Three Fundamental Mechanisms of Base-catalysed Reactions of Isocyanates with Hydrogen-acidic Compounds

Klaus Schwetlick, Rainer Noack and Fanziska Stebner
Institut für Organische Chemie und Farbenchemie, Technische Universität Dresden, D-01062 Dresden, Germany

The base-catalysed addition of H-acidic compounds HX, such as alcohols, phenols and amines, to isocyanates giving carbamates and ureas may proceed by three fundamental mechanisms depending on the acidity and nucleophilicity of the particular HX and the basicity of the catalyst B. Acidic, less nucleophilic HX, such as phenols and acidic alcohols, are transformed by the base catalyst into the anionic X^- which is then added to the isocyanate (mechanism I). HX of moderate acidity, like the common alcohols, may react in a concerted single-step reaction, in which proton transfer to the base and nucleophilic addition to isocyanate occur simultaneously (mechanism II). With strong bases as catalysts, a changeover of mechanism II into I can occur. Less acidic, stronger nucleophilic HX, such as aromatic amines, are added directly to the isocyanate followed by base-catalysed proton transfer in the resulting adduct (mechanism III).

The three mechanisms leads to different rate laws and structure–reactivity relationships. The concerted and the stepwise mechanisms II and III are susceptible to steric hindrance of HX and the catalyst B, whereas the anionic mechanism I is not influenced by steric effects of B. The relative reactivity of HX towards isocyanate rises with the basicity (decreasing acidity) of HX in mechanism III (amines: Brønsted $\beta_{nuc} > 0$), but is independent of it in mechanism II (common alcohols: $\beta_{nuc} = 0$). In mechanism I with strong acidic HX, the reactivity of HX increases with decreasing acidity (strong acidic phenols: $\beta_{nuc} > 0$), but decreases with the less acidic HX (less acidic phenols and acidic alcohols: $\beta_{nuc} < 0$).

Organic isocyanates readily react with compounds containing acidic hydrogen (HX) to produce the corresponding carbamoyl derivatives (Scheme 1). In this way, alcohols and phenols

$$R\text{-}N{=}C{=}O + H\text{-}X \rightleftharpoons R\text{-}NH\text{-}CO\text{-}X$$

Scheme 1

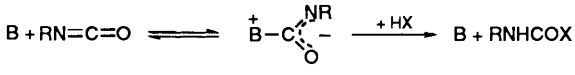
(R'OH) are transformed into carbamates (urethanes RNHCOOR'). Other hydroxylic compounds, such as water or carboxylic acids, react similarly, but the primarily formed carbamic acids (RNHCOOH) and anhydrides (RNHCOOCOR') decarboxylate giving amines and amides (RNH_2 and RNHCOR', respectively). Amines ($R'NH_2$) and amides ($R'CONH_2$) react with isocyanates to form substituted ureas (RNHCONHR' and RNHCONHCOR', respectively).

Most of these transformations are subject to catalysis by bases, acids, Lewis acids and certain metal compounds, of which tertiary amines and tin carboxylates are used on a large scale in the industrial production of polyurethanes from diisocyanates and polyalcohols.

Due to this importance, a wealth of experimental investigation has been performed into the kinetics and mechanisms of these reactions,[1] but many of these studies have been done under intricate conditions, resulting in considerable misinterpretation and open questions, which prevent a deeper insight into the relationships between structure, reaction conditions and reactivity of the compounds involved.

Most of the earlier studies have been performed in non or weakly polar solvents such as hydrocarbons and ethers. In these solvents the reactants, in particular alcohols, are associated with themselves, the catalysts and with the reaction products *via* hydrogen bonds which affect markedly their reactivity. Kinetic considerations which did not take into account these phenomena, therefore, have led to incorrect conclusions.

Thus, concerning the nature of base catalysis, Baker *et al.*, who carried out the first kinetic studies to elucidate the mechanism of catalytic action of tertiary amines (B) in dibutyl ether as solvent, assumed nucleophilic catalysis involving activation of the isocyanate by addition of B,[2] (Scheme 2).



Scheme 2

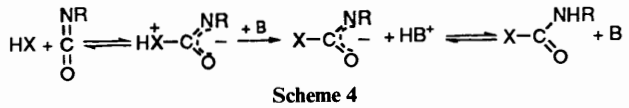
It was soon recognized, but slowly accepted, that this mechanism leads to many contradictions and cannot be valid in general.

Baker discussed but rejected a mechanism in which the base activates not the isocyanate but the alcohol through formation of a hydrogen bonded complex which is more or less ionic (Scheme 3). This mechanism was first proposed to occur in the catalysis of more acidic HX such as thiols and phenols,[3] but later also for the alcohol reaction.[4]

$$B + HX \rightleftharpoons B{\cdot}HX \rightleftharpoons BH^+X^- \xrightarrow{+RNCO} B + RNHCOX$$

Scheme 3

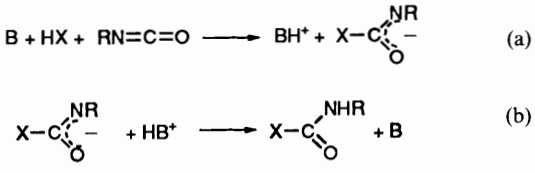
This mechanism is now generally accepted, but it can be valid only for reactions in less polar solvents, because in media of higher polarity the hydrogen bonded complexes play no role. Moreover, the detailed mechanism of the essential last step of Scheme 3 is by no means clear at present. For the amine catalysed reaction of phenyl isocyanate with aniline in acetonitrile, it was concluded by examination of hydrogen isotope effects and base structure–reactivity relationships that the base catalyst functions by accelerating the rate-limiting proton transfer from an intermediate isocyanate–aniline adduct[5] (Scheme 4).



Scheme 4

In a detailed study by Williams and Jencks,[6] this was confirmed to be true also for the reactions of cyanic acid with arylamines in water, whereas with aliphatic amines the addition of HX onto the isocyanate was rate-determining and base catalysis was completely absent.

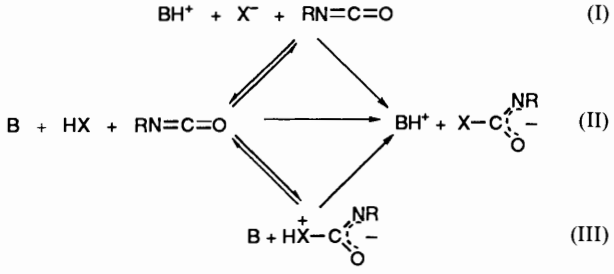
Kinetics of Base-catalysed Reactions of Isocyanates with Hydrogen-acidic Compounds.—Dealing with the problem of base catalysis of isocyanate reactions comprehensively, one can start from the fact that the general transformation (Scheme 1) proceeds at least in two steps, shown in Scheme 5, of which step



Scheme 5

(a) is rate-limiting. This step (a) involves the proton transfer from HX to B and the nucleophilic addition of X to the isocyanate with formation of the X–C bond. The timing of these two events is the essential problem of understanding the mechanisms of base catalysis of isocyanate reactions (Scheme 1).

Proton transfer and X–C bond formation may take place in one step synchronously (Scheme 6, II) or in two steps successively, in the latter case both proton transfer (I) or X–C bond formation (III) may occur as the first step.

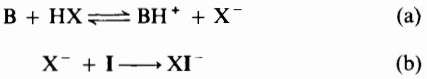


Scheme 6

It may be anticipated that, depending on the electrophilicity of the isocyanate, the acidity and nucleophilicity of HX and the basicity of B, which all are strongly solvent dependent, each of these three basic mechanisms is possible. HX Compounds of high acidity and low nucleophilicity (*e.g.* phenols) should react according to path I, those of low acidity and high nucleophilicity (*e.g.* amines) according to path III, and HX of intermediate acidity and nucleophilicity (*e.g.* alcohols) according to path II.

Criteria to differentiate between the three basic mechanisms of Scheme 6 are: (a) the rate equations; (b) the dependence of the rate on the basicity of HX in terms of β_{nuc} (β_{HX}) of a Brønsted relationship correlating lg$k$ with p$K_{H_2X^+}$; and (c) the Brønsted coefficient β_B of a correlation of lg$k$ with pK_{HB^+}, the basicity of the catalyst base.

Rate Equations.—At first we shall consider the problem for reactions *in highly polar solvents*, for example water where neither ion pair association nor $B(HX)_n$, $X^-(HX)_n$ or $(HX)_n$ complex formation occur. Under these conditions, mechanism I in which the anion X^- is formed first [Scheme 7(a)] and reacts with the isocyanate **I** in a second rate-limiting step (b),



Scheme 7

This leads to the rate eqn. (1), where k_1 is the rate constant of

$$v = k_1\{(\tfrac{1}{4}K_0^2[HX]^2 + K_0[B]_0[HX])^{\frac{1}{2}} - \tfrac{1}{2}K_0[HX]\}[\mathbf{I}] \quad (1)$$

step (b) (Scheme 7) and K_0 the equilibrium constant of the proton transfer (a). K_0 may be determined from the acidity constants of HX and HB^+ by eqn. (2).

$$\lg K_0 = pK_{HB^+} - pK_{HX} \quad (2)$$

Mechanism I may be divided into two subclasses.

Ia: For strongly acidic HX and strong bases B, where $K_0[HX] \gg [B]_0$, the base is completely transformed into HB^+ so that $[HB^+] = [X^-] = [B]_0$, and eqn. (1) simplifies to give eqn. (3), which is of zero order with respect to HX. The

$$v = k_1[B]_0[\mathbf{I}] \quad (3)$$

rate constant, k_1, of addition of X^- to the isocyanate is then directly accessible from this rate law.

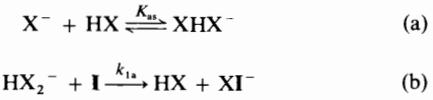
Ib: For less acidic HX, where $K_0[HX] \ll [B]_0$ and $[B] = [B]_0$, eqn. (1) reduces to eqn. (4), which is of half order in [B]

$$v = k_1(K_0[B]_0[HX])^{\frac{1}{2}}[\mathbf{I}] \quad (4)$$

and [HX]. Mechanism Ia becomes Ib when eqn. (3) = (4), that is when $K_0 = [B]_0/[HX]$ or eqn. (5) is satisfied.

$$pK_{HX} = pK_{HB^+} + \lg[HX] - \lg[B]_0 \quad (5)$$

In media of intermediate polarity, such as the common dipolar aprotic solvents acetonitrile, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), where homo-association by hydrogen bonding [Scheme 8(a)], but no formation of B·HX takes place, the second step [Scheme 7(b)] is



Scheme 8

as shown in Scheme 8(b) and the rate law, if $K_0K_{as}[HX]^2 \ll [B]_0$, becomes first order in [HX] but remains half order in [B] [eqn. (6)].

$$v = k_{1a}(K_0K_{as}[B]_0)^{\frac{1}{2}}[HX][\mathbf{I}] \quad (6)$$

Here, mechanism Ia becomes Ib when $K_0K_{as} = [B]_0/[HX]^2$ or eqn. (7) is satisfied.

$$pK_{HX} = pH_{HB^+} + \lg K_{as} + 2\lg[HX] - \lg[B]_0 \quad (7)$$

Mechanism II involving the concerted reaction of B, HX and the isocyanate **I** *via* a termolecular transition state $B\cdots H\cdots X\cdots \mathbf{I}$ leads, if $K_0[HX] \ll [B]_0$, to the simple rate equation (8).

$$v = k[B]_0[HX][\mathbf{I}] \quad (8)$$

Finally, mechanism III, involving the initial addition of HX to the isocyanate [Scheme 9(a)] followed by proton transfer to

B [Scheme 9(b)] gives, if the intermediate $HXI^{\pm}$ is short

$$HX + I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HXI \quad (a)$$

$$B + HXI^{\pm} \xrightarrow{k_2} BH^+ + XI^- \quad (b)$$

Scheme 9

lived, the rate law eqn. (9).

$$v = \frac{k_1 k_2 [B]_0}{k_{-1} + k_2 [B]_0} [HX][I] \quad (9)$$

Mechanism III also includes two subclasses.

IIIa: If $k_{-1} \gg k_2[B]_0$, equilibrium (a) (Scheme 9) is always established and eqn. (9) simplifies to eqn. (10).

$$v = K_1 k_2 [B]_0 [HX][I] \quad (10)$$

IIIb: If $k_{-1} \ll k_2[B]_0$, eqn. (9) simplifies to eqn. (11) which is

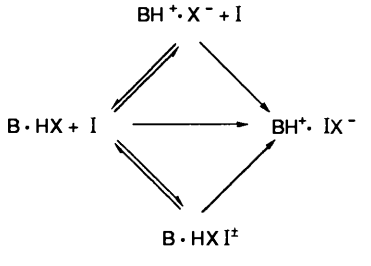
$$v = k_1 [HX][I] \quad (11)$$

of zero order in [B]. In this case, step (a) (Scheme 9) is rate determining and the reaction exhibits no base catalysis; k_1 is directly accessible.

Summarizing these kinetic considerations, it is obvious that mechanism I with strongly as well as less acidic HX (Ia and Ib, respectively) and mechanism IIIb with strongly nucleophilic HX can be easily diagnosed by means of their rate laws which are independent of [HX] in the first case, half order in [B] in the second, and independent of [B] in the last case. Mechanism II and IIIa with less nucleophilic HX, however, cannot be distinguished from each other because both follow identical rate laws. A discrimination, however, is possible by looking at structure–reactivity correlations, see below.

In weakly or non polar solvents, the kinetic conditions are both more complicated and less informative due to the formation of $(HX)_n$ and $X^-(HX)_n$ complexes and ion pair associates, *e.g.* BH^+X^-, by hydrogen bonding. A simplified mechanistic scheme is then as shown in Scheme 10.

$$B + HX \underset{}{\overset{K}{\rightleftharpoons}} B \cdot HX \quad (I)$$



(II)

(III)

Scheme 10

For the mechanisms II and III the rate laws assume the form of eqn. (12),[4] where K is the formation constant of B·HX.

$$v = \frac{kK[HX]}{1 + K[HX]} [B]_0[I] \quad (12)$$

For $K[HX] \gg 1$ this gives eqn. (13), which is independent of [HX], and for $K[HX] \ll 1$ eqn. (14) first order in [HX].[4]

$$v = kK[B]_0[HX][I] \quad (13)$$

$$v = kK[B]_0[HX][I] \quad (14)$$

The rate law for mechanism I depends on the identity of the reacting B and X^- species. If the latter is the simple homoassociate XHX^-, equations of form (12) may result. In other cases also those of half order in [HX] and $[B]_0$ may be valid.

Brønsted Relationships.—The dependence of rate constants of reactions of isocyanates with various HX in the presence of various bases B on the basicity of these HX and B in terms of the Brønsted coefficients β_{HX} (β_{nuc}) and β_B is a powerful tool to characterize the underlying reaction mechanisms and to understand structure–reactivity relationships.

In a Brønsted plot correlating the rate constants of the reactions of various HX with the pK_as of the conjugate acids H_2X^+ [eqn. (15)], the slope β_{HX} (β_{nuc}) is a composite

$$\lg k = \beta_{HX}\, pK_{H_2X^+} + c \quad (15)$$

parameter. Because HX in the base-catalysed reaction [Scheme 5(a)] acts both as an acid and a nucleophile, β_{HX} (β_{nuc}) measures the development of negative charge of X brought up by proton transfer from HX to B and of positive charge of X caused by X–C–bond formation between HX and the isocyanate. If both these events are fully synchronized, as in the concerted mechanism II, the electron density on X remains unchanged in going from reactants to transition state, and β_{HX} should be zero. The value of β_{HX} must be positive if proton transfer is ahead of X–C–bond formation, whereas if it is behind, β_{HX} is negative. So β_{HX} may vary between $+1$ and -1.

In the case of the two-step mechanisms I and III, β_{HX} is the β of that step whose rate constant appears in the actual rate equation; it may be the sum of several individual βs if the actual rate equation contains the product of several ks and Ks. So, for mechanism Ia, which holds for strong acidic HX and which follows rate eqn. (3), the value is given by eqn. (16), that is, the

$$\beta_{HX} = \beta_1 > 0, \quad (16)$$

reactivity decreases with increasing acidity of HX. For mechanism Ib, however, with less strong acids HX according to eqn. (4), the relationship is given by eqn. (17) and the

$$\beta_{HX} = \tfrac{1}{2}\beta_0 + \beta_1 < 0 \quad (17)$$

reactivity rises with increasing acidity of HX.

Mechanism IIIa with less strong nucleophiles HX following rate eqn. (10) leads to eqn. (18), and mechanism IIIb with strong

$$\beta_{HX} = \beta_{1eq} + \beta_2 > 0 \quad (18)$$

nucleophiles HX according to eqn. (11) to eqn. (19).

$$\beta_{HX} = \beta_1 > 0 \quad (19)$$

In both cases the reactivity increases with increasing basicity of HX, but this effect is more pronounced for mechanism IIIa than for IIIb.

As a whole, studying the reactions of a series of HX of different acidity and nucleophilicity, non-linear Brønsted plots should result (Fig. 1), the sections of which belong to the five classes of mechanisms Ia to IIIb characterized by different Brønsted coefficients and rate equations. Extrema and inflection points in these plots should change with the reactivity of the

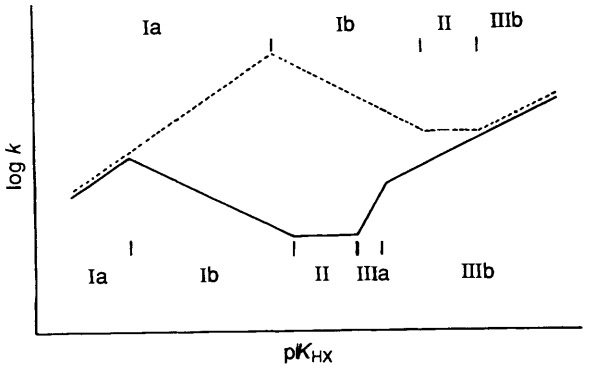


Fig. 1 Anticipated over-all Brønsted plot for base-catalysed reactions of isocyanates with H-acidic nucleophiles HX

isocyanate and the basicity and concentration of the catalyst, *cf.* eqns. (5) and (7).

The Brønsted coefficient β_B of a correlation between lg$k$ and pK_{HB^+} of reactions of a particular HX in the presence of various base catalysts B [eqn. (20)], measures, if anti-Hammond

$$\lg k = \beta_B \, pK_{HB^+} + c \qquad (20)$$

effects are absent, only the extent of proton transfer from HX to B in the course of the reaction shown as Scheme 5(a). β_B may vary between 0 and +1.

Thus, the magnitude of β_{HX} and β_B enables location of the position of the transition state of the reaction [Scheme 5(a)] in a More O'Ferrall–Jencks diagram with the four corners as in Scheme 6.

In order to elucidate the factors governing the affiliation of the reaction of a particular HX to the three mechanisms of Scheme 6, which is essential for understanding structure–reactivity relationships, we investigated the reactions of phenyl isocyanate with various alcohols, phenols and amines in the presence of various basic catalysts in acetonitrile and other aprotic solvents. Acetonitrile was chosen as the main solvent because it combines medium basicity with sufficient polarity so preventing the formation of ion pairs and hydrogen bond complexes of reactants and catalysts. Furthermore, absolute thermodynamic pK_a values for a series of compounds in acetonitrile are known from literature.[8] For compounds where such values are not available, we have estimated them by extrapolation using the corresponding pK_a values in DMSO[9] or water. These pK_a values in acetonitrile are more suitable for reactivity correlations in aprotic media than the commonly used pK_a values in water.

Experimental

Materials.—Phenyl isocyanate was refluxed over copper powder for 5 h and then distilled. The acidic impurities were ≤30 ppm. The alcohols were purified from acidic and basic impurities and dried by azeotropic distillation. *N*-Arylamines were distilled or recrystallized. Amine catalysts were used as supplied. Acetonitrile and dioxan were purified by distillation over 4,4′-diphenylmethane diisocyanate in the presence of 0.1% dibutyltin dilaurate; acetonitrile was additionally distilled over calcium hydride. Both were stored over 4 Å molecular sieves.

The standard compounds for HPLC were prepared as known in literature, special products are listed in Table 1.

Kinetic Methods.—All kinetic runs were carried out in acetonitrile or dioxan solution in a thermostatted vessel at 50 °C. Samples were taken at intervals, quenched with dibutylamine and analysed for isocyanate by titration with hydrochloric acid. For HPLC analyses, the samples were quenched with methanol or, in the case of reactions of isocyanate with alcohols and phenols, with morpholine. The quenched diluted samples were analysed by HPLC at 254 nm using a Hewlett–Packard HP 1080 LC apparatus with methanol–water as eluent. Methyl ethyl ketone and the isocyanate zero-sample functioned as standards. The concentrations of the products were monitored using externally determined extinction coefficients at 254 nm (Table 1).

Table 1 Model compounds for HPLC

Compound	Retention time (t/min)	R_f[a]	lgε_{254}
Aniline	4.25	0.46	
N-Morpholino-N′-phenylurea	4.91	0.53	3.72
Methyl *N*-phenylcarbamate	6.61	0.71	2.82
Triphenylisocyanurate	7.69	0.82	2.95
N-Morpholino-*N*′,*N*″-diphenylbiuret	7.85	0.84	4.06
N,*N*′-Diphenylurea	9.34	1.00	4.54
Methyl *N*,*N*′-diphenylallophanate	11.29	1.21	4.08
Butyl *N*-phenylcarbamate	11.43	1.22	2.92
N,*N*′,*N*″-Triphenylbiuret	13.53	1.45	4.48
Butyl *N*,*N*′-diphenylallophanate	14.66	1.57	4.12
Diphenyluretdione	16.30	1.75	

[a] Relative to diphenylurea R_f = 1.00.

Table 2 Rate constants of the triethylamine-catalysed reaction of phenyl isocyanate with butanol in acetonitrile at 50 °C. $[PhNCO]_0$ = $[BuOH]_0$ = 0.486 mol dm^{-3}

[B]/10^{-2} mol dm^{-3}	k/10^{-3} dm^3 mol^{-1} s^{-1}	k_B/dm^6 mol^{-2} s^{-1}[a]
0.95	4.3	0.418
1.08	4.9	0.424
1.72	7.0	0.388
2.02	8.2	0.390
2.18	9.4	0.416
2.80	11.9	0.414
3.55	14.8	0.408
		mean 0.408 ± 0.014

[a] $k_B = (k - k_0)/[B]$, $k_0 = 3.2 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}.

Results and Discussion

Base-catalysed Addition of Alcohols to Phenyl Isocyanate.—The addition (Scheme 11) affords the corresponding alkyl *N*-phenylurethanes.

$$PhNCO + ROH \longrightarrow PhNHCOOR$$

Scheme 11

The kinetics of these transformations differ for alcohols of different acidity. The reactions of the common, less acidic alcohols follow a second order rate law [eqn. (21)] whose rate constant depends linearly on the concentration of the catalyst base [eqn. (22)] (Table 2). Catalysis by the alcohol or the

$$-d[\mathbf{I}]/dt = k[\mathbf{I}][ROH] \qquad (21)$$

$$k = k_o + k_B[B] \qquad (22)$$

product urethane was not observed. The catalytic constants k_B determined according to eqn. (22) for the amine-catalysed addition of butanol to phenyl isocyanate in acetonitrile (Table 3) give excellent linear Brønsted plots for several catalyst families when correlated with the pK_a of the corresponding

Table 3 Kinetics of the base-catalysed addition of butanol to phenyl isocyanate in acetonitrile at 50 °C: $[BuOH]_0 = [PhNCO]_0 = 0.50$ mol dm^{-3}

Entry	Base	pK_{HB^+}(AN)	E_N[a]	[B]/10^{-3} mol dm^{-3}	$k_B/10^{-3}$ dm^6 mol^{-2} s^{-1}
	Pyridines and imidazoles				
1	4-Dimethylaminopyridine	17.5		7 ··· 14	785
2	1,2-Dimethylimidazole	17.0		9 ··· 19	590
3	1-Butylimidazole	15.8		21 ··· 28	256
4	4-Methylpyridine	13.6		58 ··· 90	41
5	2-Methylpyridine	13.4			23
6	Pyridine	12.3		83 ··· 196	22
7	3-Bromopyridine	9.8		58.5	3.0
8	3,5-Dibromopyridine	7.8		76.6	0.8
	Tertiary alkylamines				
9	DABCO[b]	18.25	−1.3	2 ··· 10	2680
10	*N*-Methylpyrrolidine	18.42	−2.7	7 ··· 36	617
11	Triethylamine	18.46	−3.8	11 ··· 35	408
12	*N*,*N*-Dimethylhexylamine	18.20	−2.2	15 ··· 30	369
13	*N*,*N*-Dimethylcyclohexylamine	18.10	−3.0		325
14	2-Dimethylaminoethyl ethyl ether	17.40		11 ··· 23	136
15	2-Dimethylaminoethyl acetate	16.9		27 ··· 54	115
16	*N*,*N*-Dimethylbenzylamine	16.6	−2.2	26 ··· 52	87
17	*N*-Methylmorpholine	15.7	−3.0	35 ··· 70	55
18	2-Dimethylaminopropionitrile	14.7		38 ··· 74	26
19	Lauroyl 2,2-dimethylhydrazide			8 ··· 15	6
20	Ethyl morpholinoacetate	12.3		18 ··· 114	3.5

[a] Steric constant, ref. 18. [b] 1,4-Diazabicyclo[2.2.2]octane.

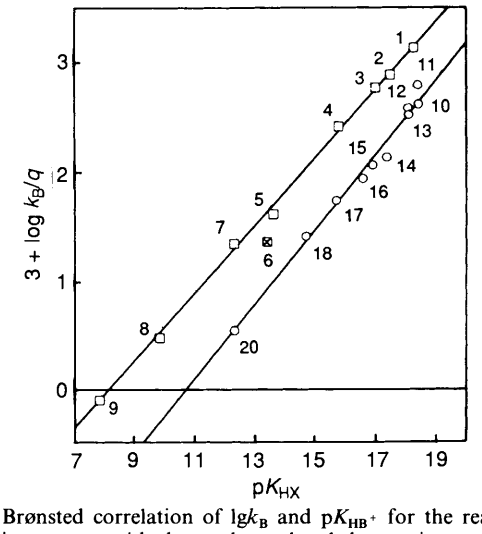


Fig. 2 Brønsted correlation of lgk_B and pK_{HB^+} for the reaction of phenyl isocyanate with butanol catalysed by tertiary amines in acetonitrile at 50 °C. (Numbering as in Table 3.) □, Nonhindered amines. ○, Dimethylamines.

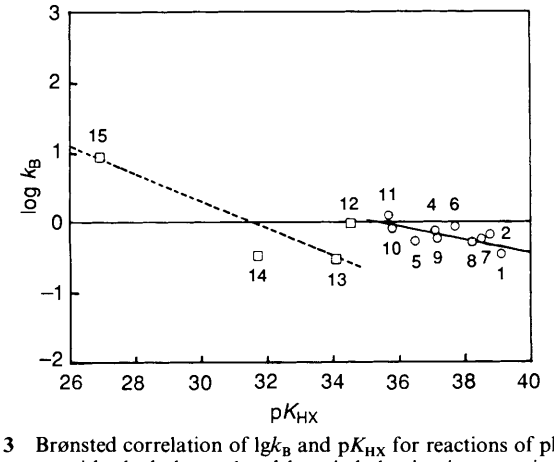


Fig. 3 Brønsted correlation of lgk_B and pK_{HX} for reactions of phenyl isocyanate with alcohols catalysed by triethylamine in acetonitrile at 50 °C. (Numbering as in Table 4.)

acids HB^+ (pK_{HB^+} in acetonitrile), see Fig. 2. The Brønsted coefficients are equal for pyridines and imidazoles ($\beta_B = 0.33$) and for substituted dimethylamines ($\beta_B = 0.34$), but the former are approximately 0.7 lgk_B units more active than the latter at the same basicity.

The β_B values show that only a partial protonation of the base has occurred in the transition state. Similar values have been obtained for the reactions of phenyl isocyanate with water in water ($\beta_B = 0.33$)[10] and in dioxan (0.2,[11] 0.4)[12,13] and with butanol in toluene (0.3),[14] tetrachloromethane (0.30)[15] and 2-ethoxyethyl acetate (0.25).[16] A somewhat higher value of $\beta_B = 0.49$ has been found for PhNCO + BuOH in tetrachloromethane, where the hydrogen bonded complex BuOH·B was studied as the attacking agent.[17]

The parallel shift of the straight lines in the Brønsted plots for different families of catalyst bases (Fig. 2) is attributed to differing steric hindrance of the particular bases, as it is also reflected by their steric parameters E_N.[18] The difference $\gamma = lgk_{DABCO} - lgk_{Et_3N}$ can be considered as a measure of the susceptibility of the catalytic reaction towards steric hindrance in the base catalyst. It amounts to $\gamma = 0.86$ in the present case of the reaction of butanol with phenyl isocyanate in acetonitrile.

The high catalytic activity of diazabicyclooctane (DABCO) in comparison with pyridines and imidazoles and the only slightly higher activity of 4-methylpyridine compared to 2-methylpyridine also suggest that the amines do not act as nucleophilic catalysts as formerly proposed by Baker *et al.*[2] However, the Brønsted coefficients, steric effects and the kinetic isotope effect $k_{HOMe}/k_{DOMe} = 2.1$ (Table 4) are consistent with a mechanism of general base catalysis.

Other simple, not too acidic alcohols react with phenyl isocyanate with rates quite similar to butanol. Some rate constants of the triethylamine-catalysed reactions are listed in Table 4. These rate constants do not depend on the acidity of the alcohol. From a Brønsted plot of lgk_B *vs.* pK_{HOR} (in acetonitrile as solvent), a β_{nuc} (β_{HX}) = −0.08 results (Fig. 3).

Similar, low Brønsted coefficients β_{HX} in the range of −0.03 to +0.09 may be calculated from a study of the amine-catalysed reactions of 2,4-tolylene diisocyanate with alcohols of

Table 4 Triethylamine-catalysed addition of alcohols to phenyl isocyanate in acetonitrile at 50 °C: $[ROH]_0 = [PhNCO]_0 = 0.50$ mol dm^{-3}

Entry	Alcohol	$pK_{HX}(AN)$[a]	$[B]/10^{-3}$ mol dm^{-3}	n_B[b]	k_B/dm^6 mol^{-2} s^{-1}	k_B/dm$^{\frac{9}{2}}$ mol$^{-\frac{3}{2}}$ s^{-1}	$\lg \frac{k_{DABCO}}{k_{Et_3N}}$[c]
1	Butanol	(39.1)	11 ··· 35	1.18	0.41		0.86
2	Ethanol	(38.7)			0.6		
3	[^{2}H]Methanol		7 ··· 18		0.35[d]		
4	Methanol	(37.1)			0.73		0.79
5	2-Methoxyethanol	(36.5)	17 ··· 28		0.53		0.55
6	Benzyl alcohol	(37.7)	17 ··· 35		0.84		0.62
7	4-Methoxybenzyl alcohol	(38.5)	7 ··· 17		0.56		0.61
8	4-Methylbenzyl alcohol	(38.2)			0.50		0.86
9	4-Chlorbenzyl alcohol	(37.2)			0.57		0.92
10	3-Nitrobenzyl alcohol	(35.8)			0.79		0.33
11	4-Nitrobenzyl alcohol	(35.7)	7 ··· 17		1.23		0.23
12	Methoxymethanol	(34.5)		0.58		0.94	−0.04
13	Propargyl alcohol	(34.1)		0.55		0.29	0.05
14	2,2,2-Trifluoroethanol	(31.7)		0.4		0.33	
15	Phenol	26.9		0.65		8.6	−0.13

[a] Estimated from pK_{HX} in DMSO or water according to correlation equations derived for 3- and 4-substituted phenols [$pK_{HX}(AN) = 1.03pK_{HX}(DMSO) + 9.8$ and $pK_{HX}(AN) = 2.14\ pK_{HX}(W) + 5.6$]. [b] Kinetic order with respect to base-catalyst. [c] Susceptibility of the reaction against steric hindrance in the base-catalyst B. [d] $k_H/k_D = 2.1$.

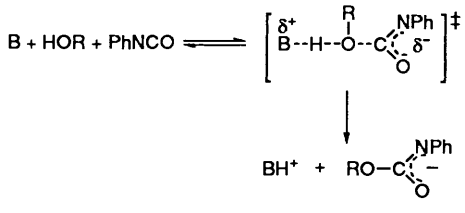
Table 5 Rate constants of the *N*-benzylpiperidine-catalysed reaction of phenyl isocyanate with 4-methylphenol in acetonitrile at 50 °C: $[PhNCO]_0 = [ArOH]_0 = 0.486$ mol dm^{-3}

$[B]/10^{-5}$ mol dm^{-3}	$k/10^{-3}$ dm^3 mol^{-1} s^{-1}	k_B/dm$^{\frac{9}{2}}$ mol$^{-\frac{3}{2}}$ s^{-1}[a]
0.75	3.7	1.35
1.20	4.4	1.27
2.40	7.1	1.45
4.01	8.4, 7.9	1.3, 1.25
5.60	9.7	1.30
		mean 1.32 ± 0.06

[a] $k_B = k/[B]^{\frac{1}{2}}$.

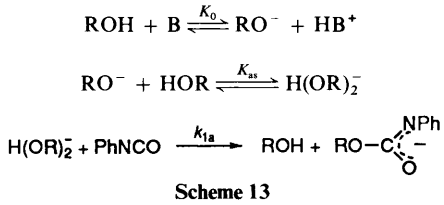
different acidities in butyl acetate reported in the literature by Zhitinkina and Shostaeva.[19]

Such low β_{nuc} are not consistent with a stepwise mechanism III with rate-limiting proton transfer in the adduct $HXI^{\pm}$, Scheme 9, for which a $\beta_{HX} \approx 0.5$ should be expected. But the low β_{HX} is compatible with the concerted mechanism II in which proton transfer from ROH to B and nucleophilic addition of ROH to PhNCO proceed synchronously, as shown in Scheme 12.



Scheme 12

For the amine-catalysed reactions of more acidic alcohols such as propargyl alcohol, trifluoroethanol and methoxymethanol with phenyl isocyanate a quite different kinetic form is observed (Table 4, Fig. 3). The kinetic order with respect to the base is no longer 1 but nearly $\frac{1}{2}$ in these cases and a larger negative value of $\beta_{HX} = -0.2$ is found. All these facts are evidence for the above mentioned stepwise anionic mechanism Ib for the reactions of these acidic alcohols with the isocyanate. In acetonitrile as solvent, the alkoxide anion X^- should be homoassociated with the alcohol HX to give the solvated HX_2^- anion, Scheme 13(b), if a value of $K_{as} = 10^4$ dm^3 mol^{-1} holds for the association constant (as in the case of phenols).[20] Rate limiting addition of HX_2^- to the isocyanate Scheme 13(c), then leads to rate eqn. (6) which has been observed experimentally.



Scheme 13

The observed decreased susceptibility of the reactions of the acidic alcohols towards steric hindrance in the amine catalyst: $\gamma = \lg(k_{DABCO}/k_{Et_3N}) \approx 0$, is also in accordance with mechanism Ib.

The anionic mechanism I so discovered does not only explain the experimental β_{HX} values but also the dominating occurrence of consecutive reactions of the formed carbamate with isocyanate giving allophanate and isocyanurate under certain conditions.[21]

The Base-catalysed Addition of Phenols to Phenyl Isocyanate.—The reactions of substituted phenols with phenyl isocyanate giving the corresponding aryl *N*-phenylurethanes take place in acetonitrile with high rates even in the presence of low concentrations of tertiary amines. Here also, the kinetics differ for the more and less acidic phenols. The reactions of the latter follow a second order rate law. As in the case of the acidic alcohols, the rate constants do not depend linearly on the catalyst concentration, but a half order dependence is found (Table 5). Phenols of higher acidity (when $\lg K_0 > -8$ in acetonitrile), however, react with decreasing rates according to a first order rate law of zero order in ArOH, and the rate constants are linearly dependent on the amine concentration. The dependence of the catalytic constants on the acidity of the phenols is also different in the two classes: k_B decreases with increasing acidity in the case of the less acidic phenols ($\beta_{HX} = -0.19$) but rises in the case of the more acidic ones ($\beta_{HX} = +0.48$), see Table 6 and Fig. 4.

All these results are evidence that the base-catalysed reactions of phenols with phenyl isocyanate follow the above mentioned stepwise anionic mechanism I involving homoassociated anions HX_2^- formed from the catalyst bases and phenols (Scheme 13).

Table 6 *N*-Benzylpiperidine-catalysed reactions of phenyl isocyanate with substituted phenols (RC_6H_5OH) in acetonitrile at 50 °C: $[RC_6H_5OH]_0 = 0.50$ mol dm^{-3}

R	pK_{HX}(AN)[a]	[B]/10^{-5} mol dm^{-3}	n_{ov}[b]	n_B[c]	k_B/dm$^{\frac{9}{2}}$ mol$^{-\frac{3}{2}}$ s^{-1}	k_{1a}/dm^3 mol^{-1} s^{-1}
4-MeO	(28.0)	4 • • • 8	2		0.90	2950
4-Me	(27.6)	1 • • • 6	2	0.49	1.32	2730
H	26.9	9 • • • 23	2	0.50	1.55	1430
4-Cl	25.8	1 • • • 4	2		3.72	680
3-Cl	25.0	3.2	2		3.09	320
3-NO_2	23.9	3.2	1			78
4-CO_2Et	(22.9)	3.2	1			13
4-CHO	(22.6)	3.2	1			3.3
4-NO_2	20.9	4.8	1			0.1

[a] Values in parentheses estimated from a Hammett-plot of the other phenols with σ_p^- constants. [b] Overall pseudo reaction order. [c] Order with respect to base-catalyst.

Table 7 Base-catalysed reactions of phenyl isocyanate with phenol in acetonitrile at 50 °C: $[PhNCO]_0 = [PhOH]_0 = 0.5$ mol dm^{-3}

Entry	Base	pK_{HB^+}	[B]/10^{-5} mol dm^{-3}	n_B[a]	k_B/dm$^{\frac{9}{2}}$ mol$^{-\frac{3}{2}}$ s^{-1}	k_{1a}/dm^3 mol^{-1} s^{-1}
1	Triethylamine	18.46	0.6 • • • 1.2	0.65	9.9	2210
2	Tributylamine	18.10	2.0 • • • 4.0	0.46	7.55	1940
3	DABCO	18.25	0.8 • • • 1.7	0.55	7.30	2080
4	2-Dimethylaminoethyl ethyl ether	17.40	3 • • • 8	0.58	2.78	2110
5	*N*-Benzylpiperidine	16.97	9 • • • 23	0.50	1.55	1950
6	*N*,*N*-Dimethylaminobenzylaniline	16.76	3 • • • 7	0.58	1.11	1810
7	*N*-Methylmorpholine	15.68	7.4		0.30	1730
						mean 1980 ± 160

[a] Order with respect to base catalyst.

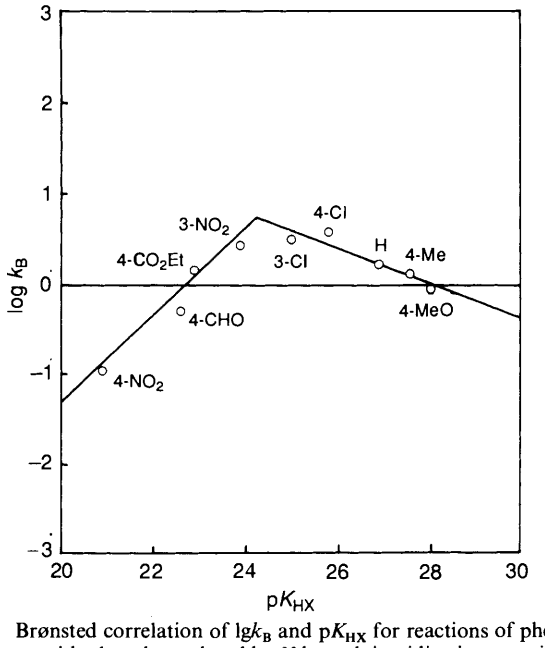


Fig. 4 Brønsted correlation of lgk_B and pK_{HX} for reactions of phenyl isocyanate with phenols catalysed by *N*-benzylpiperidine in acetonitrile at 50 °C. For the higher acidic phenols, a k_B calculated according to $k_B = k_{1a}(K_0K_{as})^{\frac{1}{2}}$ is depicted.

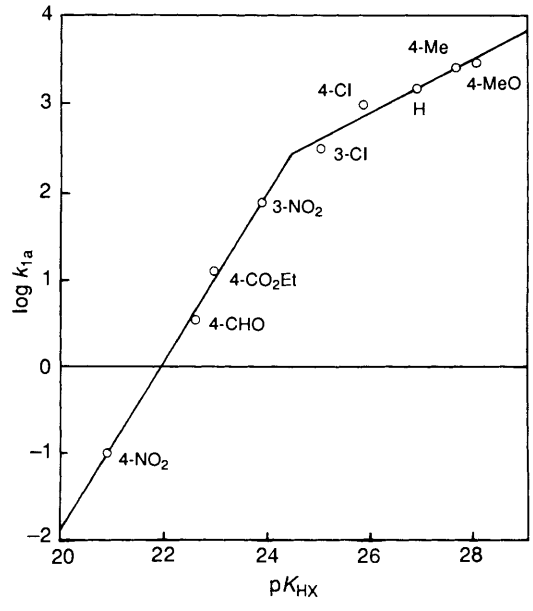


Fig. 5 Brønsted correlation of lgk_{1a} and pK_{HX} for reactions of phenolates with phenyl isocyanate in acetonitrile at 50 °C.

For weakly acidic phenols, when $\lg K_0 < -8$, rate eqn. (6) is then valid. From the catalytic constants shown by eqn. (23), the

$$k_B = K_0^{\frac{1}{2}}K_{as}^{\frac{1}{2}}k_{1a} \quad (23)$$

rate constants k_{1a} for the addition of ArO^-·HOAr to phenyl isocyanate may be calculated, taking into account an association constant of $K_{as} \approx 10^4$ dm^3 mol^{-1}.[20] The so obtained values of k_{1a} for the reactions of a series of substituted phenols with phenyl isocyanate catalysed by *N*-benzylpiperidine are summarized in Table 6. A plot of lgk_{1a} against pK_{HX} is depicted in Fig. 5, upper branch. A $\beta_{HX} = 0.31$ results which is also in agreement with the reaction mechanism Ib supposed.

Using various tertiary amines as catalysts, diverse catalytic constants k_B [eqn. (23)] result in the reaction of phenol with phenyl isocyanate in acetonitrile (Table 7), but the k_{1a} for the addition of PhO^-·HOPh to PhNCO calculated from these k_B are identical: $k_{1a} = 2.0 \times 10^3$ dm^3 mol^{-1} s^{-1} at 50 °C. A Brønsted plot of lgk_B *vs.* pK_{HB^+} results in a straight line with $\beta_B = 0.55$ (Fig. 6). These findings support the above mentioned reaction mechanism Ib but not the participation of hydrogen-bonded complexes ArOH·B or ion pairs ArO^-·HB^+ in the rate limiting step.

With the more acidic phenols, where $\lg K_0 < 8$ (in aceto-

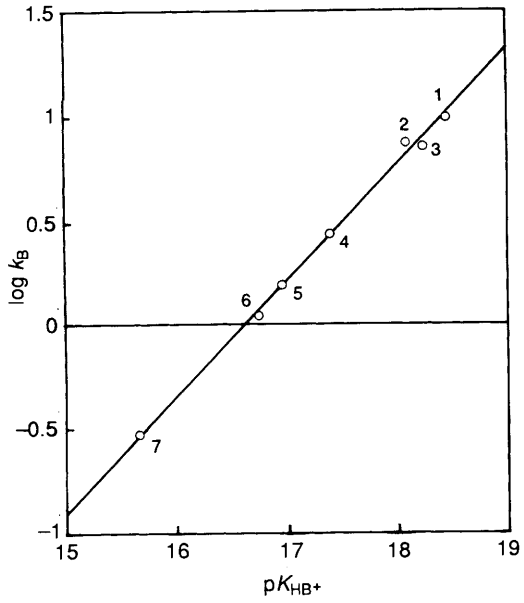


Fig. 6 Brønsted correlation of lgk_B and pK_{HB^+} for the reaction of phenyl isocyanate with phenol catalysed by tertiary amines in acetonitrile at 50 °C. (Numbering as in Table 7.)

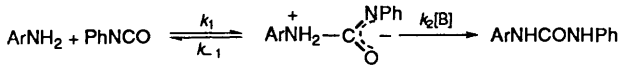
nitrile) and the base is completely transformed into HB^+, mechanism Ia with rate eqn. (3) is valid. In this case the rate law is independent of [HX], and the catalytic constant becomes eqn. (24).

$$k_B = k_{1a} \tag{24}$$

Rate constants for the reactions of a series of substituted phenols with PhNCO in acetonitrile are summarized in Table 6 and depicted in Fig. 5 (lower branch), from which a Brønsted coefficient $\beta_{HX} = 0.98$ results. A similar high value of β_{HX} has been found for the addition of phenolates to 3-nitrophenyl isothiocyanate ($\beta_{HX} = 0.81$).[22]

As is obvious from Fig. 5, the Brønsted plot for the addition of substituted phenolates (HX_2^-) to phenyl isocyanate is nonlinear, displaying a larger β_{HX} for the less basic phenolates. A closer inspection of the data of Al-Rawi and Williams[7] reveals that this is also true for the reactions of phenolates with isocyanic acid in water, where a β_{HX} of 0.3 comes out for the stronger, and a value of 0.8 for the less basic phenolates (giving an average of 0.66 quoted by these authors).[7] Such nonlinear Brønsted plots have been frequently observed for the reactions of oxyanions in acyl and proton transfer reactions, and various reasons have been made responsible for the nonlinearity.[23] In the present case, possibly a more difficult desolvation of the stronger basic homoassociated phenolates HX_2^- in the addition to the isocyanate causes the increase of the Brønsted slope for these anions.

The Base-catalysed Addition of Anilines to Phenyl Isocyanate.—All experimental observations about this reaction (Scheme 14) are in accord with the already known stepwise mechanism IIIa with rate limiting proton transfer,[5,6] *cf.* Scheme 9.



Scheme 14

Rate eqn. (9) is valid for mechanism III in polar solvents leading to a catalytic constant given by eqn. (25) which simplifies to eqn. (26) if $k_{-1} \gg k_2[B]$ [mechanism IIIa, eqn. (10)]. The

$$k_B = \frac{k_1 k_2}{k_{-1} + k_2[B]_0} \tag{25}$$

$$k_B = K_2 k_2 \tag{26}$$

value of $K_1 k_2$ can be determined from eqn. (26) or by plotting k_B^{-1} against $[B]_0$ according to the reciprocal eqn. (25).

$$\frac{1}{k_B} = \frac{1}{K_1 k_2} + \frac{[B]_0}{k_1} \tag{27}$$

The catalytic constants k_B of the triethylamine-catalysed reactions of phenyl isocyanate with a series of substituted anilines in acetonitrile and dioxan as solvents are summarized in Table 8. If lgk_B is plotted *vs.* p$K_{ArNH_3^+}$ (in acetonitrile), linear Brønsted correlations result with $\beta_{HX} = 0.46$ in acetonitrile and 0.53 in dioxan, Fig. 7. These β_{HX} are the sum of the β values for lgK_1 and lgk_2, $\beta_{HX} = \beta_{1eq} + \beta_2$. Because the rate of the proton transfer, k_2, from $HXI^{\pm}$, should be less susceptible towards the basicity of HX than K_1 of the preceding equilibrium, β_2 is anticipated to be small and negative so that β_{1eq} should make the main contribution to β_{HX}. The value

Table 8 Triethylamine-catalysed addition of substituted anilines ($RC_6H_4NH_2$ = HX) to phenyl isocyanate in acetonitrile and dioxan at 50 °C: [Et_3N] = 3···28 mmol dm^{-3}, $[PhNCO]_0 = [HX]_0$ = 0.090 mol dm^{-3}

		k_B/dm^6 mol^{-2} s^{-1}	
R	p$K_{H_2X^+}$(AN)	in acetonitrile	in dioxan
4-MeO	12.10	10	13.5
4-Me	11.25	3.32	2.73
3-Me	10.81	2.36	1.92
H	10.56	1.38	1.12
3-MeO	10.1	1.0	
4-Cl	9.56	0.70	0.48
4-Br	9.39	0.44	0.36
3-Cl	9.02	0.43	0.21
3-CF_3	8.6	0.24	0.11
4-CO_2Et	8.18	0.17	0.045
3-NO_2	7.79	0.14	0.091
4-NO_2	6.15	0.012	0.021
2,4-$(NO_2)_2$		0.4	

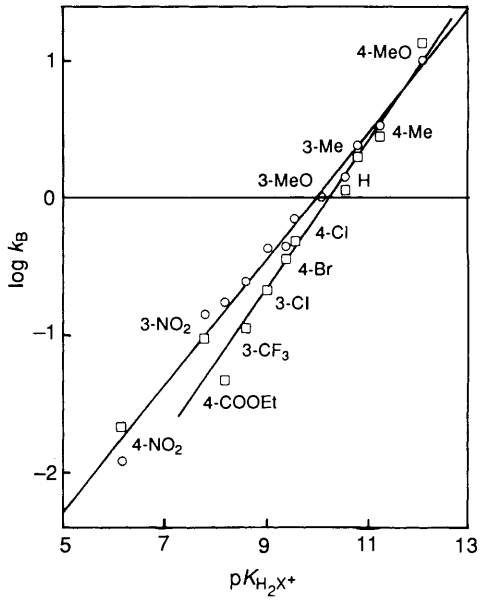


Fig. 7 Brønsted correlation of lgk_B and p$K_{H_2X^+}$ for reactions of phenyl isocyanate with substituted anilines catalysed by triethylamine in acetonitrile and dioxan at 50 °C. □, In acetonitrile. ○, In dioxan.

Table 9 Base-catalysed addition of aniline to phenyl isocyanate in acetonitrile at 50 °C: $[PhNCO]_0 = [PhNH_2]_0 = 0.09$ mol dm^{-3}

Entry	Base	pK_{HB^+}(AN)	k_B/dm^6 mol^{-2} s^{-1}
1	3-Chloroaniline	9.02	0.007
2	3-Bromopyridine	9.8	0.13
3	Pyridine	12.33	0.25
4	3-Methylpyridine	13.1	0.53
5	1-Methylimidazole	15.4	0.9
6	*N*-Methylmorpholine	15.68	0.2
7	*N*-Methylpiperidine	18.01	0.45
8	DABCO	18.25	1.94
9	Triethylamine	18.46	0.43
10	1,4,8,11-Tetramethyltetraazacyclododecane	(24)	4.6

Table 10 Base-catalysed addition of aniline to phenyl isocyanate in dioxan at 50 °C: $[PhNCO]_0 = [PhNH_2]_0 = 0.090$ mol dm^{-3}

Entry	Base	pK_{HB^+}(AN)	[B]/10^{-3} mol dm^{-3}	k_B/dm^6 mol^{-2} s^{-1}	K_1k_2/dm^6 mol^{-2} s^{-1}
1	DABCO	18.25	1 ··· 10	9.86	11.8
2	4-Dimethylaminopyridine	17.4	3 ··· 6	6.04	11.4
3	1,2-Dimethylimidazole	16.6	4 ··· 10	4.03	7.6
4	1-Butylimidazole	15.8	4 ··· 8	2.93	6.2
5	1-Methylimidazole	15.4		2.06	4.8
6	Triethylamine	18.46	4 ··· 8	1.12	1.40
7	*N*-Methylmorpholine	15.68	4 ··· 8	1.17	1.49
8	4-Methylpyridine	13.6	20 ··· 50	0.59	0.89
9	Pyridine	12.33	24 ··· 50	0.29	0.43
10	Aniline	10.60	90 ··· 480	0.022	0.024
11	Dimethylformamide	6.1	250 ··· 500	0.005	0.005

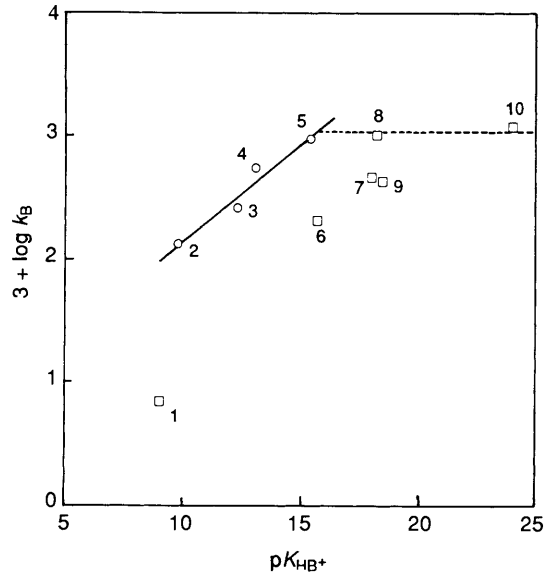


Fig. 8 Brønsted correlation of lgk_B and pK_{HB^+} for the reaction of aniline with phenyl isocyanate catalysed by tertiary amines in acetonitrile at 50 °C. (Numbering as in Table 9.)

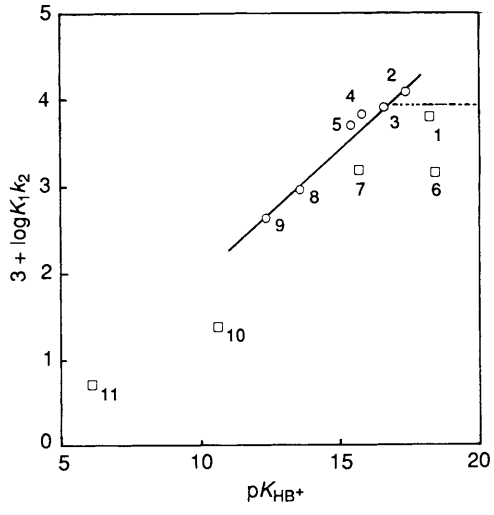


Fig. 9 Brønsted correlation of lgk_B and pK_{HB^+} for the reaction of aniline with phenyl isocyanate catalysed by tertiary amines in dioxan at 50 °C. (Numbering as in Table 10.)

of β_2 can be estimated from β_B (= 0.29 see below) to be −0.3 in dioxan, leading to a $\beta_{1eq} = 0.53 + 0.3 = 0.8$ in dioxan. This is a rather small value compared with 1.0 found for the addition of anilines to isocyanic acid in water.[6]

Catalytic constants and K_1k_2 values for various amines as catalysts of the reaction of aniline with phenyl isocyanate in acetonitrile and dioxan are listed in Tables 9 and 10 and displayed as a function of the basicity of the amines in Figs. 8 and 9. The pyridine and imidazole bases studied give approximately linear Brønsted correlations with a $\beta_B = 0.16$ in acetonitrile and $\beta_B = 0.29$ in dioxan. These values must be attributed to the proton transfer step (k_2), because K_1 is independent of the base.

For strong bases, k_B (K_2k_2) approaches limiting values of 1 dm^6 mol^{-2} s^{-1} in acetonitrile and 10 dm^6 mol^{-2} s^{-1} in dioxan which are independent of the amine basicity and obviously correspond to a K_2k_2 with diffusion-controlled k_2. Assuming a $K_1 = 1 \times 10^{-7}$ dm^3 mol^{-1}, an estimation of k_2 for the DABCO-catalysed reaction of $PhNH_2$ with PhNCO in dioxan gives $k_2 \approx 1 \times 10^8$ dm^3 mol^{-1} s^{-1} at 50 °C. This value is distinctly smaller than the possible $k_{diff} = 8 \times 10^9$ dm^3 mol^{-1} s^{-1} (dixoan, 50 °C), but of the same magnitude as similar k_2 values in aprotic solvents.[24]

The low reactivity of the sterically hindered amines *N*-methylpiperidine, *N*-methylmorpholine and triethylamine with respect to amines of similar basicity is not in accord with mechanism IIIa, because rate limiting proton transfer should not be sensitive to steric hindrance in the base catalyst. The

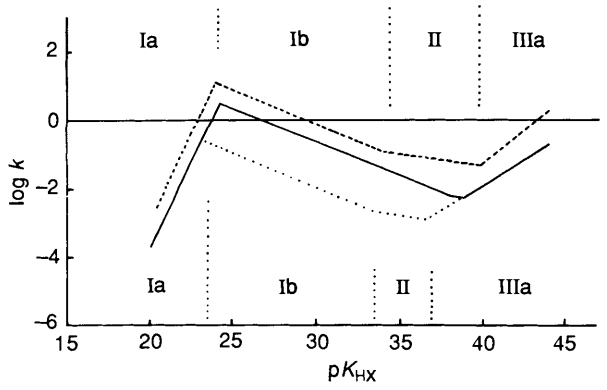


Fig. 10 Over-all Brønsted plot for reactions of phenyl isocyanate with H-acidic nucleophiles ([HX] = 1 dm^3 mol^{-1}) in acetonitrile at 50 °C. Full line: catalyst triethylamine $[B]_0$ = 0.01 mol dm^{-3}. Dashed line: catalyst triethylamine $[B]_0$ = 0.1 mol dm^{-3}. Dotted line: catalyst *N*-methylmorpholine $[B]_0$ = 0.01 mol dm^{-3}.

same has been found in the literature,[1,2] whereas the sterically hindered 2-picoline showed similar catalytic activity to the non-hindered 3- and 4-derivatives.[5,25] Why the more basic aliphatic amines do not behave in this manner is not clear.

An Overall Brønsted Plot for the Base-catalysed Addition of H-acid Compounds to Isocyanates.—On the basis of the results hitherto described, a non-linear overall Brønsted plot for the kinetics of the base-catalysed addition of H-acidic compounds to phenyl isocyanate can be constructed, the various branches of which are affiliated to the different mechanisms of these reactions.

In order to display such an overall Brønsted relationship, one has to consider that the different mechanisms obey different rate equations. The rate constants which are comparable are the ones of first order with respect to isocyanate in the general rate equation, eqn. (28).

$$v = k[\mathbf{I}] \tag{28}$$

For the different mechanisms, these *k*s are given by eqns. (29)–(33).

Ia: $$k = k_{1a}[B]_0 \tag{29}$$

Ib: $$k = k_{1a}(K_0K_{as}[B]_0)^{\frac{1}{2}} \tag{30}$$

II: $$k = k_1[B]_0[HX] \tag{31}$$

IIIa: $$k = K_1k_2[B]_0[HX] \tag{32}$$

IIIb: $$k = k_1[HX] \tag{33}$$

From the Brønsted correlations above established for the reactions of phenyl isocyanate in acetonitrile at 50 °C, eqns. (34)–(37) hold.

Ia: $$\lg k = 1.0pK_{HX} - 21.7 + \lg[B]_0 \tag{34}$$

Ib: $$\lg k = -0.2pK_{HX} + 0.5pK_{HB^+} - 2.9 + 0.5\lg[B]_0 + \lg[HX] \tag{35}$$

II: $$\lg k = -0.08pK_{HX} + 0.3pK_{HB^+} - 2.76 + \lg[B]_0 + \lg[HX] \tag{36}$$

IIIa: $$\lg k = 0.46pK_{H_2X^+} - 4.57 + \lg[B]_0 + \lg[HX] = 0.3pK_{HX} - 11.9 + \lg[B]_0 + \lg[HX] \tag{37}$$

Eqn. (38) was supposed to hold for the relationship between pK_{HX} and $pK_{H_2X^+}$ of amines.

$$pK_{ArNH_3^+} = 0.68\ pK_{ArNH_2} - 17.0 \tag{38}$$

The non-linear Brønsted plot resulting from the above relationships for the reactions of HX with PhNCO catalysed by triethylamine at $[B]_0$ = 0.01 mol dm^{-3} and [HX] = 1 dm^3 mol^{-1} in acetonitrile at 50 °C is shown in Fig. 10. The dotted line in the figure is constructed for the reactions catalysed by the weaker base *N*-methylmorpholine (pK_{HB^+} = 15.68, $[B]_0$ = 0.01 mol dm^{-3}) and the dashed line for triethylamine as catalyst in a higher concentration of $[B]_0$ = 0.1 mol dm^{-3}.

References

1 For reviews see: A. Farkas and G. A. Mills, *Adv. Catal.*, 1962, **13**, 393; S. G. Entelis and O. V. Nesterov, *Usp. Khim.*, 1966, **35**, 2178; K. C. Frisch and L. P. Rumao, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1970, **5**, 103; D. P. N. Satchell and R. S. Satchell, *Chem. Soc. Rev.*, 1975, **4**, 231.
2 J. W. Baker and J. B. Holsworth, *J. Chem. Soc.*, 1947, 713; J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 1949, **9**, 19, 24; J. W. Baker and D. N. Bailey, *J. Chem. Soc.*, 1957, 4663.
3 J. F. Smith and E. C. Friedrich, *J. Am. Chem. Soc.*, 1959, **81**, 161; Y. Iwakura and H. Okada, *Can. J. Chem.*, 1960, **38**, 2418; J. Burkus, *J. Org. Chem.*, 1962, **27**, 474.
4 A. Farkas and P. F. Strohm, *Ind. Eng. Chem., Fundam.*, 1965, **4**, 32.
5 J. M. Briody and D. Narinesingh, *Tetrahedron Lett.*, 1971, 4143.
6 A. Williams and W. P. Jencks, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1753, 1760.
7 H. Al-Rawi and A. Williams, *J. Am. Chem. Soc.*, 1977, **99**, 2671.
8 For amines see: J. F. Coetzee and G. R. Padmanabham, *J. Am. Chem. Soc.*, 1965, **87**, 5005; Z. Pawlak and G. Urbanczyk, *J. Mol. Struct.*, 1988, **177**, 401; H. Smagowski, *Pol. J. Chem.*, 1987, **61**, 449; K. T. Leffek, P. Pryszynski and K. Thanapaalasingham, *Can. J. Chem.*, 1989, **67**, 590. For phenols see: M. K. Chantooni and J. M. Kolthoff, *J. Phys. Chem.*, 1976, **80**, 1306.
9 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456; B. Valter, *Chem. Listy*, 1986, **80**, 918.
10 E. A. Castro, R. B. Moodie and P. J. Sansom, *J. Chem. Soc., Perkin Trans. 2*, 1985, 737.
11 Yu. V. Aleksandrova and O. G. Tarakanov, *Vysokomol. Soedin., Ser. A*, 1972, **14**, 23.
12 Calculated from data of J. M. Borsus, P. Merkaert, R. Jerome and P. Theyssie, *J. Appl. Polym. Sci.*, 1982, **27**, 4029.
13 R. Noack, F. Stebner and K. Schwetlick, unpublished results.
14 J. Burkus, *J. Org. Chem.*, 1961, **26**, 779.
15 R. Bacaloglu, L. Cotarca, N. Marcu and St. Tölgyi, *J. Prakt. Chem.*, 1988, **330**, 530.
16 R. Noack, unpublished results.
17 R. B. Moodie and P. J. Sansom, *J. Chem. Soc., Perkin Trans. 2*, 1981, 664.
18 S. V. Bogatkov, N. A. Belova and S. S. Medved, *Reakts. Sposobn. Org. Soedin.*, 1975, **12**, 267.
19 A. K. Zhitinkina and M. V. Shoshtaeva, *Sin. Fiz.-Khim. Polim.*, 1968, **5**, 117.
20 J. M. Kolthoff and M. K. Chantooni, *J. Am. Chem. Soc.*, 1969, **91**, 4621.
21 K. Schwetlick and R. Noack, to be published.
22 S. V. Hill, S. Thea and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1983, 437.
23 W. P. Jencks, *Adv. Chem. Ser.*, 1987, **215**, 155 and refs. therein.
24 C. D. Ritchie and S. Lu, *J. Am. Chem. Soc.*, 1990, **112**, 7748; M. M. Kreevoy and Y. J. Wang, *J. Chem. Phys.*, 1977, **81**, 1924; G. D. Burfoot, E. F. Calvin and H. Grodman, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 105.
25 N. K. Vorobev, O. K. Shebanova and N. I. Zabolotskaya, *Izv. Vyssh. Uchebn Zaved., Khim. Khim. Tekhnol.*, 1974, **17**, 814.

Paper 3/04165D
Received 16*th July* 1993
Accepted 13*th October* 1993