The Kinetics of the Addition of Ethanol to *p*-Chlorophenyl Isocyanate in Diethyl Ether Solution in the Presence of Covalent Metal Halides

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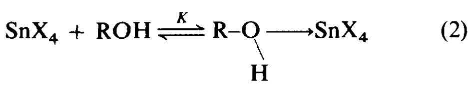
The effects of the presence of BF_3, $ZnCl_2$, $SbCl_3$, $PhSnCl_3$, $(Bu^n)_2SnCl_2$, and $(Bu^n)_3SnCl$ on the kinetics of ethanolysis of *p*-chlorophenyl isocyanate in diethyl ether solution have been studied at 25 °C. The covalent halides rapidly form 1 : 1 adducts with ethanol in ether solution and the formation constants, *K*, are 350 ± 100, 205 ± 30, 10 ± 2, 61 ± 5, 1.5 ± 0.2, and 0.50 ± 0.10 $dm^3 mol^{-1}$, respectively, at 25 °C. Under most of the concentration conditions studied, the 1 : 1 adduct and the isocyanate lead to the urethane product in a reaction (rate constant k_a) that is first order in each reactant. Except for the boron trifluoride adduct, this reaction always leads to catalysis of the alcoholysis and the value of k_a generally increases as that of *K* decreases; with the butyltin chlorides the spontaneous alcoholysis becomes negligible compared with the catalysed reaction. In solutions containing a sufficient concentration of free covalent halide, departures from the foregoing simple kinetic pattern occur. Our results and the mechanism of the alcoholysis are discussed in the light of previous work.

Numerous metal compounds are known[1,2] to catalyse the addition of alcohols to isocyanates [equation (1)]. Certain tin compounds have normally been found to be very effective catalysts and most kinetic studies of catalysis by metal compounds have concerned them.[2,3] The detailed mechanism of the catalysis is uncertain[3] but work[4] with tin-based catalysts shows that catalyst–alcohol adducts [*e.g.*, equation (2)] are probably involved. One study[5] using n-heptane as solvent suggests that catalytic reactivity is related to the magnitude of the formation constant, *K*, of the 1 : 1 adduct, reactivity being a maximum when *K* is neither too small nor too large.

$$RNCO + R'OH \longrightarrow RNHCO_2R' \qquad (1)$$



$$SnX_4 + ROH \overset{K}{\rightleftharpoons} R\text{–}\underset{\displaystyle H}{O}\longrightarrow SnX_4 \qquad (2)$$

(I)

We now compare the kinetic behaviour of some covalent tin halides with that of covalent halides of other metals in catalysing reaction (3) in diethyl ether solution at 25 °C. We report also values of *K* for the ethanol–metal halide interactions.

$$p\text{-}ClC_6H_4{\cdot}NCO + EtOH \xrightarrow[Et_2O]{MX_n} p\text{-}ClC_6H_4NHCO_2Et \qquad (3)$$

Experimental

Materials.—Di-n-butyldichlorotin and tri-n-butylchlorotin were the Fluka products and were used without further purification. The other covalent halides, the solvent, and *p*-chlorophenyl isocyanate were purified and stored as in earlier work in these laboratories.[6,7] AnalaR ethanol was further dried with a molecular sieve. All materials were handled and solutions prepared in a dry-box.

Kinetics and Equilibrium Experiments.—The kinetic experiments were conducted along lines used for the spontaneous alcoholysis.[6] The presence of the metal halide did not interfere with the monitoring of the appearance of the urethane (at 293 nm). All reactions were conducted using pseudo-first-order conditions (ethanol in excess of isocyanate) and, except with boron trifluoride and zinc chloride, the ethanol was also normally present in a considerable excess over the metal halide. All the systems displayed an accurate first-order behaviour over three or more half-lives. The observed first-order rate constant, $k_{obs.}$, was always reproducible to within ±12% (normally ± 8%). Details of the concentration and other conditions used in the runs are in the Tables and Figures.

The equilibrium adduct formation was monitored by noting the change in the alcohol monomer absorption at 3 500 cm^{-1} as increasing amounts of covalent halide were added to a (*ca.* 0.03—0.10 mol dm^{-3}) solution of the alcohol. At such concentrations in ether at 25 °C ethanol is effectively completely monomeric and is predominantly so throughout the concentration ranges used in the kinetic work.[6,8]

Spectroscopic experiments suggested that the metal halides interact very little with the isocyanate in ether solution.

Reaction Products.—Preparative-scale experiments, that simulated as far as possible the concentration conditions of the kinetic runs, led with all the covalent halides to high (>90%) yields of the expected urethane. The absorbance changes during the runs also indicated an effectively quantitative yield of urethane.

Results and Discussion

Formation Constants.—In the concentration ranges studied, all the covalent halides display simple 1:1 adduct formation with ethanol in ether [*e.g.*, equation (2)]. Our values of *K* (= [1:1 adduct]/[MX_n][EtOH]) are given in Table 1; the (qualitative) value for boron trifluoride is compatible with the value obtained from kinetic analysis of the boron trifluoride-catalysed addition of ethanol to dimethylketene in ether.[9]

Kinetics of Addition of Ethanol to p-*Chlorophenyl Isocyanate*.—(*i*) *Spontaneous addition*. The value of $k_{obs.}$ for this reaction[6] (k_s) increases rapidly with the stoicheiometric alcohol concentration, $[ROH]_s$. Over the concentration ranges used in the present

Table 1. Formation constants and reactivities of the 1:1 adducts (**I**) at 25 °C. $K = [(\mathbf{I})]/[MX_n][EtOH]$; k_a = second-order rate constant for reaction (5); solvent = diethyl ether

MX_n	K/mol^{-1} dm^3	k_a/dm^3 mol^{-1} s^{-1}
BF_3	350 ± 100	1.6×10^{-4}
$ZnCl_2$	205 ± 30	3.6×10^{-3}
$SbCl_3$	10 ± 2	7.0×10^{-2}
$PhSnCl_3$	61 ± 5	22×10^{-2}
$(Bu^n)_2SnCl_2$	1.5 ± 0.2	1.7
$(Bu^n)_3SnCl$	0.50 ± 0.10	16

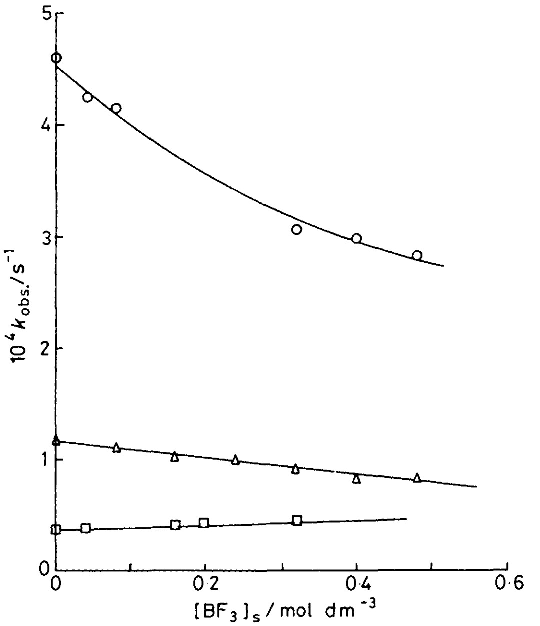


Figure 1. Plot of $k_{obs.}$ for ethanolysis in the presence of boron trifluoride at 25 °C. $[EtOH]_s$: □, 0.510; △, 0.847; and ○, 1.53 mol dm^{-3}

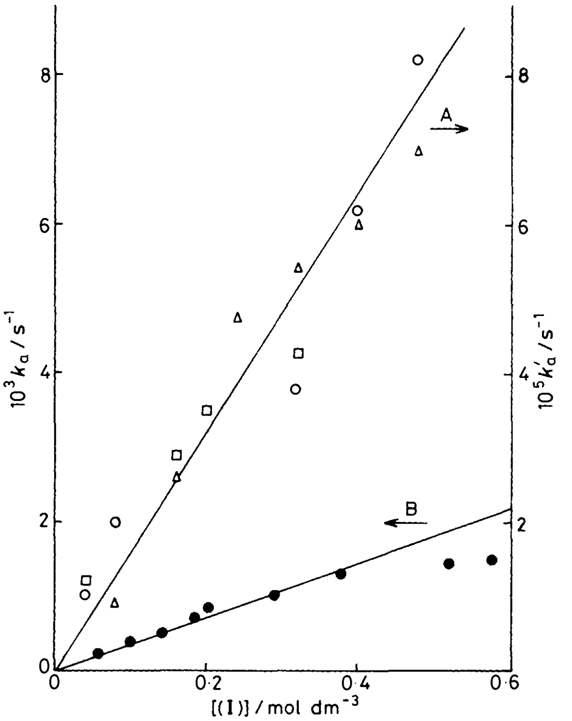


Figure 2. Plots of k_a' *versus* $[(\mathbf{I})]$ for catalysis by A, boron trifluoride ($[EtOH]_s$: □, 0.510; △, 0.847; and ○, 1.53 mol dm^{-3}) and B, zinc chloride

work the reaction displays an order in $[ROH]_s$ of between third and fourth. This stems from the fact that the spontaneous addition involves[6] predominantly the reaction of the isocyanate with self-associated alcohol. Monomeric alcohol appears to be relatively very unreactive.

(*ii*) *Addition in the presence of boron trifluoride.* Values of $k_{obs.}$ in Figure 1 show that when $[ROH]_s > ca.$ 0.5 mol dm^{-3} the addition of boron trifluoride to a reaction mixture actually leads to a decrease in $k_{obs.}$, the decrease being most marked at large values of $[ROH]_s$. This effect arises because the added boron trifluoride removes free alcohol as the 1:1 adduct, (**I**); this loss of alcohol reduces the spontaneous rate and, at large values of $[ROH]_s$, this lost contribution to the rate is not entirely made up for by reaction of the isocyanate with (**I**).

Our knowledge of K, and of k_s as a function[6] of [ROH], permits the calculation, at each value of $[ROH]_s$ and $[BF_3]_s$, of $[(\mathbf{I})]$ and of that part (k_a') of $k_{obs.}$ not attributable to the spontaneous addition of the residual free (uncomplexed) alcohol, *i.e.*, $k_a' = k_{obs.} - k_s$. In Figure 2A k_a' is plotted against $[(\mathbf{I})]$ for all the results shown in Figure 1. Figure 2A reveals that, as well as the spontaneous addition, there exists a (rather slow) route that is first order in $[(\mathbf{I})]$.

(*iii*) *Addition in the presence of zinc chloride.* Our data for this metal halide refer to a single value of $[ROH]_s$ = 0.80 mol dm^{-3}. In contrast to the results with boron trifluoride (Figure 1), the presence of zinc chloride leads to a significant increase in $k_{obs.}$ (Table 2). Calculation of $[(\mathbf{I})]$, and correction to $k_{obs.}$, as before, for k_s due to residual free alcohol, leads to the results in Figure 2B. Here also k_a' is rectilinearly related to $[(\mathbf{I})]$ up to $[ZnCl_2]_s$ *ca.* 0.4 mol dm^{-3}; thereafter further increases in $[ZnCl_2]_s$ have much less effect.

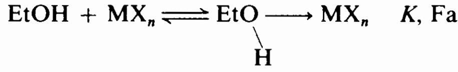
(*iv*) *Addition in the presence of phenyltrichlorotin.* At a given value of $[ROH]_s$, values of $k_{obs.}$ in the presence of this metal halide are appreciably larger than with either boron trifluoride or zinc chloride so that lower values of $[MX_n]_s$ were used (Table 2). For this system therefore relatively little of $[ROH]_s$ is converted into adduct in the reaction mixtures and the k_s correction to $k_{obs.}$ is roughly constant for a given value of $[ROH]_s$, although still significant. Results were obtained at two different values of $[ROH]_s$ and Figure 3A is a plot of k_a' against $[(\mathbf{I})]$, including all the data. Again a rectilinear dependence of k_a' on $[(\mathbf{I})]$ is evident.

(*v*) *Addition in the presence of antimony trichloride.* For this metal halide K is sufficiently small, and the adduct sufficiently reactive towards the isocyanate, for it to be practicable to reveal an equilibrium-like increase in $k_{obs.}$ as $[ROH]_s$ is increased at a fixed value of $[SbCl_3]_s$. Figure 4 shows how the increase in $k_{obs.}$ slows down when $[ROH]_s \gg [SbCl_3]_s$. The results in Figure 4, and those obtained at two fixed $[ROH]_s$ values (Table 2), all corrected for k_s, are plotted against $[(\mathbf{I})]$ in Figure 3B; a rectilinear dependence is once again observed.

(*vi*) *Addition in the presence of di-n-butyldichlorotin and tri-n-butylchlorotin.* These metal halides proved to be relatively very reactive in catalysing isocyanate alcoholysis and in ether solution the spontaneous alcoholysis can be ignored, even at quite low values of $[MX_n]_s$. Our results are in Figures 5 and 6. The data for Bu_2SnCl_2 in Figure 6 have been calculated using K = 3 (rather than 1.5 given in Table 1) as the fit is much improved. This difference in value may arise from the fact that the i.r. measurements required in this case use relatively large concentrations of MX_n. Consideration of the data shows that

$k_{obs.}$ ($= k_a'$) is proportional to [(**I**)] provided that $[MX_n]_{free} <$ *ca.* 2.5×10^{-3} mol dm^{-3}.

Reaction Mechanism.—In all the present systems the metal halides provide routes to alcoholysis that are always first order in isocyanate and also first order in the 1 : 1 alcohol–MX_n adduct over most (or all) of the MX_n concentration range studied. The outline mechanism of equations (4) and (5) therefore accounts for the observed equilibria and for the major part of the reaction orders. Values of k_a (obtained from the slopes of the plots in Figures 2, 3, and 6) are in Table 1.



$$EtOH + MX_n \rightleftharpoons \underset{H}{EtO} \longrightarrow MX_n \quad K, \text{Fast} \quad (4)$$

(**I**)

$$(\mathbf{I}) + ClC_6H_4NCO \longrightarrow ClC_6H_4NHCO_2Et \quad k_a, \text{Slow} \quad (5)$$

In general we find that the smaller the value of K the larger is k_a. The three tin-based halides are the most effective catalysts and the fact that k_a is greater for phenyltrichlorotin than for antimony trichloride (although K is smaller for the latter) suggests that there may be something especially suitable about tin in these reactions. As noted above,[1-3] tin catalysts have normally been found, in qualitative tests, to be very effective. Our finding that k_a generally rises as K falls, over the range of catalysts used, is unexpected in view of the reports of Nesterov *et al.* for heptane solutions.[5]

In heptane solutions catalysis of ethanolysis by di-n-butyltin dilaurate has a less negative entropy of activation than has the spontaneous alcoholysis and this accounts for the large increase in rate.[10] We believe[6] that in ether solution the spontaneous reaction may contain a substantial contribution from a path involving the alcohol trimer or tetramer; if so, mechanism (4)—(5) should certainly have entropic advantages; the involvement of alcohol polymers in the spontaneous reaction will probably be even more important in the aprotic solvent heptane.

Facts that require explanation are (i) the rise in k_a with fall in K, (ii) the ease with which appropriately complexed alcohol monomer, (**I**), adds to the isocyanate in view of the unreactivity[3,6] of the free monomer, (**II**); and (iii) the loss of proportionality between k_a and [(**I**)] when sufficient free MX_n is in solution.

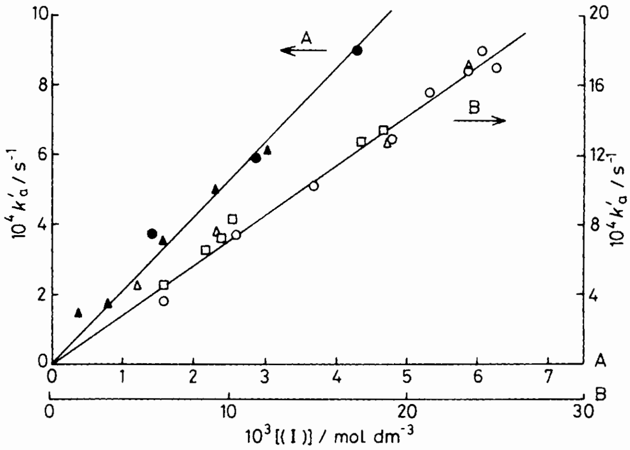


Figure 3. Plots of k_a' *versus* [(**I**)] for catalysis by A, phenyltrichlorotin and B, antimony trichloride. A: $[EtOH]_s$, ●, 0.51; ▲, 0.085 mol dm^{-3}. B: $[EtOH]_s$, □, 1.23; △, 0.85 mol dm^{-3}; $10^2[SbCl_3]_s$, ○, 2.96

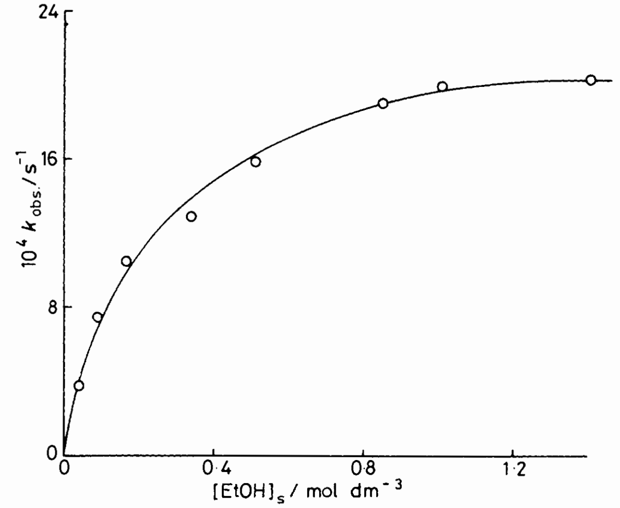


Figure 4. Plot of $k_{obs.}$ *versus* $[EtOH]_s$ in the presence of antimony trichloride at 25 °C. $10^2[SbCl_3]_s$ 2.96 mol dm^{-3}

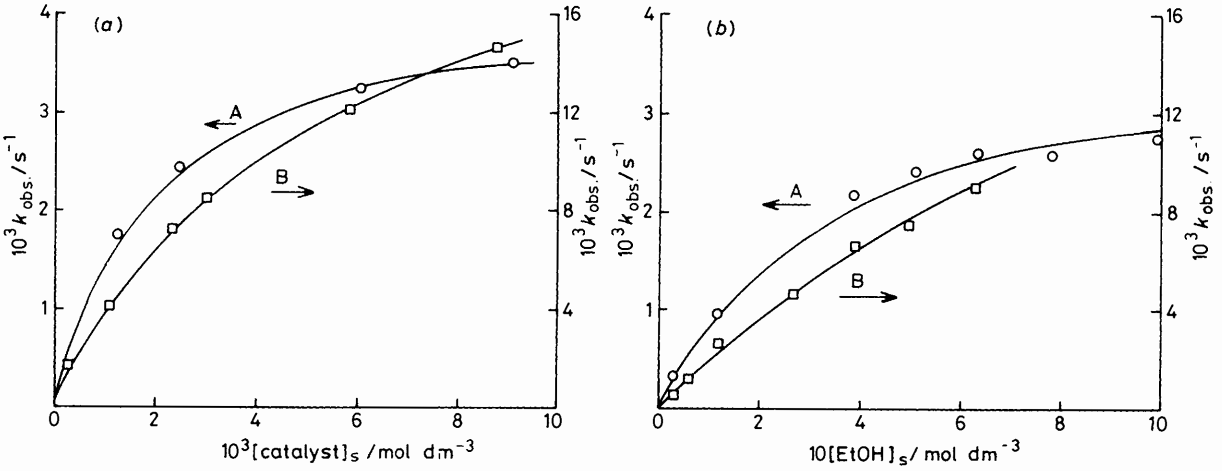


Figure 5. Catalysis by dibutyltin dichloride and tributyltin chloride at 25 °C. (*a*) $[EtOH]_s$ 0.51 mol dm^{-3}; (*b*) $10^3[catalyst]_s$ 2.4 mol dm^{-3}. A, Dibutyltin dichloride with $[EtOH]_s$ 0.51 mol dm^{-3} or $10^3[Bu_2SnCl_2]_s$ 2.4 mol dm^{-3}; B, tributyltin chloride with $[EtOH]_s$ 0.51 mol dm^{-3} or $10^3[Bu_3SnCl]_s$ 2.4 mol dm^{-3}

Table 2. Values of $k_{obs.}$ for reaction of ethanol with *p*-chlorophenyl isocyanate in the presence of covalent metal halides in diethyl ether. $k_{obs.}$ = observed first-order constant; temperature = 25 °C; $[ClC_6H_4NCO]_{init}$ *ca.* 5 × 10^{-4} mol dm^{-3}

(*i*) *Boron trifluoride* (see Figure 1)							
(*ii*) *Zinc chloride* ($[EtOH]_s$ = 0.80 mol dm^{-3})							
$10^5\ k_{obs.}/s^{-1}$	31	46	59	75	90	105	133
$10[ZnCl_2]_s$/mol dm^{-3}	0.60	1.02	1.45	1.89	2.10	3.00	3.90
$10^5 k_{obs.}/s^{-1}$	144	146					
$10[ZnCl_2]_s$/mol dm^{-3}	5.40	6.00					
(*iii*) *Antimony trichloride*							
(*a*) $[EtOH]_s$ = 1.23 mol dm^{-3}							
$10^4\ k_{obs.}/s^{-1}$	7.4	9.4	10.1	11.0	15.5	16.2	
$10^2[SbCl_3]_s$/mol dm^{-3}	0.77	1.05	1.14	1.30	2.10	2.36	
(*b*) $[EtOH]_s$ = 0.85 mol dm^{-3}							
$10^4\ k_{obs.}/s^{-1}$	5.8	8.8	13.8	18.2			
$10^2[SbCl_3]_s$/mol dm^{-3}	0.61	1.17	2.34	2.96			
(*c*) $10^2[SbCl_3]_s$ = 2.96 mol dm^{-3} (see Figure 4)							
(*iv*) *Phenyltrichlorotin*							
(*a*) $[EtOH]_s$ = 0.085 mol dm^{-3}							
$10^4\ k_{obs.}/s^{-1}$		1.5	1.7	3.6	5.0	6.1	
$10^3[PhSnCl_3]_s$/mol dm^{-3}		0.50	1.00	2.00	3.00	4.00	
(*b*) $[EtOH]_s$ = 0.51 mol dm^{-3}							
$10^4\ k_{obs.}/s^{-1}$		4.2	6.3	9.4			
$10^3[PhSnCl_3]_s$/mol dm^{-3}		1.50	3.00	4.50			

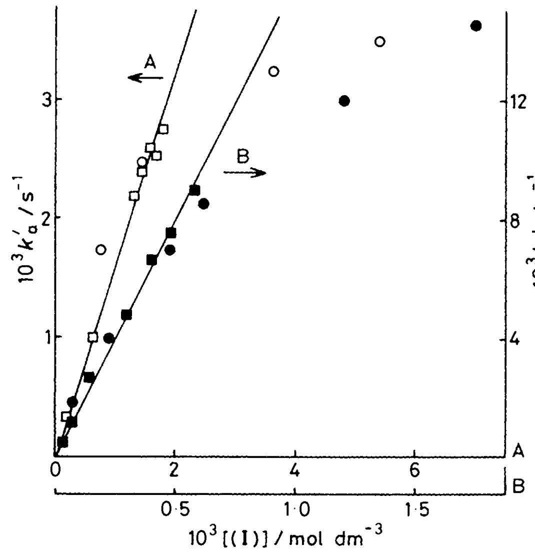
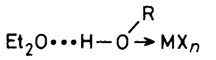
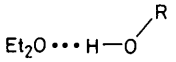
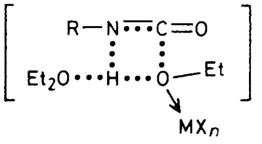
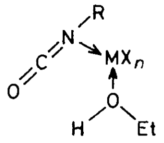


Figure 6. Plots of k_a' *versus* [(I)] for catalysis by dibutyltin dichloride and tributyltin chloride. A: ○, $[EtOH]_s$ 0.51 mol dm^{-3}; □; $10^3[Bu_2SnCl_2]_s$ 2.4 mol dm^{-3}. B: ●, $[EtOH]_s$ 0.51 mol dm^{-3}; ■, $10^3[Bu_3SnCl]_s$ 2.4 mol dm^{-3}


(I)
(solvent included)

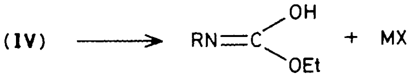

(II)


(III)

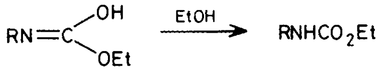

(IV)

The explanation for facts (i) and (ii) is presumably that the catalytic addition retains as its crucial energy barrier[3,6] the attack of the alcoholic oxygen atom on the carbonyl carbon atom of the isocyanate; the more firmly this oxygen atom is attached to the metal centre the bigger this barrier is likely to be. However, forming the 1:1 adduct may lengthen slightly the alcohol O–H bond[4] and so facilitate a four-centre addition, (III), that seems so difficult for the free alcohol, (II). Amongst our systems we suggest that a reaction involving a transition state such as (III) is probably only involved for the (relatively slow) reaction of $EtOH,BF_3$. All the other covalent halide–alcohol adducts can, in principle, accommodate an isocyanate molecule co-ordinated to the metal, as in (IV). We suggest that step (5) normally involves the sequence (6)—(8). The speed of this intramolecular addition could clearly depend (inversely) on the strength of the M–O bond in (I) and on the detailed

$$\mathrm{RNCO} + (\mathrm{I}) \rightleftharpoons (\mathrm{IV}) \qquad \text{Fast, (6)}$$



$$(\mathrm{IV}) \longrightarrow \mathrm{RN{=}C(OH)OEt} + \mathrm{MX}_n \qquad \text{Slow, (7)}$$



$$\mathrm{RN{=}C(OH)OEt} \xrightarrow{\mathrm{EtOH}} \mathrm{RNHCO_2Et} \qquad \text{Fast, (8)}$$

geometry of (**IV**) (which may be especially suitable in tin compounds).

A satisfactory explanation for fact (iii) is not obvious. The result is beyond experimental error and similar findings have been reported[11-13] for dibutyltin dilaurate in heptane and in dioxane, and for dibutyltin diacetate in acetonitrile and in dibutyl ether. We consider, however, that the explanations[13,14] offered for these other findings are unconvincing since one involves the assumption that (**I**) ionises to give free ions in dibutyl ether and in hexane solution whilst the other (as admitted by its authors) does not fully explain the effect and also assumes that a step corresponding to (8) will be a unimolecular prototropic rearrangement, even in the presence of a large excess of alcohol. It is probably significant that the effect sets in at relatively low free MX_n concentrations with the most reactive catalysts.

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