The Kinetics and Mechanism of the Spontaneous Alcoholysis of *p*-Chlorophenyl Isocyanate in Diethyl Ether. The Association of Alcohols in Diethyl Ether

By **S. A. Lammiman** and **R. S. Satchell**,* Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W.8

The self-association of four simple aliphatic alcohols in ether solution has been investigated. In the concentration range 0·1—1·2 mol dm^{-3} the principal polymer is in every case the dimer. At 25 °C the dimerisation constants K_2 (= [dimer]/[monomer]^2) have the values 0·49, 0·71, 0·50, and 0·72 for MeOH, EtOH, Pr^{i}OH, and Bu^{n}OH respectively. The kinetics of the spontaneous alcoholysis of *p*-chlorophenyl isocyanate by the same alcohols in ether solution has also been studied. The observed rate equation is $-d[\text{isocyanate}]/dt = d[\text{product}]/dt = \{k_2[\text{M}]^2 + k_n[\text{M}]^n\}[\text{isocyanate}]$ where [M] represents the alcohol monomer concentration, and $n = 3$ or 4 depending on the structure of the alcohol involved. The second-order term represents a route *via* dimeric alcohol. The various dimers have similar reactivities, the bulkier Bu^n and Pr^i substituents leading (at 25 °C) to species with about half the reactivity of dimeric methanol and ethanol. The higher-order term probably represents a route *via* trimeric or tetrameric alcohol. The contributions of the second- and of the higher-order terms to the overall rate are comparable, the latter dominating at high stoicheiometric concentrations. The probable mechanism of urethane formation is a slow, one-step cyclic addition of alcohol polymer to the isocyanate and is analogous to the mechanism of alcoholysis of ketens. The fact that alcoholysis of isocyanates involves, in almost all solvents, a kinetic order >1 in the stoicheiometric alcohol concentration arises from the generally greater reactivity of alcohol polymers than of monomers, and the circumstance that the relative concentration of the former inevitably rises as the stoicheiometric alcohol concentration increases.

THERE have been a number [1-8] of kinetic investigations of the spontaneous reaction (1) between alcohols and isocyanates in non-hydroxylic solvents, but there exists no general agreement about either the proper kinetic form or the reaction mechanism.[7,9] Much confusion has arisen from the use by almost all authors of the type of concentration conditions and plots employed in the early work of Baker and Gaunt.[1] These workers used roughly equimolar concentrations of alcohol and isocyanate and sought to express their results in terms of conventional second-order plots, first-order in each reactant. Unfortunately for this procedure the inherent reactivity of the alcohol normally changes, as we shall see, with its stoicheiometric concentration. This has two consequences. First, reactions conducted under conditions of comparable concentrations of alcohol and isocyanate, and which therefore lead to an appreciable reduction of the alcohol concentration during a run, lead to apparent second-order rate constants which vary throughout the run. Secondly, even when the alcohol is in sufficient excess of the isocyanate for its concentration to remain effectively constant throughout any run, the observed second-order rate constants for different stoicheiometric alcohol concentrations are not constant, and almost invariably increase with increase in $[\text{ROH}]_{\text{stoich}}$. One certain aspect of the subject is that Baker and Gaunt's explanation of the second effect cannot be correct.[5,9]

$$R^1N{=}C{=}O + R^2OH \longrightarrow R^1NHCO_2R^2 \qquad (1)$$

A reduction in velocity is observed [7,9] for reactions in co-ordinating solvents (*e.g.*, ethers) compared with non-co-ordinating solvents (*e.g.*, benzene and hexane) and most authors have suspected that some change in hydrogen-bonding with changing solvent underlies this phenomenon, but their explanations vary. Partial or exclusive reaction of the isocyanate with alcohol polymers, rather than with alcohol monomers, has been suggested,[3,7] but the nature of the polymer (dimer, trimer, *etc.*) and the percentage of polymer which exists in any particular circumstances has always been assumed; there has been no adequate correlation of reaction velocity with polymer concentration. This is largely because of the past tendency to approach the kinetics *via* the second-order rate equation. Since we believe that a general preference of the isocyanate for reaction with alcohol polymers would explain qualitatively almost all the available kinetic results, and since it is known that such a preference is found in the very similar reactions (2) of ketens with alcohols [10] and with water [10] in ethereal solvents, and also for the alcoholysis of acyl chlorides in carbon tetrachloride and other solvents,[11,12] we decided to reinvestigate the alcoholysis of isocyanates more thoroughly from this viewpoint. We have used *p*-chlorophenyl isocyanate and various alcohols as reagents in diethyl ether as solvent, and have examined both the alcohol

$$R^1_2C{=}C{=}O + R^2OH \longrightarrow R^1_2CHCO_2R^2 \qquad (2)$$

---

[1] J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 1949, 19.

[2] E. Dyer, H. A. Taylor, S. J. Mason, and J. Samson, *J. Amer. Chem. Soc.*, 1949, **71**, 4106.

[3] S. Ephraim, A. E. Woodward, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, 1958, **80**, 1326.

[4] M. Sato, *J. Org. Chem.*, 1962, **27**, 819.

[5] W. G. P. Robertson and J. E. Stutchbury, *J. Chem. Soc.*, 1964, 4000.

[6] S. G. Éntelis and O. V. Nesterov, *Kinetika i Kataliz*, 1966, **7**, 464.

[7] A. E. Oberth and R. S. Bruenner, *J. Phys. Chem.*, 1968, **72**, 845.

[8] N. N. Zolotarevskaya, E. Z. Zhuravlev, A. V. Gerega, and I. I. Konstantinov, *Kinetika i Kataliz*, 1969, **10**, 427.

[9] A. Farkas and G. A. Mills, *Adv. Catalysis*, 1962, **13**, 393.

[10] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 889.

[11] R. F. Hudson and G. W. Loveday, *J. Chem. Soc.* (*B*), 1966, 766.

[12] R. F. Hudson, G. W. Loveday, S. Fliszár, and G. Salvadori, *J. Chem. Soc.* (*B*), 1966, 769.

polymerisation and the reaction orders under simple kinetic conditions.

EXPERIMENTAL

Materials.—Anhydrous diethyl ether was fractionally distilled first from sodium and then from lithium aluminium hydride. The product had b.p. 35 °C/760 mmHg. *p*-Chlorophenyl isocyanate, fractionally distilled under reduced pressure, had b.p. 101 °C/21 mmHg. AnalaR grades of the alcohols were purified by refluxing 20 ml portions with magnesium turnings (1·2 g) activated with iodine (0·2 g) for 1 h. More alcohol (250 ml) was then added, and the whole fractionally distilled. The respective b.p.s of the alcohols were: methanol, 65 °C/760 mmHg; ethanol 79 °C/760 mmHg; propan-2-ol, 82 °C/760 mmHg; and butan-1-ol, 118 °C/760 mmHg.

Reaction Mixtures.—To prevent contamination by atmospheric moisture, which would result in removal of the isocyanate by hydrolysis and also could affect the hydrogen-bonding properties of the reaction mixtures, these mixtures were prepared in a dry-box frequently flushed with pre-dried nitrogen. Stock solutions of *p*-chlorophenyl isocyanate in ether were made up by weight. For the kinetic experiments suitable aliquot portions of the stock *p*-chlorophenyl isocyanate solution were added to 10 ml volumetric flasks containing weighed amounts of the relevant alcohol dissolved in solvent. The mixture was then made up to the mark with more solvent. For the association experiments solutions were made up in the same way with the omission of the *p*-chlorophenyl isocyanate.

Kinetic Arrangements.—Portions of reaction mixtures were transferred (in the dry-box) to a stoppered spectrophotometer cell (1 cm path) which served as the reaction vessel. The cell was quickly removed from the box, and transferred to the thermostatted cell compartment of a Unicam SP 500 (or SP 800) spectrophotometer. The blank cell always contained the same concentration of alcohol as the reaction mixture, but no isocyanate. The progress of the reaction was followed by measurement of the absorbance (D) at 293 nm (or 244 nm) where the product urethane absorbs strongly, and the isocyanate weakly. Identical results were obtained at both wavelengths. When possible D_∞ readings were taken after 10 half-lives; such measurements when checked after a further 10 half-lives showed no change. For slow reactions ($t_{\frac{1}{2}}$ several days or more) the experimental D_∞ after 10 half-lives was found to be unreliable (owing to slow evaporation of solvent) and the theoretical D_∞ based on the known product spectrum was therefore used.

In the reaction mixture the alcohol was always present in at least 10-fold excess of the isocyanate (normally [RNCO] $= 1 \times 10^{-3}$ mol dm^{-3}); this led to a pseudo-first-order loss of the isocyanate. The observed first-order rate constant (k_{obs}) was obtained from a plot of log ($D_\infty - D_t$) against t, where D_t and D_∞ were the absorbances (at 293 or 244 nm) at time t and ∞ respectively. Values of k_{obs} were reproducible normally to within $\pm 5\%$.

Reaction Products.—For each alcohol preparative scale reactions were carried out with concentration conditions (alcohol, 1 mol dm^{-3}; *p*-chlorophenyl isocyanate, 2×10^{-3} mol dm^{-3}) similar to those used in the kinetic runs. The product urethanes were obtained in very high (*ca.* 100%) yields and their m.p.s agreed with literature values. The i.r. and n.m.r. spectra of the products were also compatible with their being urethanes. Their u.v. spectra in ether solution when compared with the terminal spectra from the kinetic runs showed that the yields in the latter were also close to 100%.

Alcohol Association.—The self-association of the various alcohols in ether solution was determined by measuring the departure from Beer's law of the i.r. absorption due to the monomer.[13] Two bands were used: the fundamental O–H stretching vibration around 3500 cm^{-1} (in ether the monomer is hydrogen-bonded), and its (less intense) first overtone band around 7000 cm^{-1}. Absorption due to polymeric alcohol species appears at longer wavelengths in each case, but the identification of particular types of polymer from its position is a very uncertain procedure.[13-15] Both the 3500 cm^{-1} and 7000 cm^{-1} regions have been used in the past for the determination of the association constants of alcohols, and we have found that similar conclusions follow from measurements in either region. However, to obtain reliable values for the monomer extinction coefficients, we found it necessary to use solutions with $[\text{ROH}]_{\text{stoich}} \leqslant$ *ca.* 0·05 mol dm^{-3}. This is not feasible in the overtone region owing (*a*) to the width of the cell necessary to obtain reasonable absorbances, and (*b*) to interference from the solvent's absorption. Most of our measurements were therefore made with a Perkin-Elmer 237 spectrophotometer by use of the fundamental band. Solutions having $[\text{ROH}]_{\text{stoich}} = 5 \times 10^{-3}$—$5 \times 10^{-2}$ mol dm^{-3} were used to obtain the monomer extinction coefficients in cells of (nominal) 0·2 and 0·5 mm pathlength. A cell of variable pathlength was used to compensate for solvent absorption. Plots of absorbance against $[\text{ROH}]_{\text{stoich}}$ were straight lines over this concentration range, and the extinction coefficients were obtained from their slopes. The alcohol self-association was then studied with a series of more concentrated solutions and cells of 0·1 mm path. (An accurate comparison of the pathlength of this cell with that of the 0·2 and 0·5 mm cells was made by determining the absorbances of the same test solution in each of the cells.) As has been found,[10] plots of absorbance against $[\text{ROH}]_{\text{stoich}}$ at these higher concentrations are not rectilinear, but curve downwards. The concentration of the monomer was calculated from the observed absorbance for each solution after allowance had been made for the overlap of the polymer band.

RESULTS AND DISCUSSION

Self-association of Alcohols in Ether.—The polymeric species present in ethereal solvents have not previously been identified with certainty. Lillford and Satchell [10] favoured the trimer, but could not properly distinguish between this and the dimer. (They studied a rather small concentration range.)

We have treated our results on the assumption of a mixture of a dimer and trimer [equations (3) and (4)], so that we could test for the significant presence of both.

$$2\text{ROH} \overset{K_2}{\rightleftharpoons} (\text{ROH})_2 \qquad (3)$$

$$3\text{ROH} \overset{K_3}{\rightleftharpoons} (\text{ROH})_3 \qquad (4)$$

---

[13] A. N. Fletcher and C. A. Heller, *J. Phys. Chem.*, 1967, **71**, 3742.

[14] W. C. Coburn and E. Grunwald, *J. Amer. Chem. Soc.*, 1958, **80**, 1318.

[15] D. A. Ibbitson and L. F. Moore, *J. Chem. Soc.* (*B*), 1967, 76.

If M, D, and T refer to the monomer, dimer, and trimer respectively, and S refers to the stoicheiometric alcohol, then we obtain equation (5). Since $K_2 = [D]/[M]^2$ and $K_3 = [T]/[M]^3$, equation (6) follows and this leads to

$$[S] = [M] + 2[D] + 3[T] \qquad (5)$$

$$[S] = [M] + 2K_2[M]^2 + 3K_3[M]^3 \qquad (6)$$

$$([S] - [M])/2[M]^2 = K_2 + 3K_3[M]/2 \qquad (7)$$

equation (7). For such a system containing significant concentrations of trimer, values of $([S] - [M])/2[M]^2 = (K_2)_{app}$ should increase as [M] increases. Our values of $(K_2)_{app}$ show no such general increase (see Tables 1—4), and are, in fact, roughly constant. We conclude that the major associated species up to stoicheiometric concentrations of *ca.* 1·2 mol dm^{-3} is the dimer.* Obviously higher polymers may be present in low concentrations.

TABLE 1

Association of methanol in diethyl ether at 27 °C

$(K_2)_{app} = ([S] - [M])/2[M]^2$

[S] mol dm^{-3}	[M] mol dm^{-3}	[S] − [M] mol dm^{-3}	$10^2(K_2)_{app}$ dm^3 mol^{-1}
0·247	0·210	0·037	46·2
0·414	0·324	0·090	44·4
0·517	0·379	0·138	48·1
0·673	0·458	0·215	51·2
0·757	0·512	0·245	46·7
0·892	0·562	0·336	53·2
1·039	0·614	0·425	56·4
1·120	0·682	0·438	47·1
			Av. 49 ± 4

TABLE 2

Association of ethanol in diethyl ether at 27 °C

[S] mol dm^{-3}	[M] mol dm^{-3}	[S] − [M] mol dm^{-3}	$10^2(K_2)_{app}$ dm^3 mol^{-1}
0·138	0·117	0·021	76·7
0·148	0·123	0·025	82·4
0·175	0·144	0·031	74·7
0·227	0·179	0·048	74·9
0·375	0·287	0·088	53·4
0·441	0·312	0·129	66·2
0·478	0·332	0·146	66·3
0·541	0·364	0·177	66·8
0·625	0·406	0·219	66·7
0·696	0·430	0·266	71·9
0·814	0·485	0·329	70·0
0·897	0·512	0·385	73·4
1·041	0·561	0·480	76·3
1·200	0·621	0·579	75·1
			Av. 71 ± 7

TABLE 3

Association of propan-2-ol in diethyl ether at 27 °C

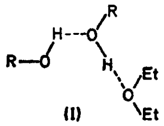
[S] mol dm^{-3}	[M] mol dm^{-3}	[S] − [M] mol dm^{-3}	$10^2(K_2)_{app}$ dm^3 mol^{-1}
0·276	0·226	0·050	49·0
0·406	0·321	0·085	41·3
0·471	0·352	0·119	48·0
0·523	0·396	0·127	40·4
0·602	0·422	0·180	50·6
0·667	0·452	0·215	52·4
0·785	0·519	0·266	49·4
0·869	0·539	0·330	56·8
0·904	0·571	0·333	51·1
1·161	0·651	0·510	60·2
			Av. 50 ± 6

TABLE 4

Association of butan-1-ol in diethyl ether at 27 °C

[S] mol dm^{-3}	[M] mol dm^{-3}	[S] − [M] mol dm^{-3}	$10^2(K_2)_{app}$ dm^3 mol^{-1}
0·236	0·186	0·050	72·3
0·265	0·202	0·063	76·0
0·353	0·252	0·101	79·5
0·459	0·327	0·132	61·8
0·551	0·369	0·182	66·9
0·664	0·419	0·245	69·8
0·756	0·460	0·296	69·9
0·873	0·502	0·371	73·6
0·978	0·528	0·450	80·7
1·077	0·602	0·475	65·5
			Av. 72 ± 6

In ethereal solvents the dimer would be expected to have an open-chain structure [*e.g.* (I)]. Higher polymers are likely to be cyclic.[15] This idea is supported by the i.r. spectra. Up to 2 mol dm^{-3} our polymer absorbance was centred around 3420 cm^{-1}, but at very much higher concentrations ($[ROH]_{stoich} > [Et_2O]$) the absorbance moved to the region of 3350 cm^{-1}, where cyclic polymers have been reported to absorb.[15]



(I)

Our average values of K_2 for the various alcohols are in Table 5. The values are in the sequence BuOH ≏ EtOH > Pr^iOH ≏ MeOH.

TABLE 5

Values of the dimerisation constants and the rate constants in diethyl ether. See text for definitions of symbols; values of K_2 are at 27 °C, and values of the rate constants at 25 °C

Alcohol	10^2K_2 mol^{-1} dm^3	10^5k_2 mol^{-2} dm^6 s^{-1}	10^5k_3 mol^{-3} dm^9 s^{-1}
MeOH	49 ± 4	10	
EtOH	71 ± 7	10	
Pr^iOH	50 ± 6	5	37
Bu^nOH	72 ± 6	7	

Alcohol	10^5k_4 mol^{-4} dm^{12} s^{-1}	10^3k_D mol^{-1} dm^3 s^{-1}
MeOH	54	0·20
EtOH	158	0·14
Pr^iOH		0·10
Bu^nOH	186	0·10

Kinetics of Urethane Formation.—In any reaction mixture the alcohol was present in large excess of the isocyanate, and the observed loss of isocyanate always obeyed the first-order rate law (8) accurately during several half-lives. The value of the observed first-order rate constant (k_{obs}) was found to depend upon

$$-d[RNCO]/dt = k_{obs}[RNCO] \qquad (8)$$

---

* Above 1·2 mol dm^{-3} it was not possible to obtain accurate monomer absorbances owing to the extent of overlap with the polymer absorption band.

$[ROH]_{stoich}$ (Tables 6—9). It is evident that k_{obs} increases more rapidly than the stoicheiometric alcohol concentration [S]; this suggests that polymeric alcohol species may be involved in the reaction, since the fraction of self-associated alcohol must rise as [S] is increased. If it is first assumed that the monomer, dimer, and trimer can all react with isocyanate as in equation (9), then the rate equation will be (10), where k_M, k_D, and k_T are the

$$(R^1OH)_n + RNCO \longrightarrow RNHCO_2R^1 + (R^1OH)_{n-1} \qquad (9)$$

$$-d[RNCO]/dt = (k_M[M] + k_D[D] + k_T[T])[RNCO] \qquad (10)$$

second-order rate constants for reaction of the monomer, dimer, and trimer respectively. Hence we obtain

$$\begin{aligned} k_{obs} &= k_M[M] + k_D[D] + k_T[T] && (11)\\ &= k_M[M] + k_DK_2[M]^2 + k_TK_3[M]^3 && (12)\\ &= k_1[M] + k_2[M]^2 + k_3[M]^3 && (13)\\ k_{obs}/[M] &= k_1 + k_2[M] + k_3[M]^2 && (14) \end{aligned}$$

equations (11) and (12). The latter can be written as (13) where $k_1 = k_M$, $k_2 = k_DK_2$, and $k_3 = k_TK_3$, and we thus obtain equation (14). To test if the monomer is reactive, $k_{obs}/[M]$ was plotted against [M] (Figure 1), the values of [M] being obtained from our results for the self-association equilibria. The plots are curves, but each curve passes through the origin. Therefore k_M must be relatively very small and we conclude that the monomer does not take any significant part in the reaction. For each alcohol studied the plot curves upward as [M] increases indicating that, in addition to the dimer, the trimer or perhaps a higher polymer is involved.

TABLE 6

Values of k_{obs} for methanolysis of *p*-chlorophenyl isocyanate in diethyl ether at 25 °C. [M] was calculated from the value of K_2 (Table 5)

$\frac{[S]}{mol\ dm^{-3}}$	$\frac{[M]}{mol\ dm^{-3}}$	$10^5k_{obs}/s^{-1}$
0·319	0·255	0·788
0·340	0·269	1·05
0·418	0·319	1·50
0·543	0·392	2·68
0·781	0·518	7·87
0·928	0·589	10·6
1·030	0·635	14·2
1·056	0·644	13·2
1·17	0·696	18·0
1·27	0·737	21·2
1·39	0·785	28·3
1·98	1·00	63·7

TABLE 7

Values of k_{obs} for ethanolysis of *p*-chlorophenyl isocyanate in diethyl ether at 25 °C

$\frac{(S)}{mol\ dm^{-3}}$	$\frac{[M]}{mol\ dm^{-3}}$	$10^5k_{obs}/s^{-1}$
0·166	0·139	0·195
0·187	0·154	0·317
0·222	0·177	0·510
0·367	0·266	1·75
0·407	0·289	2·08
0·496	0·336	3·57
0·511	0·343	3·15
0·586	0·381	5·53
0·847	0·497	12·6
0·887	0·513	15·1
1·04	0·573	19·2
1·09	0·589	22·3
1·23	0·643	28·4
1·36	0·689	37·2

TABLE 8

Values of k_{obs} for propan-2-olysis of *p*-chlorophenyl isocyanate in diethyl ether at 25 °C

$\frac{[S]}{mol\ dm^{-3}}$	$\frac{[M]}{mol\ dm^{-3}}$	$10^5k_{obs}/s^{-1}$
0·149	0·132	0·152
0·167	0·146	0·224
0·276	0·225	0·552
0·351	0·275	1·21
0·407	0·311	1·61
0·523	0·379	2·70
0·632	0·439	4·03
0·709	0·479	4·75
0·782	0·516	5·92
0·913	0·578	8·98
1·04	0·636	11·0
1·07	0·649	12·3
1·29	0·740	17·7
1·67	0·886	29·3

TABLE 9

Values of k_{obs} for butan-1-olysis of *p*-chlorophenyl isocyanate in diethyl ether at 25 °C

$\frac{[S]}{mol\ dm^{-3}}$	$\frac{[M]}{mol\ dm^{-3}}$	$10^5k_{obs}/s^{-1}$
0·150	0·127	0·160
0·208	0·168	0·360
0·245	0·192	0·560
0·347	0·254	1·36
0·440	0·306	2·38
0·559	0·366	4·65
0·643	0·408	6·33
0·764	0·460	10·2
0·853	0·497	15·2
0·968	0·543	19·0
1·09	0·590	25·5
1·17	0·619	28·7

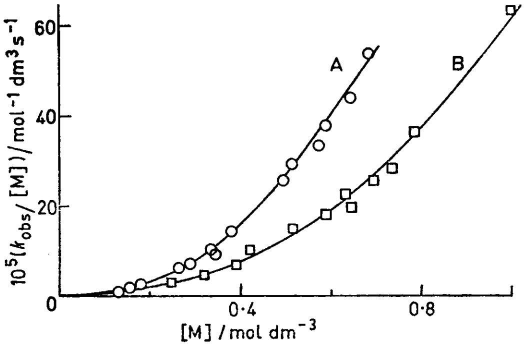


FIGURE 1 Plot of $k_{obs}/[M]$ against [M]; A, EtOH; B, MeOH

To test whether the contributions of the dimer and trimer are sufficient to account for the variation in k_{obs}, $k_{obs}/[M]^2$ was plotted against [M] (Figure 2). The plot for propan-2-ol is satisfactorily rectilinear and has an intercept on the $k_{obs}/[M]^2$ axis. The primary alcohols, however, lead to plots whose curvature suggests that a higher polymer than the trimer is involved for them. For these alcohols a plot of $k_{obs}/[M]^2$ against $[M]^2$ is satisfactorily rectilinear with an intercept on the ordinate axis (Figure 3). These results show that the rate equation for propan-2-ol has the form (15), and for the primary alcohols the form (16). These equations suggest that for primary alcohols the higher polymer is

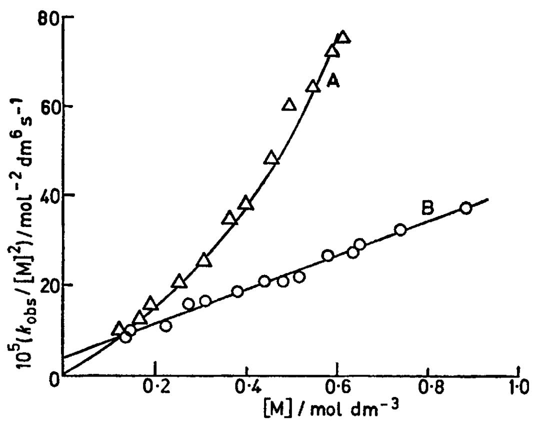


FIGURE 2 Plot of $k_{obs}/[M]^2$ against [M]; A, Bu^{n}OH; B, Pr^{i}OH

$$-d[RNCO]/dt = k_{obs}[RNCO] = (k_2[M]^2 + k_3[M]^3)[RNCO] \quad (15)$$

$$-d[RNCO]/dt = k_{obs}[RNCO] = (k_2[M]^2 + k_4[M]^4)[RNCO] \quad (16)$$

predominantly the tetramer, but for secondary alcohols the trimer. This seems reasonable for although the factors controlling such polymerisation are not understood it is recognised that chain branching will help to determine any preferences observed.

Values of k_2, k_3, and k_4 (Table 5) were obtained from the relevant slopes and intercepts respectively of the rectilinear plots in Figures 2 and 3. Since $k_2 = K_2k_D$, and K_2 is known from the association experiments, k_D can be calculated. Values of k_D are included in Table 5 and show the dimers of the bulkier alcohols to be roughly half as reactive towards the isocyanate as those of MeOH and EtOH. The values of k_2, k_3, and k_4 show that although both dimer and higher polymer contribute significantly to the reaction rate at the lower alcohol concentrations, the latter dominates at the higher alcohol concentrations. Since our independent experiments on alcohol self-association show that our reaction mixtures contain much monomer and dimer, but undetectable amounts of trimer and tetramer, the question arises whether (say) the third-order dependence on [M] does, in fact, result from a single-step reaction between the isocyanate and a small amount of very reactive trimer as in equation (9), or whether it results from a scheme like (17)—(18) or (19)—(20). Both schemes (17)—(18) and (19)—(20) lead to an expected third-order dependence * on alcohol monomer *provided* that the pre-equili-

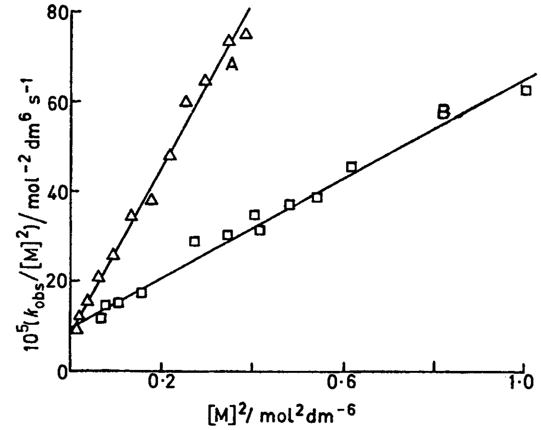
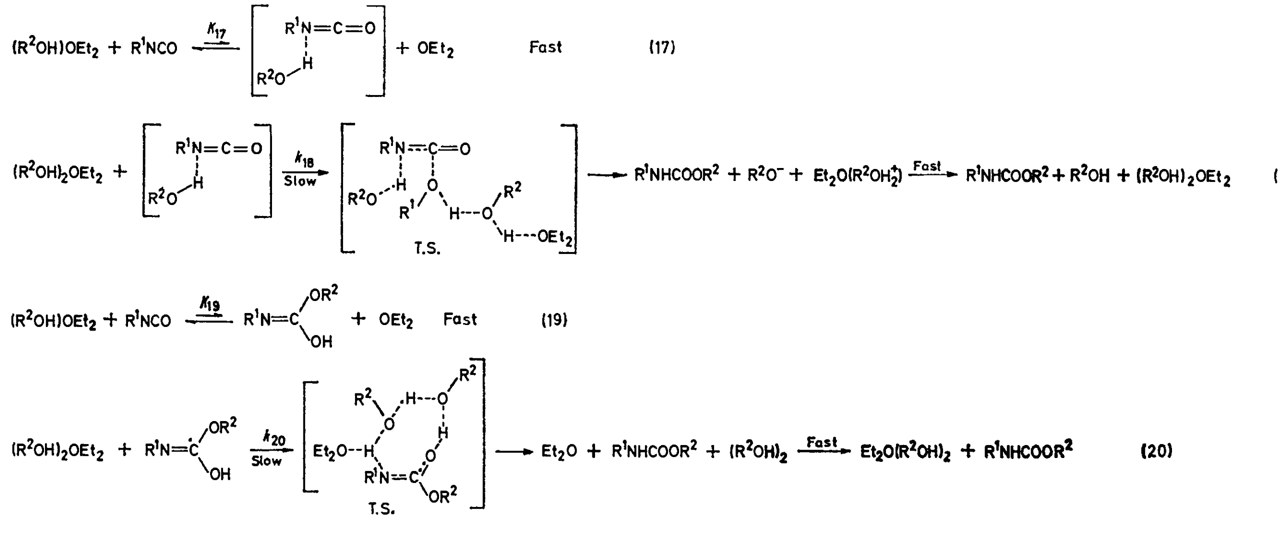


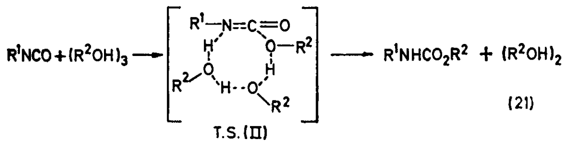
FIGURE 3 Plot of $k_{obs}/[M]^2$ against $[M]^2$; A, Bu^{n}OH; B, MeOH



---

* Analogous schemes can be written to account for a fourth-order dependence.

bria are fast and lie well to the left. Neither scheme is particularly attractive chemically in ethereal solvents: (17)—(18) owing to the involvement of charged species,* and (19)—(20) owing to the steric crowding likely in the transition state near the substituent R′, to the unlikelihood of the dimer (already hydrogen-bonded to the solvent) facilitating this type of prototropic rearrangement, to the evidence against carbonyl addition routes found in the analogous reactions of ketens,[16] and to the fact that step (20) is effectively a slow proton transfer between O and N centres. A further most important point should be noted: owing to the required position of the pre-equilibria (17) and (19), both schemes involve reaction of dimer with a *low concentration* (*i.e.*, $\leqslant$ *ca.* 10^{-4} mol dm^{-3}) intermediate. Hence these schemes, in fact, offer no concentration advantages over the direct reaction of the isocyanate with a low concentration (perhaps 10^{-2} mol dm^{-3}) of (probably) cyclic trimer [equation (9)].† The one-step route *via* cyclic trimer [equation (21)] (or cyclic tetramer for primary alcohols) has the advantage of involving (i) minimal charge separation, and (ii) a polymer species not stabilised and encumbered by solvent. A similar scheme cannot be written involving the solvent-bonded dimer (I) and the direct addition of solvent-bonded monomer necessitates a four-membered ring transition state, as well as loss of solvent. The great reactivity of the trimer and tetramer, relative to both monomer and dimer, which has to be assumed if (21) is the main type of reaction path reflected by the third- and fourth-order terms, is therefore chemically reasonable. It probably arises essentially from their freedom from solvent. In heptane where monomer and polymer appear to be roughly equally reactive (k_{obs} is directly proportional to [S] over a range of [S] values [6,17]) both monomer and polymer will be solvent-free. (However, the nature of the polymers present in this and other solvents requires more investigation.) The contributions from the term in $[M]^2$ in our system may arise from the reaction of the very small quantity of solvent-free dimer which can readily form a cyclic transition state similar to (II). We shall present further evidence for cyclic, one-step addition in subsequent papers on the acid-catalysed alcoholysis of isocyanates.



(21)

[2/895 *Received*, 24*th April*, 1972]

---

* If step (18) is made cyclic to avoid this, one is effectively back to the addition of trimer.

† For a similar reason schemes involving the solvent-free dimer in steps (18) and (20) are likely to be even less advantageous.

[16] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 897.

[17] S. G. Éntelis, O. V. Nesterov, and V. B. Zabrodin, *Kinetika i. Kataliz*, 1966, 7, 627.