Kinetics and Mechanism of the Lewis Acid-catalysed Addition of Alcohols to Ketenes in Diethyl Ether Solution

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A kinetic study is reported of the addition of alchols to dimethyl- and diphenyl-ketene in diethyl ether solution at 25 °C in the presence of $HgCl_2$, $ZnCl_2$, $SbCl_3$, and $Bu^n_2SnCl_2$. Except for $HgCl_2$, which forms insoluble complexes with the reactants, the metal halides catalyse the addition to dimethylketene. The catalysed addition involves the reaction of metal halide–alcohol adducts with the ketene. In general, the stronger the adduct as a Brønsted acid, the faster is the addition of the alcohol to the ketene, although C–O, as well as C–H, bond formation is probably significant kinetically. A cyclic transition state is suggested. For diphenylketene, strongly acidic adducts transfer alcohol to the ketene so slowly that inhibition of alcoholysis is observed. Inhibition arises because the spontaneous alcoholysis is reduced as free alcohol is removed as unreactive adduct. However, weak-metal halide acids probably lead to catalysis. It is concluded (a) that the different behaviour of the two ketenes in these reactions is in keeping with their behaviour observed when they react with carboxylic acids in ether, and (b) that metal halide-catalysed alcoholysis of ketenes is generally similar to that observed with aryl isocyanates, except that tin-based catalysts are relatively more effective with isocyanates.

Additions to ketenes and to isocyanates possess many common kinetic and mechanistic features.[1] The alcoholysis of isocyanates is powerfully catalysed by certain metal compounds and especially by compounds such as di- and tri-butyltin halides.[2,3] However, an attempt to use these tin derivatives, and other similar compounds, to catalyse the alcoholysis of ketenes was unsuccessful.[4] Since we have shown recently[5] that, in diethyl ether solution, boron trifluoride strongly catalyses the alcoholysis of dimethylketene but inhibits that of diphenylketene, we considered that further study of these systems, using other covalent metal halides as potential catalysts, might throw light on the apparent difference in behaviour between ketenes and isocyanates noted above. We report now on the effects of $HgCl_2$, $ZnCl_2$, $SbCl_3$, and Bu_2SnCl_2 on the alcoholysis of dimethyl- and diphenyl-ketenes in diethyl ether solution.

Experimental

We used methods developed previously in this laboratory in work with alcohols,[6] ketenes,[1] and covalent metal halides.[3,7] In the kinetic work the ketene was always in deficit and the observed first-order rate constant for its loss, k_{obs}, was normally reproducible to within $\pm 12\%$. Typical results, together with the corresponding concentration and other conditions, are given in the Tables and Figures. Most of the k_{obs} values are the averages of two, or more, determinations.

In the systems where catalysis is observed, preparative experiments using the alcohol, ketene, and metal halide at concentrations similar to those of the kinetic experiments led to high yields of the expected ester [equation (1)]. It has previously

$$R'_2C{=}C{=}O + ROH \xrightarrow{MX_n} R'_2CHCO_2R \qquad (1)$$
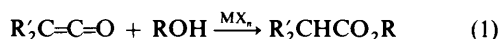
been established[5,6] that high yields are obtained during spontaneous alcoholyses, and also when the catalyst is BF_3.

U.v. and i.r. spectroscopic studies of mixtures of the metal halides and ketenes in ether solution show that rapid adduct formation between these species occurs to a negligible extent under the concentration conditions of the kinetic experiments. However, for $ZnCl_2$ with dimethylketene, and for $SbCl_3$ and Bu_2SnCl_2 with diphenylketene, a slow loss of ketene (possibly as dimer) occurs in the absence of alcohol. For these systems a

correction was therefore necessary to k_{obs} obtained in the presence of alcohol. For the $ZnCl_2$–dimethylketene system this correction was smaller than the experimental uncertainty in k_{obs} and was normally $<5\%$. For the diphenylketene systems the necessary corrections complicated study of the alcoholyses.

Results and Discussion

(a) *Dimethylketene.*—(i) $HgCl_2$. All the metal halides used acted as catalysts for the alcoholysis of dimethylketene, except $HgCl_2$. When the latter compound is present in an ethereal solution containing dimethylketene and either methanol or ethanol, a precipitate rapidly forms. This precipitate interferes with the spectroscopic monitoring of ketene loss and therefore we did not study this metal halide further. The precipitate only forms when all three components (ketene, alcohol, and $HgCl_2$) are present together. It may be significant that the failure of the previous attempt[4] to catalyse the methanolysis of ketene itself with this and other metal halides, using toluene as solvent, was attributed to the formation of inactive compounds.

(ii) $ZnCl_2$. Our results with this metal halide are in Table 1 and Figure 1. Catalysis is evident, but the spontaneous alcoholysis contributes slightly to k_{obs}. Zinc chloride rapidly forms a 1:1 adduct with ethanol in diethyl ether solution [equation (2)]

$$ZnCl_2 + EtOH \xrightleftharpoons{K_1} EtO{-}ZnCl_2 \atop {}^{\backslash}H \qquad (2)$$
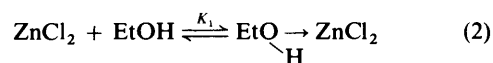
for which spectroscopic measurements suggest[3] $K_1 \simeq 200\ mol^{-1}\ dm^3$ at 25 °C. (The equilibrium constant for 2:1 adduct formation is small.) Using this value of K_1, we can calculate the concentration of free ethanol in each reaction mixture and so correct k_{obs} for the contribution of the spontaneous rate,[5,6] k_s; the corrected values $k_c = (k_{obs} - k_s)$ are in Table 1.

For the boron trifluoride-catalysed alcoholyses of dimethylketene[5] we found that the (strongly acidic) 1:1 adduct (ROH, BF_3) is the species which reacts with the ketene. However, in the present case, the detailed dependence of k_c on the stoicheiometric alcohol and $ZnCl_2$ concentrations, $[EtOH]_s$ and $[ZnCl_2]_s$, shows that reaction of the 1:1 adduct with the ketene cannot alone account for the results: k_c is too large when the ratio $[EtOH]_s/[ZnCl_2]_s$ is large, and it does not approach a

Table 1. Zinc chloride-catalysed ethanolysis of dimethyl ketene in diethyl ether solution at 25 °C. $[Ketene]_{initial} \simeq 10^{-3}M$; k_{obs} = observed first-order rate constant (see text); $k_c = k_{obs}$ corrected for the spontaneous alcoholysis (see text); $[\ ]_s$ represents the stoicheiometric (total) concentration used

(i) 10^2 $[ZnCl_2]_s$ = 4.50M

10 $[EtOH]_s$/M	0.65	0.98	1.30	1.64	1.97	2.29	2.62
10^4 k_{obs}/s^{-1}	1.7	2.5	3.7	5.5	7.3	10.1	11.7
10^4 k_c/s^{-1}	1.6	2.4	3.5	5.3	7.0	9.4	11.1

10 $[EtOH]_s$/M	2.95	3.28
10^4 k_{obs}/s^{-1}	12.6	14.1
10^4 k_c/s^{-1}	11.8	13.0

(ii) 10 $[EtOH]_s$ = 1.97M

10^2 $[ZnCl_2]_s$/M	2.3	12.2	15.2	22.8
10^4 k_{obs}/s^{-1}	5.3	10.1	10.3	12.0
10^4 k_c/s^{-1}	5.0	10.0	10.3	12.0

Table 2. Antimony trichloride-catalysed alcoholysis of dimethylketene in diethyl ether solution at 25 °C. $[Ketene]_{initial} \simeq 10^{-3}M$; k_{obs} = observed first-order rate constant

(a) 2,2,2-Trifluoroethanol

(i) 10^2 $[CF_3CH_2OH]_s$ = 4.20M

10 $[SbCl_3]_s$/M	0.70	1.39	2.09	2.79
10^4 k_{obs}/s^{-1}	1.2	2.4	3.7	4.5

(ii) 10^2 $[SbCl_3]$ = 6.90M

10 $[CF_3CH_2OH]_s$/M	0.42	1.28	1.71	2.10
10^4 k_{obs}/s^{-1}	1.1	3.3	4.0	5.6

(b) Phenylmethanol

(i) 10^2 $[PhCH_2OH]_s$ = 6.40M

10 $[SbCl_3]_s$/M	0.38	0.94	1.32	1.89	2.46
10^3 k_{obs}/s^{-1}	0.65	1.3	2.3	3.0	4.1

(ii) 10^2 $[SbCl_3]_s$ = 3.8M

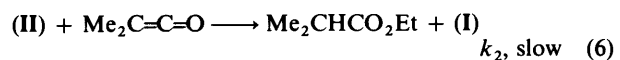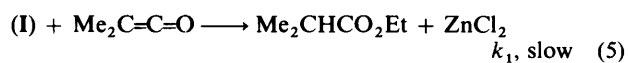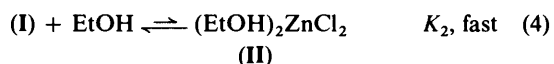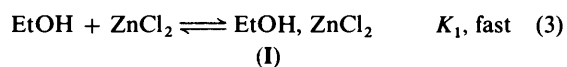| 10 $[PhCH_2OH]_s$/M	0.64	0.96	1.29	1.58	2.20	3.16
10^3 k_{obs}/s^{-1}	0.65	0.91	1.3	1.6	2.4	3.3

(c) Methanol (See Figure 2)
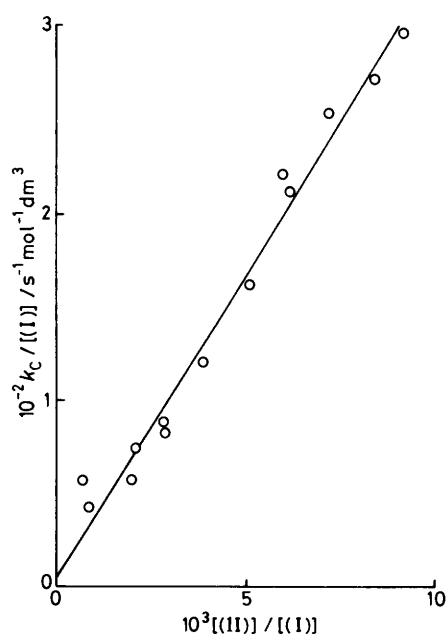
Figure 1. Plot of equation (7) for the zinc chloride–ethanol–dimethylketene system

constant value under conditions where virtually all the $ZnCl_2$ added will exist as the 1:1 adduct. The results suggest that a higher adduct, e.g. a 2:1 alcohol–$ZnCl_2$ species, is contributing to the reaction (Scheme 1).

$$EtOH + ZnCl_2 \rightleftharpoons EtOH, ZnCl_2 \qquad K_1, \text{fast} \quad (3)$$
$$\text{(I)}$$

$$\text{(I)} + EtOH \rightleftharpoons (EtOH)_2ZnCl_2 \qquad K_2, \text{fast} \quad (4)$$
$$\text{(II)}$$

$$\text{(I)} + Me_2C=C=O \longrightarrow Me_2CHCO_2Et + ZnCl_2$$
$$k_1, \text{slow} \quad (5)$$

$$\text{(II)} + Me_2C=C=O \longrightarrow Me_2CHCO_2Et + \text{(I)}$$
$$k_2, \text{slow} \quad (6)$$

Scheme 1.

The rate equation for Scheme 1 is (7). If this Scheme is correct,

$$-d[Ketene]/dt = \{k_1[\text{(I)}] + k_2[\text{(II)}]\}[Ketene]$$
$$= k_c[Ketene] \qquad (7)$$

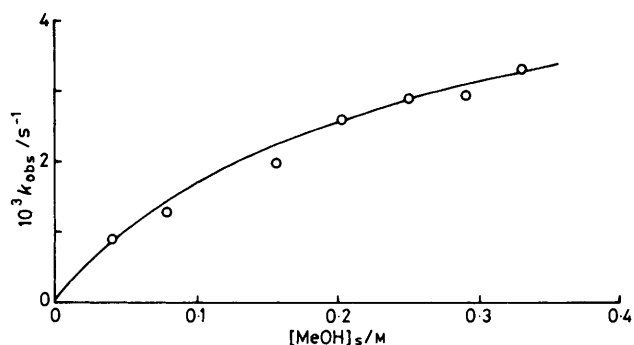a plot of $k_c/[\text{(I)}]$ against $[\text{(II)}]/[\text{(I)}]$ should be rectilinear (with

Figure 2. Antimony trichloride-catalysed addition of methanol to dimethylketene in diethyl ether at 25 °C. $[SbCl_3]_s = 0.026M$; for k_{obs}, see text; continuous line for $K_1 = 6$ mol^{-1} dm^3 and $k_1 = 0.2$ mol^{-1} dm^3 s^{-1} in equation (10)
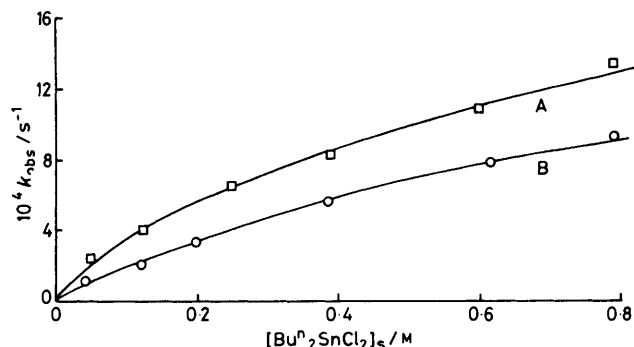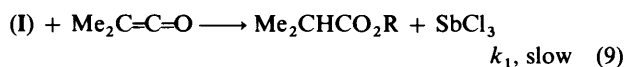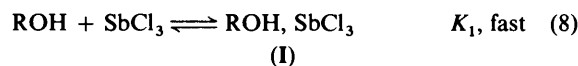

Figure 3. Dibutyltin dichloride-catalysed addition of alcohols to dimethylketene in diethyl ether at 25 °C. A $[MeOH]_s = 0.041M$; B $[EtOH]_s = 0.052M$; for k_{obs}, see text

slope k_2 and intercept k_1). Values of $[(I)]$ and $[(II)]$ can be calculated from the values of $[EtOH]_s$ and $[ZnCl_2]_s$ used in the reaction mixtures, for any chosen values of K_1 and K_2. Figure 1 results when $K_1 = 160$ and $K_2 = 3.3 \times 10^{-2}$ mol^{-1} dm^3. These values are in reasonable agreement with the spectroscopic study of the EtOH–ZnCl$_2$ system in ether.[3] Figure 1 indicates that $k_1 = (5 \pm 5) \times 10^{-4}$ and $k_2 = 3.2 \pm 0.1$ mol^{-1} dm^3 s^{-1}; (I) is therefore relatively very unreactive compared with (II).

(*iii*) SbCl$_3$. This metal halide was studied with three alcohols: methanol, phenylmethanol, and 2,2,2-trifluoroethanol. Our values of k_{obs} are in Table 2 and Figure 2. Catalysis is again evident and the spontaneous alcoholyses contributed negligibly to k_{obs}. The results for each alcohol are compatible with Scheme 2 for the catalysed reaction. The rate equation for this Scheme is (10).

$$\text{ROH} + \text{SbCl}_3 \rightleftharpoons \text{ROH, SbCl}_3 \qquad K_1, \text{ fast} \quad (8)$$
$$\text{(I)}$$

$$\text{(I)} + \text{Me}_2\text{C=C=O} \longrightarrow \text{Me}_2\text{CHCO}_2\text{R} + \text{SbCl}_3$$
$$k_1, \text{ slow} \quad (9)$$

Scheme 2.

$$-\text{d[Ketene]}/\text{d}t = k_1[(I)][\text{Ketene}] = k_{obs}[\text{Ketene}] \quad (10)$$

For phenylmethanol and trifluoroethanol plots of k_{obs} against $[ROH]_s$ (or $[SbCl_3]_s$), under otherwise constant concentration conditions, are rectilinear. This suggests that, for these alcohols, K_1 is small since, with equilibrium (8) lying well to the left, equation (10) can be written as (11). Values of k_1K_1 obtained

$$-\text{d[Ketene]}/\text{d}t = k_1K_1[\text{ROH}]_s[\text{SbCl}_3]_s[\text{Ketene}]$$
$$= k_{obs}[\text{Ketene}] \quad (11)$$

either from the plot at constant $[ROH]_s$, or from that at constant $[SbCl_3]_s$, are in good agreement. We find $k_1K_1 = 0.27 \pm 0.01$ and $(3.72 \pm 0.08) \times 10^{-2}$ mol^{-2} dm^6 s^{-1} for phenylmethanol and trifluoroethanol, respectively.

Our k_{obs} values for methanol (Figure 2) suggest that equilibrium (8) does not lie so far to the left with this alcohol. The results are well fitted by equation (10) with $K_1 = 6$ mol^{-1} dm^3 and $k_1 = 0.2$ mol^{-1} dm^3 s^{-1}. For ethanol K_1 is known[3] to be ca. 10 mol^{-1} dm^3, so this derived value for methanol is of the correct order of magnitude.

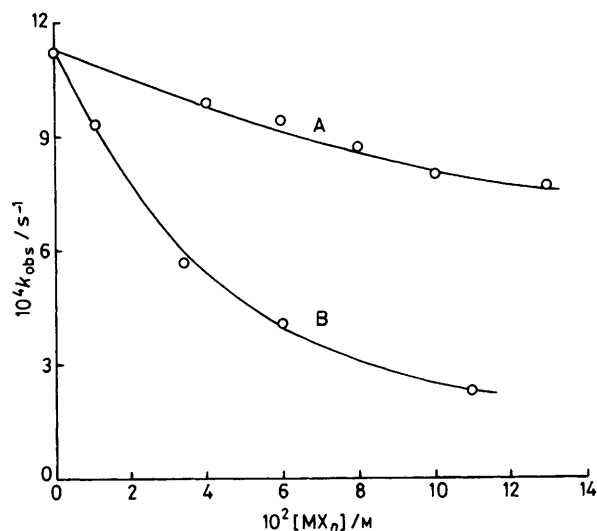(*iv*) Bu$^n_2$SnCl$_2$. This compound was studied with methanol

Figure 4. Effects of Lewis acids on the ethanolysis of diphenylketene in diethyl ether solution at 25 °C. $[EtOH]_s = 0.29M$; A HgCl$_2$; B ZnCl$_2$; for k_{obs}, see text

and ethanol. Catalysis of alcoholysis was observed, but a significant correction to k_{obs} is needed, except at low values of $[ROH]_s$, to allow for the contribution of the spontaneous reaction. By working at fixed, low alcohol concentrations, so that the corrections were negligible, we obtained the results in Figure 3. Assuming a catalytic mechanism analogous to Scheme 2, the results for this (rather feeble) catalyst are best fitted by $K_1 = 1.7$ mol^{-1} dm^3 and $k_1 = 0.03$ mol^{-1} dm^3 s^{-1} for ethanol and by $K_1 = 1.6$ mol^{-1} dm^3 and $k_1 = 0.06$ mol^{-1} dm^3 s^{-1} for methanol. The K_1 value for ethanol is similar to that obtained previously from other kinetic and equilibrium measurements.[3]

(b) *Diphenylketene.*—(i) HgCl$_2$ *and* ZnCl$_2$. These metal halides behave analogously to BF$_3$: their addition to a reaction mixture leads to inhibition of ethanolysis (Figure 4). As for BF$_3$, the results suggest that the metal halide–alcohol adducts are unreactive towards diphenylketene and that k_{obs} arises from the residual free ethanol. The fall in k_{obs} with increase in $[ZnCl_2]_s$ is slightly greater than for the BF$_3$ system and this is (qualitatively) compatible with the evidence given above for the formation of some $(EtOH)_2ZnCl_2$. The results for HgCl$_2$ suggest a value of $K_1 \simeq 1$—2 mol^{-1} dm^3 for equilibrium (12), assuming the adduct is completely unreactive.

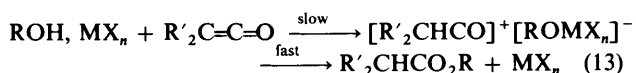$$EtOH + HgCl_2 \xrightarrow{K_1} EtOH, HgCl_2 \qquad (12)$$

(ii) $SbCl_3$ *and* Bu_2SnCl_2. Diphenylketene is unstable in solutions containing these halides (see Experimental section). This made quantitative study of their effects on alcoholysis unprofitable. Qualitatively, however, our results (with ethanol) suggest that these halides do not produce the marked inhibition caused by BF_3 and $ZnCl_2$, and, to a lesser extent, by $HgCl_2$. Under conditions when a significant amount of the alcohol is present as adduct, a small increase in k_{obs} is probable.

(c) *Conclusions.*—Our present and previous work[5] points to the following conclusions.

(i) Covalent metal halides, when they do not form insoluble complexes with the reactants, catalyse the alcoholysis of di-methylketene. With this ketene, the stronger the halide as a Lewis acid, the stronger its catalytic effect. The catalysed reaction proceeds *via* attack on the ketene by alcohol–metal halide adducts and, in general, the stronger the adduct as a Brønsted acid, the more rapid is that attack. Thus for EtOH, BF_3 $k_1 = 1.2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, whereas for EtOH, Bu_2SnCl_2 $k_1 = 0.03$ $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.
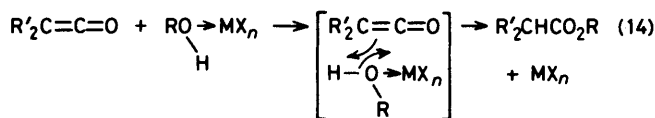
(ii) Our previous suggestion[5] (made by analogy with the addition[7] of CCl_3CO_2H) that the detailed mechanism of the slow step of the addition follows equation (13), now appears

$$ROH, MX_n + R'_2C=C=O \xrightarrow{\text{slow}} [R'_2CHCO]^+[ROMX_n]^-$$
$$\xrightarrow{\text{fast}} R'_2CHCO_2R + MX_n \qquad (13)$$

unlikely to be correct, or to apply generally to these catalysed reactions. This is because it is now known[8] that species ROH,BF_3 are much stronger Brønsted acids than is CCl_3-CO_2H, yet they add to dimethylketene at rates comparable to that found for CCl_3CO_2H. This suggests that for ROH, MX_n the proton-transfer aspect of the addition is not wholly rate-determining, and that the removal of RO^- from $[ROMX_n]^-$ is also kinetically significant. This may underlie the relatively great reactivity of $(EtOH)_2ZnCl_2$ compared with $EtOH,ZnCl_2$.

(iii) With diphenylketene the pattern of reactivity is roughly the opposite of that found with dimethylketene: the adducts ROH, MX_n containing the strongest metal halides add very slowly, whilst adducts of some weak metal halides may add faster than the free alcohol. This difference in behaviour of dimethyl- and diphenyl-ketenes is in keeping with the difference previously observed towards addition of carboxylic acids.[9]

(iv) The mechanism of addition may approximate to equation (14). As discussed for carboxylic acid addition,[9] the importance

$$R'_2C=C=O + RO\!\!\rightarrow\!\!MX_n \; \underset{H}{\overset{}{\longrightarrow}} \; \left[\begin{array}{c} R'_2C=C=O \\ \nearrow \\ H-O\!\!\rightarrow\!\!MX_n \\ \backslash \\ R \end{array} \right] \rightarrow R'_2CHCO_2R \quad (14)$$
$$+ MX_n$$

of C–O and C–H bond formation in the transition state will depend upon the ketene and upon the complex acid involved.

(v) These metal halide-catalysed additions to ketenes do not appear therefore to be entirely different from those to aryl isocyanates.[3] The principal difference is the relatively great reactivity of tin derivatives as catalysts for the isocyanates.

References

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