# Kinetics and Catalysis of Consecutive Isocyanate Reactions. Formation of Carbamates, Allophanates and Isocyanurates

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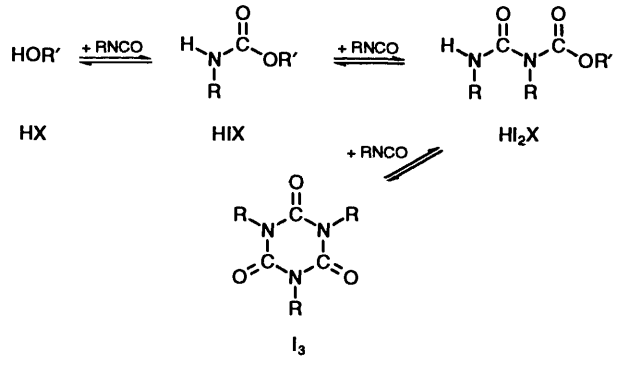
Organic isocyanates (**I**) react with alcohols and phenols (HX) in a sequence of reactions to give carbamates, allophanates and isocyanurates. Rate and equilibrium constants of the individual steps have been determined. The partitioning of the reaction products predominantly depends on the **I**:HX ratio and the nature of the catalyst applied. At equimolar **I**:HX ratios, the carbamate is the dominating product in the absence and in the presence of catalysts like tin carboxylates and common tertiary amines including 1,4-diazabicyclo[2.2.2]octane (DABCO). In these cases, the rate constant of carbamate formation ($k_1$) is larger than those of allophanate and isocyanurate formation ($k_2$ and $k_3$). With catalysts such as aminals, aminoalcohols, amidines and carboxylate, phenolate and alkoxide anions, however, the isocyanurate is mainly formed. With these catalysts the ratio of rate constants is $k_1 < k_2 \approx k_3$. For base catalysts, the $k_1:k_2:k_3$ ratios depend on the mechanism of catalysis. Tertiary amines react in the alcohol–isocyanate reaction by a concerted termolecular mechanism, whereas the anionic catalysts react by a stepwise mechanism *via* alcoholate anions. In the reactions of the isocyanate with phenols, carbamates and allophanates, all base catalysts react by the stepwise anionic mechanism, but the anionic ones are more efficient because their conjugate acids form hydrogen-bonded homoassociate complexes in higher extend.

At high **I**:HX ratios, the isocyanurate is the only final product formed *via* the carbamate and allophanate as detectable intermediates. The kinetics of cyclotrimerisation is mainly governed by the $k_1:k_2:k_3$ ratios and the magnitude of the equilibrium constants $K_1$, $K_2$ and $K_3$. The kinetic order with respect to isocyanate may vary from 1 to 3.

Organic isocyanates (**I**) are extremely reactive agents which transform compounds containing active hydrogen (HX) into the corresponding carbamoyl derivatives.[1–3] In the case of alcohols and phenols, the primarily formed carbamates (urethanes, HIX) are capable of reacting with additional isocyanate to give allophanates ($HI_2X$) which are further transformed into isocyanurates, the cyclotrimers of the isocyanate ($I_3$).[1a,d,e,2]




The cyclotrimer is built up *via* a linear trimer adduct $HNRCONRCONRCO_2R'$ ($HI_3X$), so that the full sequence of reactions is:

$$\mathbf{I} + HX \rightleftharpoons HIX \quad (1)$$

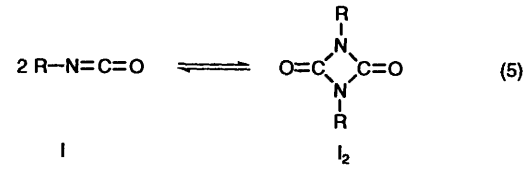
$$\mathbf{I} + HIX \rightleftharpoons HI_2X \quad (2)$$

$$\mathbf{I} + HI_2X \rightleftharpoons HI_3X \quad (3)$$

$$HI_3X \rightleftharpoons I_3 + HX \quad (4)$$

**Scheme 1**

1,3-Diazetidine-2,4-diones (uretdiones), the cyclodimers of the isocyanate, may be formed as by-products in the course of reaction[1a,d,e,4] giving rise to additional routes to the allophanate and isocyanurate. Because reaction (5) is always in equilibrium under the common reaction conditions, the uretdione disappears as the isocyanate is consumed and, therefore, does not appear in the endproducts of the **I** + HX reaction.




$$I_2 + HX \rightleftharpoons HI_2X \quad (6)$$

$$I_2 + HIX \rightleftharpoons HI_3X \quad (7)$$

All these consecutive isocyanate reactions are subject to catalysis by bases (tertiary amines, alkoxides, carboxylates), metal compounds (tin carboxylates, metal acetylacetonates) and other compounds,[1,2] the detailed reaction mechanisms of which are, with the exception of reaction (1),[3] widely unknown.

Which of the three products HIX, $HI_2X$ or $I_3$ is formed predominantly in the **I** + HX reaction depends on a number of factors, the most important of which are the **I** to HX concentration ratio, the temperature and the nature of catalyst.

All reactions (1) to (4) are, in principle, reversible and their equilibrium constants decrease with temperature. At medium temperatures (< 150 °C) the carbamate equilibrium [reaction

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(1)] with alcohols and phenols lies almost completely on the product side.[5]

The equilibrium constants of allophanate formation [reaction (2)] are smaller than those of reaction (1)[6] and should have a similar order of magnitude to those of reaction (3), which could not be determined because the linear trimer always reacts very fast to give the cyclotrimer $\mathbf{I}_3$, in the entropically favoured reaction (4). This cyclisation reaction is irreversible up to temperatures of 200 °C. At such temperatures, therefore, the isocyanurate is formed as the thermodynamically controlled endproduct in reactions of isocyanates with alcohols or phenols, and carbamates and allophanates are also transformed into isocyanurates under these conditions.[6a,7]

At lower temperatures on the other hand, the course of reaction is completely controlled by the nature of catalyst. In the absence of catalysts, and in the presence of catalysts such as the familiar tin carboxylates or 1,4-diazabicyclo[2.2.2]octane (DABCO), the isocyanate–alcohol reaction affords carbamates selectively. With carboxylate anions and some multifunctional tertiary amines (*e.g.* hexahydrotriazines) as catalysts, however, isocyanurates are formed as main products in the isocyanate–alcohol reaction, carbamates and allophanates appearing as by-products and intermediates.[8] It is not quite clear at present how the different behaviour of the various catalysts can be rationalized.

The overall kinetics of cyclotrimerisation of isocyanates has been studied repeatedly and is in general very intricate.[2] Mostly, the reaction is of first or second order with respect to isocyanate. However, the factors that control the overall order are currently not well understood.

We have, therefore, performed a series of experiments in which the base-catalysed reactions of phenyl isocyanate with alcohols and phenols were studied under various conditions to elucidate the factors which govern the course and mechanism of the underlying transformations.[9]

## Experimental and Computations

High performance liquid chromatography (HPLC) was used as the method of choice for analyses. This method allows detection of all reactants, products and longer living intermediates directly and their change in concentration throughout the course of the reaction. The isocyanates were determined as urethanes or ureas after quenching of the reaction mixture with an alcohol or secondary amine. The conditions of HPLC analyses have been described elsewhere.[3]

The products of the reaction of phenyl isocyanate with butanol in the presence of *N*,*N*-dimethylaminocyclohexane in acetonitrile at 50 °C are shown as an example in Fig. 1.

From the measured concentration–time functions of the reactants, intermediates and products, the rate and equilibrium constants of the individual reaction steps (1) to (4) are accessible by computer aided kinetic simulation. Owing to the low scatter of points, these constants may also be calculated from the slopes of the concentration–time curves in their dependence on the concentrations of reactants and intermediates, using the differential rate equations directly, which were combined to give eqns. (8)–(10) and transformed so that linear correlations result, *e.g.* (9*a*).

$$\frac{d[\mathbf{I}_3]}{dt} - \frac{d[HX]}{dt} = k_1[HX][I] - k_{-1}[HX]^{\frac{1}{2}}[HIX]^{\frac{1}{2}} \quad (8)$$

$$\frac{d[\mathbf{I}_3]}{dt} + \frac{d[HI_2X]}{dt} = k_2[HX]^{\frac{1}{2}}[HIX]^{\frac{1}{2}}[I] - k_{-2}[HX]^{\frac{1}{2}}[HI_2X]^{\frac{1}{2}} \quad (9)$$

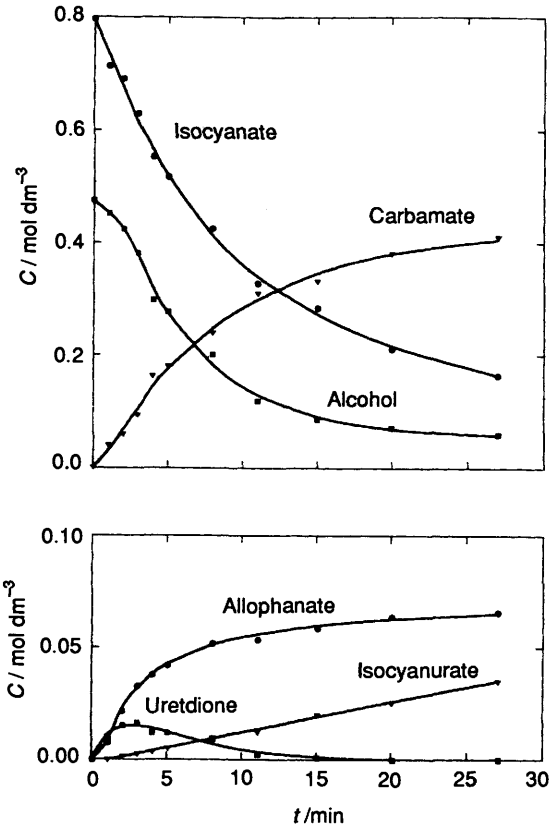



**Fig. 1** Products of reaction of phenyl isocyanate and butanol catalysed by *N*,*N*-dimethylcyclohexylamine (0.0181 mol dm$^{-3}$) in acetonitrile at 50 °C

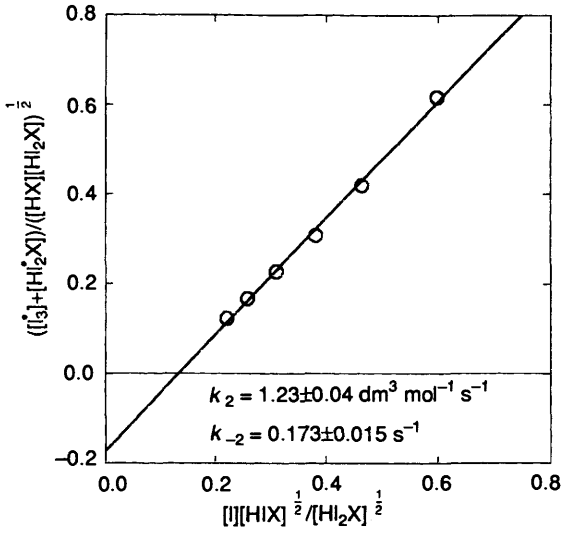



**Fig. 2** Evaluation of rate constants $k_2$ and $k_{-2}$ in the reaction of phenyl isocyanate with butanol catalysed by tetramethylammonium octanoate ($3.77 \times 10^{-4}$ mol dm$^{-3}$) in acetonitrile at 50 °C (Fig. 4)

$$\frac{d[\mathbf{I}_3]}{dt} = k_3[HX]^{\frac{1}{2}}[HI_2X]^{\frac{1}{2}}[I] \quad (10)$$

$$\frac{[I_3^{\bullet}] + [HI_2^{\bullet}X]}{[HX]^{\frac{1}{2}}[HI_2X]^{\frac{1}{2}}} = \frac{[I][HIX]^{\frac{1}{2}}}{[HI_2X]^{\frac{1}{2}}}k_2 - k_{-2} \quad (9a)$$

From the slopes and intercepts of these linear correlations, the rate constants of the individual steps and their reverse reactions can be easily evaluated (Fig. 2). The standard errors of

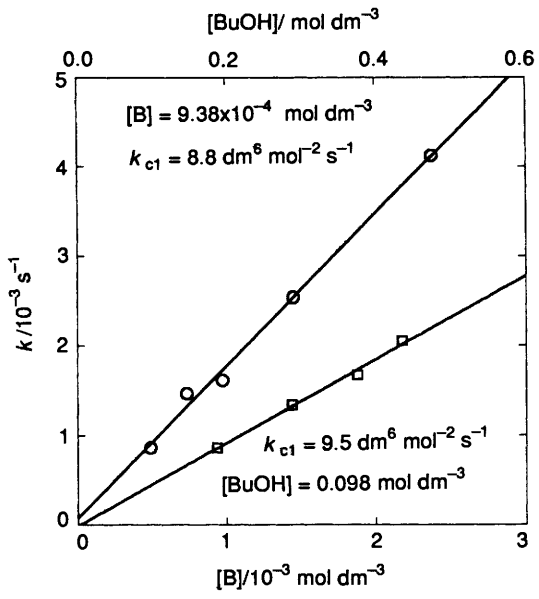



**Fig. 3** Dependence of the first order rate constant $k$ on the catalyst and butanol concentration in the reaction of phenyl isocyanate with butanol catalysed by tetramethylammonium octanoate in acetonitrile at 50 °C

the so determined $k$s were about 1–3% for $k_1$ and $k_3$, 3–10% for $k_2$, and 6–20% for $k_{-2}$.

The corresponding catalytic constants $k_c$ result by dividing the $k$s by a certain power of the catalyst concentration [C]$^m$, if necessary taking into account the portion of the reaction not catalysed according to eqn. (11).

$$k = k_0 + k_c[C]^m \qquad (11)$$

The kinetic orders with respect to reactants and catalysts have been determined separately. Examples are shown in Figs. 2 and 3. For the trimerisation of phenyl isocyanate in the presence of tetramethylammonium octanoate and butanol in acetonitrile, in which the isocyanate–butanol reaction (1) is rate determining, the orders with respect to catalyst and butanol are unity (Fig. 3). In the formation of butyl *N*,*N*′-diphenylallophanate from phenyl isocyanate and butyl *N*-phenylcarbamate (HIX) catalysed by triethylamine in the presence of butanol (HX) in acetonitrile, the kinetic orders with respect to HX and HIX are $\frac{1}{2}$ resulting in a straight line in a plot according to eqn. (9*a*), Fig. 2.

## Results and Discussion

*Kinetics and Mechanisms of Catalytic Reactions of Phenyl Isocyanate with Alcohols and Alkyl* N-*Phenylcarbamates.*—The course and products of the reactions depend on the nature of catalyst and the reaction conditions, especially the **I**:HX ratio, temperature and solvent.

At nearly equimolecular isocyanate:alcohol ratios in the presence of catalysts, such as tin carboxylates and the common tertiary amines including DABCO, carbamates are formed as main products and allophanates and isocyanurates appear only in very small portions (Fig. 1). Diazetidinediones are built up in low concentrations in the early stages of the reaction, but are completely consumed in the later stages. The rate constants determined for reaction steps (1) and (2) are displayed in Table 1. (For better comparability, the rate constants $k_{c2}$ are quoted as third order constants, first order in catalyst, carbamate and isocyanate for the given concentrations.) It is seen that these

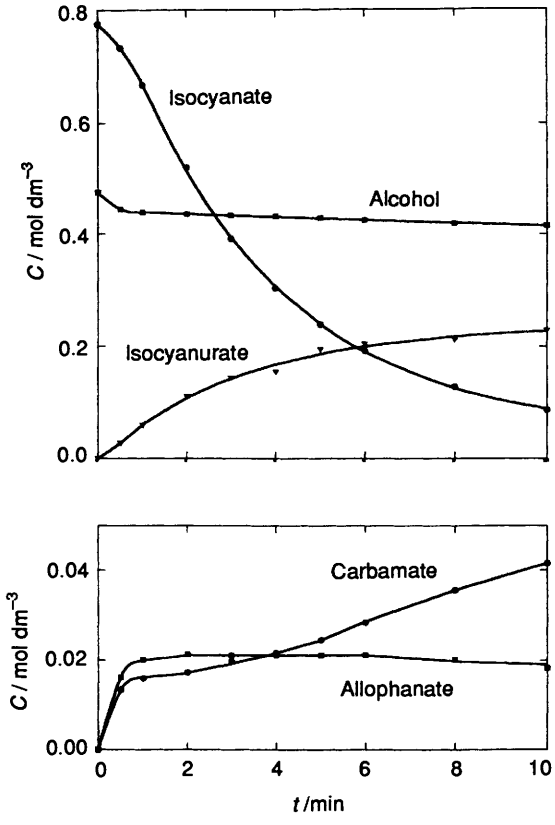



**Fig. 4** Products of reaction of phenyl isocyanate with butanol catalysed by tetramethylammonium octanoate (3.77 × 10$^{-4}$ mol dm$^{-3}$) in acetonitrile at 50 °C

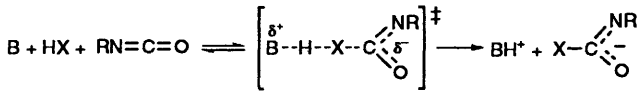
catalysts enhance more effectively reaction (1) of the isocyanate with alcohol than reaction (2) with the carbamate.

Other catalysts, however, such as carboxylates, phenolates and alkanolates, amidines, aminals and alkanolamines, accelerate reaction (2) more than (1) and allophanates and isocyanurates are formed as the main products. The alcohol is only partly consumed (Fig. 4).

The rate constant ratios are solvent and temperature dependent. Some selected values for the phenyl isocyanate–butanol–ammonium octanoate system are summarized in Table 2. In dioxan and methyl ethyl ketone as solvent, the rate constants of the reactions of isocyanate with alcohol, carbamate and allophanate, steps (1) to (3), are of the same order of magnitude. In acetonitrile, however, the rate constants of reactions (2) and (3) rise much more than that of (1) so that the ratio $k_1/k_2$ becomes much less than 1. From $k_2$ and $k_{-2}$ the equilibrium constant $K_2$ for allophanate formation is obtained (last column). It increases with decreasing temperature in accordance with an exothermic reaction; $\Delta H^\circ = -19$ kJ mol$^{-1}$ in acetonitrile. $K_1$, the equilibrium constant of carbamate formation, is always much larger than one.

The different $k_1/k_2$ ratios are due to different mechanisms of catalysis.

As we have shown previously,[3] the usual alcohols (HX) react with isocyanate in the presence of tertiary amines (B) as catalysts in acetonitrile by a concerted termolecular mechanism (II in our terminology, Scheme 2) following a third order rate law, first order with respect to B, HX and isocyanate.




**Scheme 2**

**Table 1** Rate constants (in $dm^6\ mol^{-2}\ s^{-1}$) of catalysed reactions of phenyl isocyanate with butanol and butyl *N*-phenylcarbamate in acetonitrile at 50 °C

| Entry | Catalyst | $pK_a$(AN)[10] | $k_{c1}$ | $k_{c2}$[a] | $k_2/k_1$ |
|---|---|---|---|---|---|
| | *Oxyanions* | | | | |
| 1 | Tetramethylammonium phenolate | 27.2 | 6.0 | 240 | 40 |
| 2 | Tetramethylammonium 3-nitrophenolate | 23.8 | 13.0 | 432 | 33 |
| 3 | Tetramethylammonium 2-ethylhexanoate | 23.2 | 9.7 | 355 | 37 |
| 4 | 2-Hydroxyethyltrimethylammonium 2-ethylhexanoate | 23.2 | 3.2 | 89 | 28 |
| 5 | 4-Dimethylsulfoniophenolate | 21.6 | 12.3 | 345 | 28 |
| 6 | Tetramethylammonium formate | 21.0 | 5.1 | 251 | 49 |
| 7 | Tetramethylammonium benzoate | 20.7 | 3.43 | 123 | 36 |
| 8 | Tetramethylammonium phenoxyacetate | 19.2 | 2.26 | 38 | 17 |
| 9 | Trimethylammonioacetate | 17.0 | 0.67 | 12.5 | 19 |
| | *Tertiary Amines* | | | | |
| 10 | 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) | 23.8 | 6.5 | 20.6[b] | 3.2 |
| 11 | *N,N,N′,N″,N″*-Pentamethyldi-1,3-propylenetriamine | 19.1 | 1.39 | 0.60[b] | 0.43 |
| 12 | Triethylamine | 18.5 | 0.288 | 0.23[b] | 0.80 |
| 13 | 1,4-Diazabicyclo[2.2.2]octane (DABCO) | 18.2 | 2.41 | 0.20[b] | 0.08 |
| 14 | *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine | 18.2 | 0.69 | 0.7[b] | 1.0 |
| 15 | *N,N*-Dimethylcyclohexylamine | 18.0 | 0.325 | 0.081[b] | 0.25 |
| 16 | 2-Dimethylaminoethoxymethyl butyl ether | 17.0 | 0.149 | | |
| 17 | *N,N*-Dimethyl-2-methoxyethylamine | 16.8 | 0.098 | 0.048[b] | 0.49 |
| 18 | *N,N*-Dimethylbenzylamine | 16.6 | 0.089 | 0.039[b] | 0.44 |
| 19 | *N*-Methylmorpholine | 15.7 | 0.048 | 0.022[b] | 0.46 |
| | *Special Amines* | | | | |
| 20 | *N,N′,N″*-Tris(3-dimethylaminopropyl)hexahydro-1,3,5-triazine | 19.2 | 2.0 | 36.4 | 18 |
| 21 | *N*-(2-Dimethylaminoethyl)-*N*-methylaminoethanol | 18.3 | 0.72 | 8.0 | 11 |
| 22 | Bis(2,6-dimethylaminomethyl)-4-methylphenol | 15.8 | 0.07 | 1.00 | 14 |
| 23 | 3,6-Dimethyl-8-dimethylaminomethyl-3,4-dihydro-2*H*-1,3-benzoxazine | 15.6 | 0.046 | 2.30 | 50 |
| | *Tin Carboxylates* | | | | |
| 24 | Tin(II) 2-ethylhexanoate | | 6.7 | < 0.1 | < 0.01 |
| 25 | Dibutyltin dilaurate | | 785 | < 0.01 | $< 10^{-5}$ |

[a] [HIX] = 0.025 mol $dm^{-3}$, [HX] = 0.430 mol $dm^{-3}$. [b] [B] = 0.010 mol $dm^{-3}$.

**Table 2** Rate constants (in $dm^6\ mol^{-2}\ s^{-1}$) and activation parameters of the reactions of phenyl isocyanate with butanol, butyl *N*-phenylcarbamate and butyl *N,N′*-diphenylallophanate catalysed by tetramethylammonium octanoate. Equilibrium constants (in $dm^3\ mol^{-1}$) and thermodynamic reaction parameters for the *N,N′*-diphenylallophanate formation in acetonitrile

| Solvent | *T*/°C | $k_{c1}$ | $k_{c2}$ | $k_{c-2}$ | $k_{c3}$ | $k_1/k_2$ | $K_2$ |
|---|---|---|---|---|---|---|---|
| Dioxan | 50 | 5.3 | 6.6 | 4.1 | 8.5 | 0.79 | 1.6 |
| Methyl ethyl ketone | 50 | 5.7 | 7.8 | 4.1 | 7.2 | 0.73 | 1.9 |
| Acetonitrile | 50 | 9.7 | 355 | 62 | 148 | 0.027 | 5.7 |
| Acetonitrile | 40 | 3.2 | 203 | 26 | 60 | 0.016 | 7.7 |
| Acetonitrile | 30 | 2.4 | 113 | 13 | 34 | 0.021 | 8.7 |
| Acetonitrile | 20 | 1.6 | 42 | 4.2 | 21 | 0.038 | 10.3 |
| $E_A$/kJ $mol^{-1}$ (in AN) | | 44 | 57 | 76 | 62 | −13 | $\Delta H^{\ddagger}$ −19 |
| $\Delta S^{\ddagger}$/J $K^{-1}$ $mol^{-1}$ | | −163 | −85 | −60 | −80 | −78 | $\Delta S^{\ddagger}$ −25 |

In this case, the activities of the amine catalysts should increase with their basicity and decrease with steric hindrance. A Brønsted $\beta_B = 0.39$ is found in the present study, Fig. 5 (□). The sterically unhindered DABCO (Table 1, entry 13), although slightly less basic, is catalytically more active than the sterically hindered triethylamine (Table 1, entry 12).

In the presence of anionic base catalysts, however, the alcohol–isocyanate reaction (1) proceeds according to a stepwise mechanism (I in our terminology[3]) *via* alcoholate ($X^-$) anions (Scheme 3).

In acetonitrile the oxyanions $B^-$ and $X^-$ are completely hydrogen-bonded to HB and HX, respectively, ($K_{as} \approx K_{bs} \approx 10^4$ $dm^3\ mol^{-1}$).[10] It then follows that the rate equation for the carbamate formation is as given by eqn. (12), which is confirmed experimentally (*cf.* Fig. 3).

$$v = (K_0 K_{as} K_{bs})^{1/2} k_{1a} [B^-]_0 [HX][I] \qquad (12)$$

$$B^- + HX \rightleftharpoons BH + X^- \qquad (0)$$

$$B^- + HB \rightleftharpoons B^-\cdot HB \qquad (bs)$$

$$X^- + HX \rightleftharpoons X^-\cdot HX \qquad (as)$$

$$I + X^-\cdot HX \longrightarrow XI^- + HX \qquad (1a)$$

**Scheme 3**

The anionic bases are catalytically more active than tertiary amines of equal basicity. They exhibit a separate Brønsted correlation with a $\beta_B = 0.24$, Fig. 5 (○). Contrary to the tertiary amine catalysed reaction, the reactivities of different alcohols increase with their acidities as can be seen in Fig. 9 (▽).

The base catalysed reaction (2) of phenyl isocyanate with carbamate to give allophanate should also follow the anionic mechanism I. But in acetonitrile, the allophanate formation is

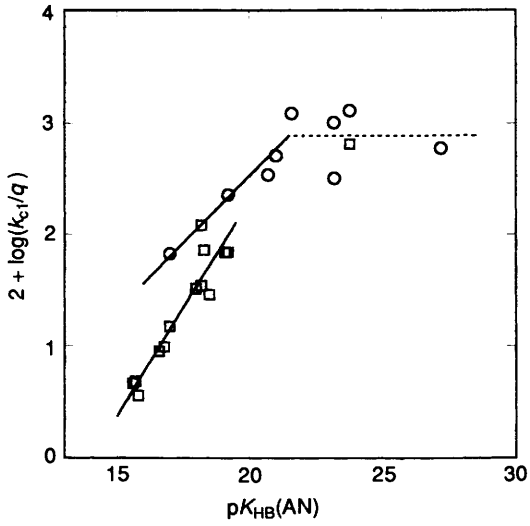



**Fig. 5** Brønsted correlations of $\lg(k_{c1}/dm^6\ mol^{-2}\ s^{-1})$ and $pK_{HB}$ for reactions of phenyl isocyanate with butanol catalysed by anionic bases (○) and tertiary amines (□) in acetonitrile at 50 °C

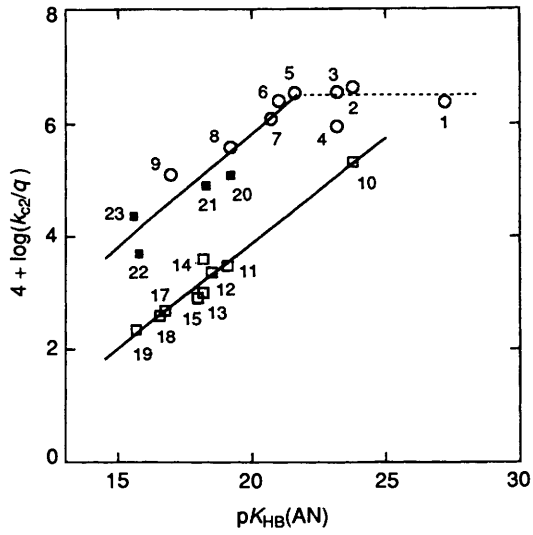



**Fig. 6** Brønsted correlations of $\lg(k_{c2}/dm^6\ mol^{-2}\ s^{-1})$ and $pK_{HB}$ of base catalysed reactions of phenyl isocyanate with butyl *N*-phenylcarbamate in acetonitrile at 50 °C (numbering of the catalysts as in Table 1)

catalysed by alcohol HX and the kinetic orders with respect to HX and carbamate were $\frac{1}{2}$. Therefore, a modified Scheme 3 is valid for the allophanate formation in the presence of alcohol, in which the alcohol HX and not the carbamate HIX function as the proton-donor for the carbamate ion $XI^-$, Scheme 3a.

$$B^- + HIX \rightleftharpoons HB + XI^- \quad (0)$$

$$B^- + HB \rightleftharpoons BH{\cdot}B^- \quad (bs)$$

$$XI^- + HX \rightleftharpoons XI^-{\cdot}HX \quad (as)$$

$$I + XI^-{\cdot}HX \rightleftharpoons XI_2^- + HX \quad (2a)$$

**Scheme 3a**

The alcohol is favoured because it is less sterically hindered and present in a higher concentration than the carbamate.

From Scheme 3a, rate eqn. (13) follows for the anion

$$v = (K_0K_{as}K_{bs})^{1/2}k_{2a}[B^-]_0[HX]^{1/2}[HIX]^{1/2}[I] \quad (13)$$

catalysed allophanate formation in the presence of alcohol showing kinetic orders of $\frac{1}{2}$ with respect to carbamate and alcohol.

According to eqn. (13), the more acidic carbamate [$pK_{HIX}$(AN) ≈ 30]§[11] reacts faster with isocyanate than an alcohol [$pK_{HX}$(AN) ≈ 39].[11,12] For a $\beta_{HX} \approx -0.2$, $\lg(k_{c2}/k_{c1}) = \beta_{HX}(pK_{HIX} - pK_{HX})$ should equal 1.8 and $k_{c2}/k_{c1} \approx 63$, if the association constants $K_{as}$ for $X^-{\cdot}HX$ and $XI^-{\cdot}HX$ would be equal. The found values of $k_{c2}/k_{c1}$ = 15–50 (Table 1) demonstrate that, as expected, $K_{as}$ for the carbamate anion is lower than for the stronger basic alcoholate.

In the allophanate formation reaction (2), the special amine catalysts such as aminals and aminoalcohols (entries 20 to 23 in Table 1) join, though with some scatter, the anionic bases in the same Brønsted plot with a $\beta_B = 0.4$ (Fig. 6), contrary to their behaviour in the urethane formation reaction (1), where they reacted as the usual tertiary amines (Fig. 5).

The common tertiary amines act in the allophanate formation reaction (2) by the same catalysis mechanism I (Scheme 3a) as the anionic bases. A $\beta_B = 0.37$ (Fig. 6) is found, and sterical hindrance in B plays no role, DABCO and triethylamine exhibit equal catalytic activities (Table 1). Tertiary amines are, however, catalytically less active than anionic bases of the same basicity (Fig. 6) and the kinetic order with respect to B is $\frac{1}{2}$. This is because the homoassociation constants $K_{as}$ of the neutral bases $B{\cdot}HB^+$ are lower than those of the anionic bases $B^-{\cdot}HB$,[10] so that rate eqn. (14) is valid. The proton transfer

$$v = (K_0K_{as})^{1/2}k_{2a}[B]_0^{1/2}[HX]^{1/2}[HIX]^{1/2} \quad (14)$$

from HIX giving the reactive complexed $XI^-$ ions is then less pronounced by a factor of $K_{bs}$. This decrease in activity is so strong that the catalytic constants $k_{c2}$ of tertiary amines in the allophanate formation are lower than the $k_{c1}$ in the urethane formation.

The rate constants $k_c$ for the strongest catalyst bases with $pK_{HB}$(AN) > 22 deviate towards smaller values from the correlation lines of both Fig. 5 and Fig. 6. Obviously, these bases $B^-$ are completely transformed with HX into hydrogen-bonded $B^-{\cdot}HX$ and/or HB and $X^-$ so that their basicity does not influence their reactivity and $\beta_B$ becomes zero.

*Kinetics and Mechanism of Base-catalysed Cyclotrimerisation of Isocyanates in the Presence of Proton Donors (HX).*—At high isocyanate:HX ratios, the isocyanurate ($I_3$) is always the mainproduct of the reaction, which then appears as a cyclotrimerisation of the isocyanate ($3I \longrightarrow I_3$) catalysed by bases B and cocatalysed by the H-acidic compounds HX. The cyclotrimer is formed *via* the carbamate (HIX), the allophanate ($HI_2X$) and sometimes, depending on catalyst and temperature, the cyclodimer ($I_2$) as detectable intermediates (Figs. 1 and 4). The linear trimer, $HI_3X$, could never be detected by liquid chromatography.

Instead of alcohols and phenols, also carbamates and allophanates may be used as cocatalysts in cyclotrimerisation (Fig. 7). They exhibit equal cocatalytic activity and function as precursors of HX, as can be seen in Fig. 8, where the products are shown resulting in the base-catalysed cyclotrimerisation of phenyl isocyanate cocatalysed by ethyl 4-chlorophenylcarbamate. The substituted carbamate is consumed in the course of reaction and the substituted cyclotrimer, 4-chlorophenyl diphenyl isocyanurate, and ethanol are formed. This is completely in accordance with Scheme 1 consisting of reactions (1) to (4) and evidence against a scheme in which the isocyanurate is

§ Estimated from the $pK_a$ in DMSO using the expression $pK_a(AN) = 1.03\ pK_a(DMSO) + 9.8$ derived for 3- and 4-substituted phenols.

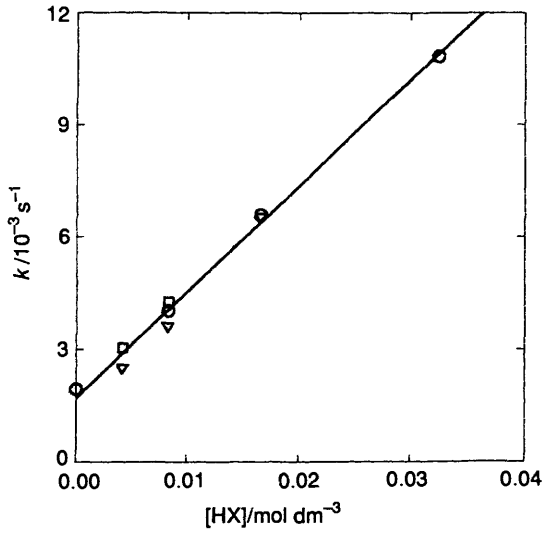



**Fig. 7** Cocatalysis of the cyclotrimerisation of phenyl isocyanate by benzyl alcohol (○), benzyl *N*-phenylcarbamate (▽) and benzyl *N*,*N*'-diphenylallophanate (□). Catalyst: Tetramethylammonium octanoate ($1.50 \times 10^{-3}$ mol dm$^{-3}$), solvent: acetonitrile, $T$ = 50 °C).

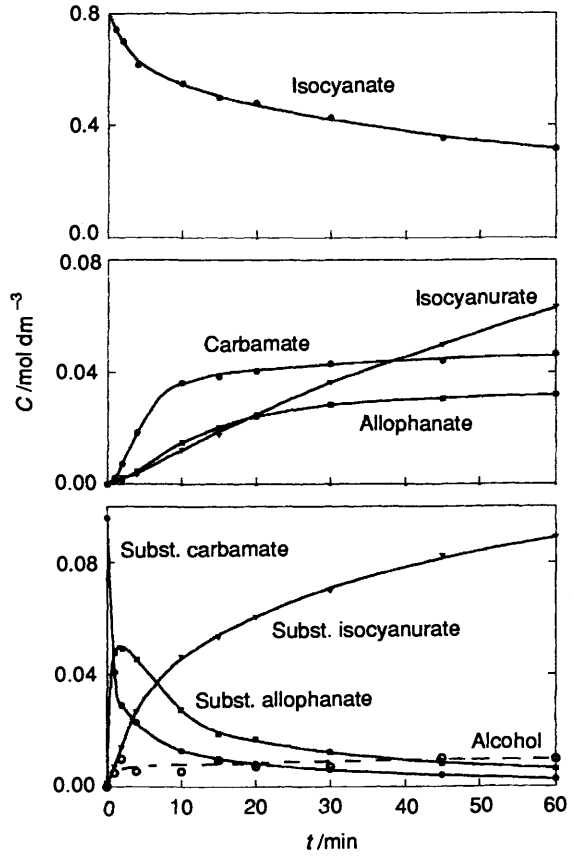



**Fig. 8** Products of reaction of phenyl isocyanate with ethyl 4-chlorophenylcarbamate catalysed by *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (0.0172 mol dm$^{-3}$) in acetonitrile at 50 °C

formed by expelling carbamate ($\mathbf{I} + HI_3X \longrightarrow I_3 + HIX$) which has been postulated by reason of the carbamate cocatalysis.[13] In case of the cyclotrimerisation cocatalysed by 4-chlorophenylcarbamate (HJX), no substituted cyclotrimer ($I_2J$), no unsubstituted carbamate (HIX) and no ethanol (HX) should then be formed (Scheme 4) whereas these products must result

**Table 3** Cyclotrimerisation of phenyl isocyanate catalysed by tetramethylammonium octanoate and HX. Allophanate formation constants $K_2$ (in dm$^3$ mol$^{-1}$) and kinetic orders with respect to isocyanate ($n$)

| Solvent | $T$/°C | HX | $K_2$ | $n$ |
|---|---|---|---|---|
| Dioxan | 50 | Phenol | 0.6 | 2.8 |
| Dioxan | 50 | Methanol | 1.0 | 1.9 |
| Dioxan | 50 | Butanol | 1.6 | 1.8 |
| Acetonitrile | 50 | Butanol | 5.7 | 1.4 |
| Acetonitrile | 20 | Butanol | 10.3 | 0.8 |

**Table 4** Cyclotrimerisation of 2,4-tolylene diisocyanate ($[\mathbf{I}]_0 = 0.670$ mol dm$^{-3}$) catalysed by triethylamine (0.068 mol dm$^{-3}$) and various cocatalysts (0.065 mol dm$^{-3}$) in methyl ethyl ketone at 60 °C

| Cocatalyst | $10^3 k$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|
| Methanol | 0.73 |
| Ethanol | 0.49 |
| Phenol | 1.37 |
| 4-Nitrophenol | 0.62 |
| Formic acid | 0.58 |
| Benzamide | 0.63 |
| Benzene sulfonamide | 0.45 |
| Ethyl *N*-phenylcarbamate | 0.26 |
| Ethyl *N*,*N*'-diphenylallophanate | 0.48 |
| Urea | 2.83 |
| Phenylurea | 1.00 |
| *N*,*N*'-Diphenylurea | 1.20 |
| *N*,*N*-Ethylene-*N*'-phenylurea (0.0089 mol dm$^{-3}$) | 12.5 |

$$\mathbf{I} + HJX \rightleftharpoons HIJX$$

$$\mathbf{I} + HIJX \rightleftharpoons HI_2JX$$

$$\mathbf{I} + HI_2JX \rightleftharpoons HI_3JX$$

$$HI_3JX \rightleftharpoons I_3 + HJX$$

**Scheme 4**

if the cyclotrimer is built up *via* the linear trimer by elimination of HX according to Scheme 1:

$$HI_2JX \rightleftharpoons I_2J + HX$$

$$\mathbf{I} + HX \rightleftharpoons HIX$$

From Scheme 1 the general rate eqn. (15) can be derived for the trimerisation supposing the intermediates HIX, $HI_2X$, and $HI_3X$ to be in stationary states and provided that the former derived rate equations are valid for the reactions (1) to (4). Furthermore, it is assumed that $K_1 \gg 1$ ($k_1 \gg k_{-1}$), which is always true for alcohols and phenols as HX, and $k_3 \ll k_4 \gg k_{-3}$, which follows because $HI_3X$ is a short-living intermediate.

$$v = \frac{(K_2^2 k_3^2/k_1)[HX]_0[\mathbf{I}]^3}{1 + (2k_3/k_{-2})[\mathbf{I}] + \{(k_3/k_{-2})^2 + [1 + (k_3/k_1)^2]K_2^2\}[\mathbf{I}]^2} \quad (15)$$

All rate constants are subject to catalysis according to eqn. (11). $m = 1$ for anionic bases in any case. For tertiary amines in acetonitrile, $m$ equals $\frac{1}{2}$ except for $k_1$ where it is 1 if alcohols of low acidity are used as HX.

Depending on the relative magnitude of the rate and equilibrium constants in the denominator of (15), overall reaction orders of 1 to 3 with respect to isocyanate result from equation (15).

If $k_3 \gg k_1 \ll k_2$, which holds for the anionic and special amine catalysts, eqn. (15) simplifies to (16). In this case step

$$v = k_1[HX]_0[\mathbf{I}] \quad (16)$$

**Table 5** Cyclotrimerisation of phenyl isocyanate catalysed by tetramethylammonium octanoate and various cocatalysts in acetonitrile at 50 °C

| Cocatalyst | $pK_{HX}(AN)^a$ | $k_{c1}/dm^6\ mol^{-2}\ s^{-1}$ |
|---|---|---|
| Butanol | 39.1 | 8.1 |
| Ethanol | 38.7 | 10.1 |
| 4-Methoxybenzyl alcohol | 38.5 | 31.8 |
| Benzyl alcohol | 37.7 | 61.4 |
| 4-Chlorobenzyl alcohol | 37.2 | 171 |
| Methanol | 37.1 | 27.9 |
| 2-Methoxyethanol | 36.5 | 12 |
| 2-Acetyloxyethanol | 36.5 | 32.4 |
| *N*-(2-Hydroxyethyl)-*N*-methylformamide | 35.8 | 67 |
| 4-Nitrobenzyl alcohol | 35.7 | 290 |
| Methoxymethanol | 34.5 | 148 |
| Propargyl alcohol | 34.1 | 230 |
| 4-Dimethylaminophenyl *N*-phenylcarbamate | 30 | 465 |
| 4-Methoxyphenyl *N*-phenylcarbamate | 28 | 626 |
| 4-Methylphenyl *N*-phenylcarbamate | 27.6 | 769 |
| 4-*tert*-Butylphenyl *N*-phenylcarbamate | 27.5 | 698 |
| Phenol | 26.9 | 1929 |
| 4-Phenylphenyl *N*-phenylcarbamate | 26.9 | 1239 |
| 4-Chlorophenyl *N*-phenylcarbamate | 25.8 | 2326 |
| 3-Chlorophenyl *N*-phenylcarbamate | 25.0 | 1350 |
| 4-Acetyloxyphenyl *N*-phenylcarbamate | 23.9 | 1200 |
| 3-Nitrophenyl *N*-phenylcarbamate | 23.8 | 1988 |
| 4-Dimethylsulfoniophenol chloride | 21.2 | 113 |
| 4-Nitrophenyl *N*-phenylcarbamate | 20.9 | 137 |

[a] The $pK_{HX}$s of the alcohols in acetonitrile have been estimated from the values in DMSO or water.[3]

(1), the formation of the carbamate, is rate determining for the cyclotrimerisation, which then follows a rate law first order with respect to isocyanate.

If on the other hand, $k_3 \ll k_1$, which holds for the common tertiary amine or tin carboxylate catalysts, eqn. (15) becomes (17), which is approximately (18).

$$v = \frac{(K_2^2 k_3^2/k_1)[HX]_0[I]^3}{1 + (2k_3/k_{-2})[I] + [K_2^2 + (k_3/k_{-2})^2][I]^2} \quad (17)$$

$$v \approx \frac{(K_2^2 k_3^2/k_1)[HX]_0[I]^3}{1 + 2K_2[I] + 2K_2^2[I]^2} \quad (18)$$

The approximation holds because $k_3 \approx k_2$ (see Table 2) so that $k_3/k_{-2} \approx K_2$. The kinetic order $n$ with respect to isocyanate is then controlled by the order of magnitude of $K_2[I]$. When $2K_2[I] \gg 1$, eqn. (18) becomes (19) and $n = 1$, and (20) when

$$v = (k_3^2/2k_1)[HX]_0[I] \quad (19)$$

$2K_2[I] \ll 1, n = 3$:

$$v = (K_2^2 k_3^2/k_1)[HX]_0[I]^3 \quad (20)$$

It may happen that the order increases with decreasing isocyanate concentration during the course of reaction and assumes an overall number between 1 and 3. In any case, the rate is almost independent of $k_1$ because $k_3/k_1 \approx k_2/k_1$ are nearly constant for the common amine catalysts (*cf.* Table 1) so that the cocatalytic activity of various HX should be almost identical.

Altogether, the kinetics of cyclotrimerisation are mainly governed by the $k_1/k_3$ ratio and the magnitude of $K_2$ both of which strongly depend on temperature and solvent. The influence of these parameters on the cyclotrimerisation of phenyl isocyanate catalysed by tetramethylammonium octoate in the presence of alcohols and phenol can be recognized in Table 3. The equilibrium constant $K_2$ varies from 0.6 to 10.3 and the kinetic order $n$ with respect to isocyanate from 2.8 to 0.8.

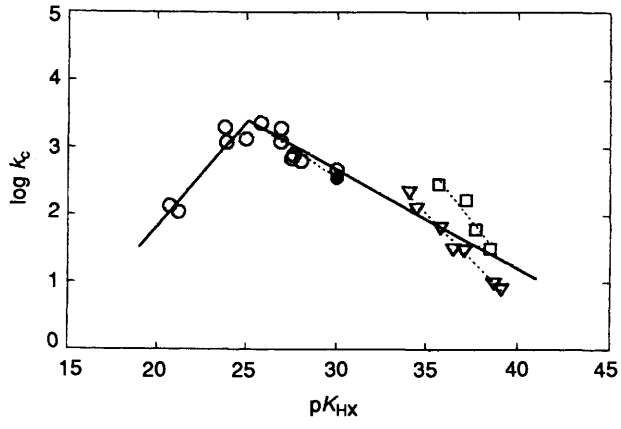



**Fig. 9** Brønsted correlation of $lg(k_{c1}/dm^6\ mol^{-2}\ s^{-1})$ and $pK_{HX}$ for the cyclotrimerisation of phenyl isocyanate catalysed by tetramethylammonium octanoate and alcohols (▽), benzyl alcohols (□), phenols and phenyl *N*-phenylcarbamates (○) in acetonitrile at 50 °C. ●: $k_{c2}$ for butyl *N*-phenylcarbamate.

Second order rate constants for the triethylamine catalysed cyclotrimerisation of 2,4-tolylene diisocyanate in the presence of various H-acidic cocatalysts are summarised in Table 4. The cocatalytic activities of the proton donors differ only by a factor of five although their acidities vary within nine orders of magnitude. With triethylamine as catalyst, $k_1 > k_3 \approx k_2$ holds (Table 1) and these reactions, therefore, follow rate eqn. (19).

The cocatalytic activity of the last compound in Table 4 is extraordinarily high because this aziridine derivative reacts, as known, by a mechanism involving ring opening of the aziridine.[14]

In the cyclotrimerisation catalysed by tetramethylammonium octanoate in the presence of various alcohols and phenols, however, the differences in the activity of the cocatalysts are very much more pronounced (Table 5). In this case, $k_1 < k_2$ is valid (Table 1), the reaction follows rate equation (16), and the experimentally observed first order rate constants equal $k_1[HX]_0$. If the logarithms of $k_{c1}$ are plotted *versus* the $pK_a$ of HX, a Brønsted plot results (Fig. 9) which nicely corresponds

to that for the directly determined $k$s of the stoichiometric reactions of phenols with phenyl isocyanate catalysed by tertiary amines (*cf.* ref. 3, Fig. 4). The plot is non-linear showing a maximum of $k_{c1}$ at $pK_{HX}(AN) = 25$. All this is in accord with an anionic mechanism I (Scheme 3) for step (1). On the left hand side of the maximum, the reactivity of the HX increases with decreasing acidity ($\beta_{HX} = -0.3$), whereas with increasing acidity on the right hand side ($\beta_{HX} = 0.3$) due to a change of the kinetics from Ia to Ib.[3] The $k_{c2}$ for the reaction of butyl *N*-phenylcarbamate with phenyl isocyanate catalysed by tetramethylammonium octanoate (Table 1), moreover, fits very well to the plot (●) indicating that carbamate and phenols react by the same mechanism I as it was concluded for the carbamate from Fig. 6.

The correlation of the right hand side of Fig. 9 with an overall $\beta_{HX} = -0.15$ is not very good. Better correlations result when the various types of HX are treated separately giving also larger numbers for $\beta_{HX}$: phenols −0.29, benzyl alcohols −0.35, other alcohols −0.28. Possibly, this might be also due to a not quite correct estimation of the $pK_{HX}$s of the alcohols in acetonitrile.

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