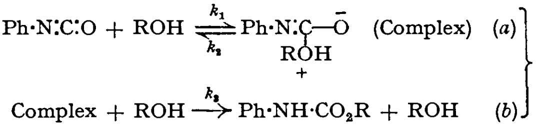
4. *The Mechanism of the Reaction of Aryl* iso*Cyanates with Alcohols and Amines. Part III. The "Spontaneous" Reaction of Phenyl* iso*Cyanate with Various Alcohols. Further Evidence relating to the Anomalous Effect of Dialkylanilines in the Base-catalysed Reaction.*

By JOHN W. BAKER and J. GAUNT.

The "spontaneous" reaction between phenyl *iso*cyanate and methyl, ethyl, *iso*propyl, and *tert.*-butyl alcohols and phenol in di-*n*-butyl ether has been studied kinetically at 20° and 30°. The reaction is catalysed by the reactant alcohol itself acting as a base, the mechanism being of the type shown in (I). Stationary-state conditions being used, the second-order velocity coefficient for the reaction is $k_0 = k_1k_3[\mathrm{ROH}]/(k_2 + k_3[\mathrm{ROH}])$, whence $[\mathrm{ROH}]/k_0 = k_2/k_1k_3 + [\mathrm{ROH}]/k_1$, and this straight-line relationship has been experimentally verified when R = Me, Et, and Pr^{β}. The significance of the values of k_1, k_2/k_3, E_0, E_1, and $E_3 - E_2$ (the Arrhenius activation energies for the various stages) thus determined is discussed on the basis of the combined operation of polar and steric effects of the group R, and it is shown that the experimental velocity order $\mathrm{R} = \mathrm{Me} < \mathrm{Et(max.)} > \mathrm{Pr}^{\beta} \gg \mathrm{Bu}^{\gamma}$ is in harmony with the theoretical deductions.

Confirmatory evidence that the failure of the dialkylanilines to catalyse the *iso*cyanate–alcohol reaction is due to the high compression energy which prevents the formation of the *iso*cyanate–base complex (Part I, *J.*, 1947, 713) is provided by the observations (1) that the same values of k_0 and the same velocity order $\mathrm{R} = \mathrm{Me} < \mathrm{Et} > \mathrm{Pr}^{\beta} \gg \mathrm{Bu}^{\gamma}$ are obtained both for the spontaneous reaction and for reaction in presence of dimethylaniline ($k_c = 0{\cdot}0$), and (2) that *N*-dimethyl-*m*-2-xylidine, in which the assumption of a planar configuration (present in dimethylaniline) is prevented by the steric effects of the two *o*-methyl substituents (Thomson, *J.*, 1946, 1113), *is* an effective catalyst ($k_c^{20°} = 0{\cdot}015$), the pyramidal configuration of this base permitting its sufficiently close approach to the *iso*cyanate molecule to form the intermediate complex.

THE mechanism deduced for the base-catalysed reaction between phenyl *iso*cyanate and alcohols (Part II, preceding paper) and the earlier observation (Part I, *J.*, 1947, 713) that the "spontaneous" reaction exhibits autocatalysis by the very weakly basic urethane product, suggested that, in the "uncatalysed" reaction, the alcohol itself, with its basic oxygen atom, might function both as a weak basic catalyst and as a reactant, the reaction proceeding by a mechanism of the type



$$\left.\begin{array}{ll}\mathrm{Ph{\cdot}N{:}C{:}O + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ph{\cdot}N{:}\underset{\overset{+}{\mathrm{ROH}}}{C}{-}\bar{O}} \quad \text{(Complex)} & (a)\\ \mathrm{Complex + ROH \xrightarrow{k_3} Ph{\cdot}NH{\cdot}CO_2R + ROH} & (b)\end{array}\right\} \quad \ldots\ldots \quad (\mathrm{I})$$

This view was supported by the observation that, like k_{bi} in the catalysed reaction, the second-order velocity coefficient, k_0, for the spontaneous reaction is also dependent on the initial alcohol concentration.

On using stationary-state conditions mechanism (I) would give an expression for k_0 of a type very similar to that for k_{bi} in the catalysed reaction, *viz.*

$$\begin{aligned} k_0 &= k_1k_3[\mathrm{ROH}]/(k_2 + k_3[\mathrm{ROH}]) \quad \ldots\ldots \quad (\mathrm{i})\\ &= k_1k_3/(k_2/[\mathrm{ROH}] + k_3)\end{aligned}$$

As before, k_0 would then approximate to a constant, and the reaction thus simulate second-order kinetics, if $k_2/[\mathrm{ROH}]$ were small in comparison with k_3, or, in the early stages of the reaction, when [ROH] is not changing greatly.

Equation (i) may be transposed thus :

$$[\mathrm{ROH}]/k_0 = k_2/k_1k_3 + [\mathrm{ROH}]/k_1 \quad \ldots\ldots \quad (\mathrm{ii})$$

The validity of mechanism (I) can thus be tested by a study of the effect of varying the concentration ratio [ROH]/[Ph·NCO], and a plot of $[\mathrm{ROH}]/k_0$ against [ROH] should give a straight line of slope $1/k_1$ and intercept k_2/k_1k_3. The results obtained when the initial concentration of *iso*cyanate was maintained at 0·24M and that of the alcohol was varied between 0·12 and 2·4M, for methyl, ethyl, and *iso*propyl alcohols, are given in Table I, and the plots of $[\mathrm{ROH}]/k_0$ against [ROH] are shown in the figure. *All values of velocity coefficients are expressed in g.-mol.$^{-1}$ l. min.$^{-1}$ units.*

TABLE I.

Effect of varying [ROH] *on the velocity of the spontaneous reaction between* ROH *and* Ph•NCO (0·24M) *in di-*n*-butyl ether at* 20° *and* 30°.

[ROH], g.-mol./l.	MeOH.				EtOH.				Pr$^{\beta}$OH.			
	10^2k_0.				10^2k_0.				10^2k_0.			
	20°.	30°.	$k_0^{30°}/k_0^{20°}$.	E_0 (kcals.).	20°.	30°.	$k_0^{30°}/k_0^{20°}$.	E_0 (kcals.).	20°.	30°.	$k_0^{30}/k_0^{20°}$.	E_0 (kcals.).
0·12	0·06	0·16	—	—	0·09	0·34	—	—	0·07$_5$	0·248	—	—
0·24	0·17	0·29	1·71	9·5	0·29	0·51	1·76	10·0	0·14	0·24$_5$	1·70	9·5
0·48	0·26	0·44	1·69	9·3	0·56	1·00	1·79	10·3	0·21	0·40	1·82	10·5
0·96	0·47	0·84	1·82	10·5	0·84	1·59	1·90	11·3	0·33	0·55	1·70	9·5
1·92	0·76	1·37	1·81	10·5	1·12	2·17	1·94	11·7	0·39	0·68	1·74	9·8
2·4	0·87	1·52	1·75	9·9	1·18	2·30	1·95	11·9	0·4	0·73	1·80	10·3
		Mean	1·76	10·0		Mean	1·87	11·0		Mean	1·75	10·0

From the above data the values of $[\mathrm{ROH}]/k_0$ are :

[ROH] =		2·4	1·92	0·96	0·48	0·24	0·12
$[\mathrm{MeOH}]/k_0$	20°	276	253	209	185	141	200
	30°	164	140	114	109	82·7	75
$[\mathrm{EtOH}]/k_0$	20°	203	171	114	86	81	133
	30°	103	88·5	60·4	48	47	35·3
$[\mathrm{Pr^{\beta}OH}]/k_0$	20°	589	489	294	225	167	160
	30°	327	281	175	120	98	48

The expected straight-line relationship is observed at both 20° and 30° with all three alcohols for values of [ROH] $>$ 0·24M. When the initial [ROH] $\not>$ 0·24M the concentration of alcohol may be insufficient to satisfy both stages (*a*) and (*b*) in the mechanism (I) and the points corresponding to reaction with 0·12 and 0·24M-alcohol usually deviate from the straight line.

The values of k_1 and k_3/k_2 at 20° and 30°, derived from the plots of $[\mathrm{ROH}]/k_0$ against [ROH] in the figure, are summarised in Table II.

TABLE II.

Values of k_1 *and* k_3/k_2 *in the reaction mechanism* (I), *between* Ph•NCO *and* ROH *in di-*n*-butyl ether at* 20° *and* 30°.

R =	Me.	Et.	Pr$^{\beta}$.	R =	Me.	Et.	Pr$^{\beta}$.
$k_1^{20°}$	0·0217	0·0168	0·0052	$(k_3/k_2)^{20°}$ (x)	0·28	1·08	1·56
$k_1^{30°}$	0·0313	0·032	0·0095	$(k_3/k_2)^{30°}$ (y)	0·40	0·97	1·46
$k_1^{30°}/k_1^{20°}$	1·44	1·99	1·82	y/x	1·43	0·90	0·94
E_1 (kcals.)	6·5	11·6	10·5	E_3-E_2 (kcals.)	6·4	−1·1	−0·7

DISCUSSION.

In contrast to the base-catalysed reaction (Part II, preceding paper) but in agreement with the mechanism (I) (p. 19), the second-order velocity coefficient of the spontaneous reaction between phenyl *iso*cyanate and an alcohol *increases* with increase in the initial concentration of the alcohol.

On the basis of the suggested mechanism the overall Arrhenius critical energy of activation for the reaction

$$E_0 = \frac{RT_2T_1}{T_2 - T_1} . \ln \left\{ \frac{k_1^{30°}k_3^{30°}[\mathrm{ROH}]}{k_2^{30°} + k_3^{30°}[\mathrm{ROH}]} \cdot \frac{k_2^{20°} + k_3^{20°}[\mathrm{ROH}]}{k_1^{20°} . k_3^{20°}[\mathrm{ROH}]} \right\}$$

$$= E_1 + E_3 + \frac{RT_2T_1}{T_2 - T_1} . \ln \left\{ \frac{k_2^{20°} + k_3^{20°}[\mathrm{ROH}]}{k_2^{30°} + k_3^{30°}[\mathrm{ROH}]} \right\} . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(iii)}$$

The values of x and y in the expression $k_3^{20°} = xk_2^{20°}$ and $k_3^{30°} = yk_2^{30°}$ are given in Table II and hence the expression (iii) may be transposed into the form

$$E_0 = E_1 + E_3 - E_2 + \frac{RT_2T_1}{T_2 - T_1} . \ln \left\{ \frac{1 + x[\mathrm{ROH}]}{1 + y[\mathrm{ROH}]} \right\} . \quad . \quad . \quad . \quad . \quad . \qquad \text{(iv)}$$

where E_1, E_2, and E_3 are the activation energies of the corresponding stages in mechanism (I).

Insertion of the appropriate values for x, y, and [ROH] in this expression makes possible the evaluation of the term ε, the concentration-dependent term in the composite evaluation of E_0 for various initial concentrations of alcohol. The values of ε thus obtained are given in Table III.

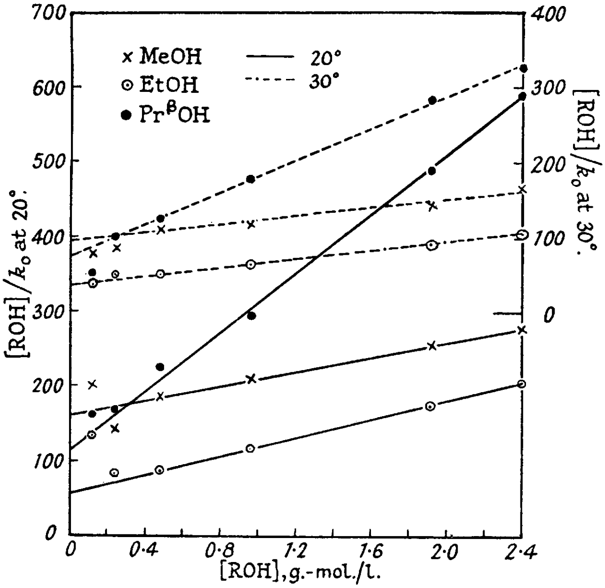
TABLE III.

Values of $\varepsilon = [\boldsymbol{R}T_2T_1/(T_2 - T_1)]\ln(1 + x[\mathrm{ROH}])/(1 + y[\mathrm{ROH}])$ *kcals./mol. for the spontaneous reaction between* Ph·NCO *and* ROH *in di-*n*-butyl ether between* 20° *and* 30°.

[ROH], g.-mol./l. =	MeOH.		EtOH.		$Pr^{\beta}OH$.	
	ε.	$E_0 - \varepsilon$.	ε.	$E_0 - \varepsilon$.	ε.	$E_0 - \varepsilon$.
2·4	−2·81	12·7	+0·7	11·2	0·95	9·3
1·92	−2·46	13·0	+0·7	11·0	0·90	8·9
0·96	−1·54	12·0	+0·5	10·8	0·72	8·8
0·48	−0·69	10·0	+0·3	10·0	0·51	10·0
0·24	−0·47	10·0	+0·25	9·75	0·32	9·2
0·12	−0·24	—	+0·14	—	0·19	—
	Mean	11·5±1·2		10·5±0·5		9·2±0·3

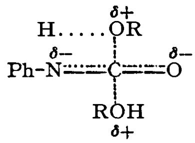
The values of ε for the spontaneous reaction are of much smaller magnitude than those of the corresponding term in the base-catalysed reaction (Part II, *loc. cit.*), and the theoretical variation of E_0 with alcohol concentration, except in the case of methyl alcohol (when the maximum variation is only 2·6 kcals.), is of the same order as the probable experimental error for values determined at only two temperatures. In agreement with this, but in contradistinction to the observations in the base-catalysed reaction, the data in Table I show that, for the spontaneous reaction, the ratio $k_0^{30°}/k_0^{20°}$, and hence the Arrhenius activation energy E_0, is approximately constant and is thus essentially independent of the initial alcohol concentration. In consequence the values of $E_0 - \varepsilon = E_1 + E_3 - E_2$ show a small downward drift with decreasing [ROH] when R = Me or Et. Such a difference between the two reactions would be expected since, in the spontaneous reaction, complications arising from reversible complex-formation between an amine catalyst and the alcohol are absent; the entity involved in the complex formation in stage (I, *a*) of the mechanism can only be the alcohol itself. Unfortunately, there are still reasons why the values of k_1 and k_3/k_2, derived from the straight-line relationships in the figure, may not have the straightforward significance suggested by the reaction scheme given. Infra-red absorption data (cf. Part IV, following paper) clearly indicate the occurrence of considerable association of the alcohol molecules with the solvent ether and, possibly, with each other, and this complication will almost certainly affect the activity coefficients of the alcohols. Differential solvation of the intermediate complex $Ph{\cdot}N{:}C(\overset{+}{O}HR) - \overset{-}{O}$ by different alcohols is also a potential factor. Hence, once again, it would be unwise to attach anything more than a qualitative significance to the values of k_1, k_3/k_2, and the derived values of E_1 and $E_3 - E_2$.

Spontaneous reaction between Ph·NCO *and* ROH *in di-*n*-butyl ether at* 20° *and* 30°.



The failure of methyl alcohol to exhibit the theoretical variation of 2·6 kcals. in the value of E_0 over the concentration range studied, exemplified by the greater variation of $E_0 - \varepsilon$ for this reaction (Table III) may possibly be attributable to such causes.

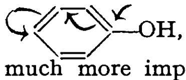
Analysis of the expected effects of alteration in the polar character and size of the alkyl group in the alcohol on the reaction velocity suggests the incidence of the following features. In stage (I, *a*) the alcohol is acting as a weakly basic catalyst and the ease of complex formation and the stability of the *iso*cyanate–alcohol complex would both be expected to increase with increase in the strength of the alcohol as an oxygen base. Increasing electron-release ($+I$ effect) in the series R = Me $<$Et $<$Pr$^\beta$$<Bu^\gamma$ should cause a corresponding increase in the basic strength of the alcohol ROH, so that the operation of this polar factor *alone* should facilitate the forward reaction in stage (I, *a*) to give a velocity order MeOH $<$EtOH $<$Pr$^\beta$OH $<$Bu$^\gamma$OH. In this series, however, the *size* of the group R is steadily increasing and this steric factor will hinder the necessary close approach of the alcohol to the *iso*cyanate molecule. The small maximum value of E_1, observed with ethyl alcohol (MeOH, 6·5; EtOH, 11·6; Pr$^\beta$OH, 10·5 kcals.), given in Table II, suggests that compression energy between the non-bonding groups may already be significant even when R = Et, although it must be remembered that differential solvation of the intermediate complexes by the different alcohols, may modify their order of stability.



In stage (I, *b*) the second molecule of alcohol * functions in a manner analogous to that in the corresponding stage of the base-catalysed reaction, the transition complex being of the general type (II). Hence, both the polar effect, due to the decreasing *acid* strength MeOH$>$ EtOH$>$ Pr$^\beta$OH$>$ Bu$^\gamma$OH, and the steric effect, arising from the increasing size of the alkyl group from methyl to *tert.*-butyl, will tend to inhibit stage (I, *b*). Thus, whereas in the base-catalysed reaction *all* factors, polar and steric, combine to predict a reaction velocity sequence R = Me$>$ Et$>$ Pr$^\beta$$>$ Bu$^\gamma$, yet in the spontaneous reaction the polar effect of increasing electron-release by the group R facilitates stage (I, *a*), but tends to inhibit stage (I, *b*), and the steric factor has a retarding influence on both stages. The problem of assessing quantitatively the relative magnitudes of these opposing polar and steric factors, especially if modified by solvation effects, is insoluble, but a general consequence of such opposing factors is the existence of a maximum velocity at some point in the graded polar series. Data for methyl, ethyl, and *iso*propyl alcohols have already been given, and the case of *tert.*-butyl alcohol was also studied under the standard conditions of initial [Ph·NCO] = [ROH] = 0·24M. The combined results are as follows :

R =	Me.	Et.	Pr$^\beta$.	Bu$^\gamma$.	Ph.
$10^2k_0^{20°}$	0·17	0·29	0·14	$0·005_5$	0·006
$10^2k_0^{30°}$	0·29	0·51 (max.)	$0·24_5$	$0·008_5$	—

At both 20° and 30° the reaction velocity coefficient does pass through a maximum value at R = Et, in contrast to the regular velocity sequence R = Me$>$ Et$>$ Pr$^\beta$$>$ Bu$^\gamma$, observed for the base-catalysed reaction.

The very weakly basic character of phenol and, possibly, its planar configuration due to resonance OH, which would make it a very inefficient catalyst in stage (I, *a*), are evidently much more important than any facilitating influence, due to its strongly acidic character, on stage (I, *b*), because the reaction velocity is of the same low order as that with *tert.*-butyl alcohol. This behaviour suggests that the facility of the reaction is *mainly* influenced by the ease with which the initial *iso*cyanate–alcohol complex can be formed, and gives added significance to the maximum velocity observed with ethyl alcohol, since it is in this stage of the mechanism that the conflict between polar and steric effects arises.

The Anomalous Catalytic Effect of Dialkylanilines.—In Part I (*loc. cit.*) it was found that the dialkylanilines, in spite of their basic strength (which is comparable to that of α-picoline) exert

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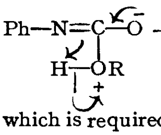
* Formation of the urethane by direct rearrangement of the alcohol–*iso*cyanate complex thus,



$\longrightarrow$ Ph·NH·CO$_2$R cannot be correct, since it would fail to explain the term [ROH]^2 which is required by the experimentally proved kinetic relationship

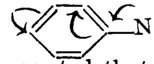
$$-\frac{d[\mathrm{Ph{\cdot}NCO}]}{dt} = \frac{k_1k_3[\mathrm{Ph{\cdot}NCO}][\mathrm{ROH}]^2}{k_2 + \mathrm{k}_3[\mathrm{ROH}]}.$$

no catalytic effect on the reaction between phenyl *iso*cyanate and methyl alcohol, the velocity being the same (within experimental error) as that of the uncatalysed, " spontaneous " reaction. This observation has now been confirmed for the reaction of phenyl *iso*cyanate with all the four alcohols studied and at two temperatures. The results are tabulated in Table IV.

TABLE IV.

Velocity of reaction between Ph·NCO *and* ROH (*both* 0·24M), (a) *without catalyst and* (b) *with dimethylaniline, in di-*n*-butyl ether at* 20° *and* 30°.

		10^2k_0 exp.			
ROH.	Temp.	(*a*).	(*b*) 0·0307M-NPhMe$_2$.	(*b*) 0·0614M-NPhMe$_2$.	Mean 10^2k_{exp}.
MeOH	20°	0·170	0·174	0·175	0·17
	30	0·290	0·308	0·315	0·30
EtOH	20	0·287	0·298	0·297	0·29
	30	0·428	0·455	0·434	0·44
Pr$^\beta$OH	20	0·144	0·111	0·110	0·12
	30	0·239	0·186	0·184	0·20
Bu$^\gamma$OH	20	0·0062	0·0050	0·0046	0·0055
	30	0·0091	0·0076$_5$	0·0074	0·0083

In Part I quantitative evidence was adduced that the failure of the dialkylanilines to catalyse the reaction is due to the high compression energy between non-bonding groups in the approach of the dialkylaniline molecule, flattened by resonance  NR$_2$, to within the transition state distance to the *iso*cyanate molecule. It was suggested that this steric factor made the formation of the base–*iso*cyanate complex so difficult that the whole reaction proceeded by the " spontaneous " mechanism, the base playing no part. In other words, the lack of catalytic activity of these bases was due entirely to the enormous decrease in the value of the forward velocity coefficient k_1 in the equilibrium Ph·NCO + base $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ complex, caused by the high compression energy involved in the formation of this complex. Hence any similar effect on k_2 (which could not be determined from the data available) was considered irrelevant to the problem. Confirmation of this view is now provided by the data in Table IV, which show that the relative velocity order with different alcohols in the presence of dimethylaniline is Me $<$ Et $>$ Pr$^\beta$ $>$ Bu$^\gamma$, identical with that observed for the "spontaneous" reaction, but differing from that, Me $>$ Et $>$ Pr$^\beta$ $>$ Bu$^\gamma$, for the base-catalysed reaction.

Recently, Thomson (*J.*, 1946, 1113) has investigated the question of the steric inhibition of resonance in dialkylanilines and its relationship to their basic strength. Although physical properties such as dipole moment (Hampson and Ingham, *J.*, 1939, 981), and the atomic refractivity of the nitrogen (which, in *N*-dimethyl-*m*-2-xylidine, approaches very closely the value for nitrogen in a tertiary aliphatic amine; Thomson, *J.*, 1944, 408) show that resonance of the dimethylamino-group with the benzene nucleus is almost completely suppressed by vicinal methyl groups, yet the basic strength of *N*-dimethyl-*m*-2-xylidine (p*K* 4·69) differs but slightly from that of *N*-dimethyl-*m*-5-xylidine (p*K* 4·48) and is, moreover, not greatly different from that of dimethylaniline itself (p*K* 4·26), all p*K* values being in 50% alcohol. Dimethyl-*m*-2-xylidine is thus an excellent tertiary base with which to test the suggestion that the lack of catalytic activity of the dialkylanilines depends entirely on the planar configuration of such molecules preventing their sufficiently close approach to the *iso*cyanate molecule to form the requisite *iso*cyanate–base complex. Its basic strength is closely similar to that of dimethylaniline itself (and, also to that of the catalytically *active* base α-picoline), but the suppression of resonance, giving it a configuration closely similar to that of a tertiary aliphatic amine, should greatly diminish the large compression energy involved in its close approach to the *iso*cyanate molecule. It would be anticipated, therefore, that unlike dimethylaniline, dimethyl-*m*-2-xylidine should be an effective catalyst for the *iso*cyanate–alcohol reaction.

We are greatly indebted to Dr. Thomson for a gift of a small quantity of his specimen of this base with which to test this conclusion. The results given on p. 24 confirm our expectations.

The value of k_0 at 20° for the xylidine is considerably lower than that (0·6) for α-picoline, but it would be expected that the two *o*-methyl substituents would, *themselves*, hinder the close approach of the molecule to the *iso*cyanate, especially if, by analogy, it is assumed that the base may be solvated with alcohol molecules, but the reality of a small catalytic effect of dimethyl-*m*-2-xylidine is beyond doubt.

Reaction between Ph·NCO *and* MeOH (*both* 0·24M) *in presence of* (*a*) 0·03M-, (*b*) 0·06M-*base in di*-n-*butyl ether at* 20° *and* 30°.

Base.	10^2k_{exp}. (*a*).	10^2k_{exp}. (*b*).	10^2k_0.	10^2k_{bl}. (*a*).	10^2k_{bl}. (*b*).	Mean value of k_c.
			At 20°.			
$NPhMe_2$	0·17	0·17	0·17	0·00	0·00	0·00
$C_6H_3Me_2{\cdot}NMe_2$	0·22	0·26	0·17	0·05	0·09	0·015
			At 30°.			
$NPhMe_2$	0·29	0·29	0·29	0·00	0·00	0·00
$C_6H_3Me_2{\cdot}NMe_2$	0·39	0·47	0·29	0·10	0·18	0·03

EXPERIMENTAL.

Materials.—The solvent, alcohols, and dimethylaniline used were purified as previously described (Parts I and II, *locc. cit.*). The sample of *N*-dimethyl-*m*-2-xylidine was a pure specimen kindly supplied by Dr. Thomson, of the Department of Physical Chemistry, The University, Glasgow. It was again refluxed over solid potassium hydroxide and then fractionated through a Widmer column, the fraction, b. p. 86·8°/18 mm., being used.

Velocity Determinations.—These were carried out, using the micro-technique, in exactly the same manner as those described in Part II except, of course, that no base catalyst was added in the determination of the velocities of the spontaneous reaction. The mean values of k_0, the second-order velocity coefficient, were determined, as before, from the straight-line plot of the experimental values of $x/(a - x)$, obtained in 6—9 individual determinations of the phenyl *iso*cyanate present, against time, measured in minutes. The samples of reaction mixture were, in general, taken during the earlier stages of the (slow) reactions, *i.e.*, before any disturbance arising from slight autocatalysis by the urethane formed (Part I) became significant. A satisfactory straight-line plot was always obtained. The number of individual experiments is, again, so large, that it is impracticable to give details of each experiment and the mean values of the velocity coefficients obtained have already been recorded earlier in this paper.

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