_{obs} values in Figure 4B are compatible with those expected for the spontaneous addition of the free ethanol remaining after the formation of the 1 : 1 adduct. The adduct is $\gtrsim 10^4$ times less reactive towards diphenyl- than towards dimethyl-ketene. These results are consistent both with our assumptions about the essentially electrophilic nature of the attack of the $\mathrm{R\underset{H}{O}\rightarrow BF_3}$ adducts on ketenes [equation (11)] and with our previous findings for diphenylketene.[10,11]

(iii) *Comparison with Water.*—The addition of water to dimethyl- and to diphenyl-ketene in ether in the presence of boron trifluoride revealed[11] kinetic behaviour similar to that now reported for alcohols. We found $K \simeq 150$ l mol^{-1} for water, a value which seems to fit well into the data in Table 2; however, $k_2 = 0.18$ l mol^{-1} s^{-1} for water, which is the same value as that now found for t-butyl alcohol. This result suggests that the $H_2O : BF_3$ adduct is less acidic than might be expected simply on the basis of substituent effects.

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