

6. *The Mechanism of the Reaction of Aryl isocyanates with Alcohols and Amines. Part V. Kinetic Investigations of the Reaction between Phenyl isocyanate and Methyl and Ethyl Alcohols in Benzene Solution.*

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The kinetics of both the "spontaneous" and the base-catalysed (0.01M-NEt<sub>3</sub>) reactions between phenyl isocyanate and methyl and ethyl alcohols have been studied in benzene solution at 20° and 30°, and the values for the various velocity coefficients and corresponding Arrhenius activation energies in the mechanisms given in Parts II and III (this vol., pp. 9, 19) have been compared with those obtained under comparable conditions in di-*n*-butyl ether as solvent.

The values of  $k_1$  and  $E_1$  are of the same order in both solvents, and the faster velocity of both

the spontaneous and the base-catalysed reactions in benzene is found to be due mainly to a large increase in the value of the  $k_3/k_2$  ratio, corresponding to the observation that, in benzene  $E_2 \gg E_3$ . This probably arises from a large decrease in  $E_3$  in benzene solution, rather than from any significant change in  $E_2$ , and may be correlated with the attack of monomeric alcohol molecules on the intermediate base-isocyanate (or, in the spontaneous reaction, alcohol-isocyanate) complex, since the infra-red absorption spectra (Part IV, preceding paper) show a considerable concentration of monomeric alcohol in benzene solution but none in di-*n*-butyl ether, in which solvent the alcohol is solvated with the solvent ether.

Other features of the data are shown to be in qualitative agreement with the mechanisms previously proposed (Parts II and III, *loc. cit.*) modified by the different degrees of association and solvation of alcohol and amine catalyst in the two solvents.

THE infra-red absorption data recorded in Part IV (preceding paper) confirmed the earlier suggestion that exact interpretation of the kinetics of the isocyanate-alcohol reactions in di-*n*-butyl ether would be difficult since, in that solvent, the results are complicated by alcohol-amine (in the catalysed reaction), alcohol-solvent, and, possibly, alcohol-alcohol association. No unassociated alcohol molecules could be detected in that medium by spectroscopic examination. In benzene, however, it was found that alcohol-solvent association is absent, but, at the same time, unassociated alcohol molecules are definitely present and amine-alcohol association is more pronounced than it is in the ether solvent. Both these factors, and particularly the varying degree of complex formation at different concentrations of the alcohol, should have significant effects on the velocity of the reaction when the di-*n*-butyl ether is replaced by dry benzene as the solvent. The results of kinetic investigations of both the catalysed and uncatalysed reactions in benzene are described in this communication.

(A) *Uncatalysed Reaction.*—Application of the kinetic test previously applied showed that the reaction between phenyl isocyanate and methyl or ethyl alcohol follows the same type of reaction mechanism in benzene as in the ether; the plot of  $[\text{ROH}]/k_0$  against  $[\text{ROH}]$  always gave a good straight line as required by the relationship  $[\text{ROH}]/k_0 = k_2/k_1k_3 + [\text{ROH}]/k_1$ , where  $k_0$ ,  $k_1$ ,  $k_2$ , and  $k_3$  have the same significance as in Part III (*loc. cit.*), the units being g.-mol.<sup>-1</sup> l. min.<sup>-1</sup> as before. Similarly  $E_0$ ,  $E_1$ ,  $E_2$ , and  $E_3$  and the concentration-dependent energy term  $\epsilon$  have the same meaning as before, the time units in the calculation of  $(PZ)_1$  being in minutes: the only change is the solvent employed.

TABLE I.

Reaction between varying concentrations of ROH with phenyl isocyanate (0.24M) in  
(a) di-*n*-butyl ether and (b) benzene, at 20° and 30°.

	(I) Methyl alcohol, g.-mol./l.											
	2.4.		1.92.		0.96.		0.48.		0.24.		0.12.	
	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.
$10^2 k_0^{30^\circ}$ .....	1.52	3.65	1.37	3.69	0.84	2.97	0.44	2.04	0.29	1.01	0.16	0.45
$10^2 k_0^{20^\circ}$ .....	0.87	2.20	0.76	2.09	0.47	2.03	0.26	1.39	0.17	0.71	0.06	0.36
$k_0^{30^\circ}/k_0^{20^\circ}$ .....	1.75	1.66	1.80	1.77	1.83	1.46	1.70	1.46	1.70	1.42	(2.7)	1.25
$E_0$ , kcals. ....	9.9	8.9	10.3 <sub>5</sub>	10.1	10.6 <sub>5</sub>	6.7	9.3 <sub>5</sub>	6.7	9.3 <sub>5</sub>	6.2	—	4.0
$\epsilon$ , kcals. ....	-2.8	12.3	-2.5	11.8 <sub>5</sub>	-1.5	10.1	-0.7	7.8 <sub>5</sub>	-0.5	5.4	-0.2	3.4
$E_0 - \epsilon$ , kcals.	12.7	-3.4	13.0	-1.7 <sub>5</sub>	12.0	-3.4	10.0	-1.1 <sub>5</sub>	10.0	+0.8	—	+0.6
	$k_1^{30^\circ}$	$k_1^{20^\circ}$	$k_1^{30^\circ}/k_1^{20^\circ}$	$E_1$ , kcals.	$(PZ)_1$	$(k_3/k_2)^{30^\circ} = y$	$(k_3/k_2)^{20^\circ} = x$	$y/x$	$E_3 - E_2$ , kcals.			
In Bu <sup>a</sup> <sub>2</sub> O .....	0.0313	0.0217	1.44	6.5	$1.6 \times 10^3$	0.400	0.280	1.43	6.4			
In C <sub>6</sub> H <sub>6</sub> .....	0.0467	0.024	1.95	11.8	$1.6 \times 10^7$	1.68	3.79	0.443	-14.2			
	(II) Ethyl alcohol, g.-mol./l.											
	2.4.		1.92.		0.96.		0.48.		0.24.		0.12.	
	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.
$10^2 k_0^{30^\circ}$ .....	2.30	3.26	2.16	3.30	1.60	2.83	1.00	1.94	0.50	1.04	0.34	0.41
$10^2 k_0^{20^\circ}$ .....	1.18	1.89	1.12	1.97	0.84	1.76	0.56	1.33	0.29	0.71	0.09	0.29
$k_0^{30^\circ}/k_0^{20^\circ}$ .....	1.95	1.72	1.93	1.67 <sub>5</sub>	1.90	1.61	1.79	1.46	1.73	1.46	(3.9)	1.41
$E_0$ , kcals. ....	11.9	9.6	11.7	9.1	11.3	8.4	10.3	6.6 <sub>5</sub>	10.0	6.7	—	6.1
$\epsilon$ , kcals. ....	0.7	10.0	0.7	9.7	0.5	8.5	0.3	6.8	0.25	4.9	0.14	3.1
$E_0 - \epsilon$ , kcals.	11.2	-0.4	11.0	-0.6	10.8	-0.1	10.0	-0.15	9.75	(-1.8)	—	(-3.0)
	$k_1^{30^\circ}$	$k_1^{20^\circ}$	$k_1^{30^\circ}/k_1^{20^\circ}$	$E_1$ , kcals.	$(PZ)_1$	$(k_3/k_2)^{30^\circ} = y$	$(k_3/k_2)^{20^\circ} = x$	$y/x$	$E_3 - E_2$ , kcals.			
In Bu <sup>a</sup> <sub>2</sub> O .....	0.032	0.0168	1.99	11.6	$8.2 \times 10^6$	0.97	1.08	0.90	-1.1			
In C <sub>6</sub> H <sub>6</sub> .....	0.0402	0.0201	1.91	11.4	$6.6 \times 10^6$	2.27	4.32	0.52 <sub>5</sub>	-11.7			

The results obtained for the "spontaneous" reaction between phenyl isocyanate and methyl and ethyl alcohols in benzene solution are summarised (*italics*) in Table I. For purposes of easy reference in discussion the corresponding data in di-*n*-butyl ether are included in the same table.

It has already been noted (Part III, *loc. cit.*) that the postulated mechanism is unlikely to occur normally when  $[ROH]$  is  $< [Ph \cdot NCO]$  and hence, in the following discussion, data for  $[ROH] \gg 0.24M$  are discounted.

#### DISCUSSION.

It is immediately apparent that, other conditions being the same, the velocity of the reaction is always greater in benzene than in di-*n*-butyl ether and that the relative velocity increase is greater in the reaction with methyl than with ethyl alcohol. This might be expected on general grounds owing to the presence of monomeric alcohol molecules and the absence of alcohol-solvent association in the former solvent. In both these factors infra-red absorption data suggest a greater differentiation between the two solvents for methyl than for ethyl alcohol. The absence of alcohol-solvent association in benzene, and its importance in di-*n*-butyl ether, are also revealed by the observations that the decrease in the value of  $k_0$  with decreasing initial alcohol concentration is smaller in benzene than it is in the ether. Thus at 20° the ratio of the values of  $k_0$  at 2.4 and 0.24M-alcohol concentration is, for methyl alcohol,  $2.2/0.71 = 3$  in benzene, and  $0.87/0.17 = 5$  in butyl ether, whilst, for ethyl alcohol, the corresponding values are  $1.89/0.71 = 2.5$  and  $1.18/0.29 = 4$ , respectively. The contrast on this point with the catalysed reaction, discussed below, may be noted in passing.

The need for caution in making any deductions from the values of  $k_1, k_3/k_2$ , and their derived values of  $E_1$  and  $E_3 - E_2$  has been stressed in earlier parts of this series, but the effect of the solvent change on these entities is so striking that certain qualitative deductions can be made with some confidence. The values of  $k_1$ , and the derived value of the Arrhenius activation energy  $E_1$ , are of the same order of magnitude in both solvents. It is in the value of the ratio  $k_3/k_2$  and its temperature coefficient that the most striking differences between the two solvents are exhibited. In butyl ether the value of  $E_3 - E_2$  is relatively small and positive, or nearly zero (within the limits of experimental error), *i.e.*,  $E_2 \lesssim E_3$ , and, in harmony with this  $k_2$  is either  $> k_3$  (MeOH) or of the same order as  $k_3$  (EtOH), but in benzene  $E_3 - E_2$  has a large negative value. The necessary deduction that, in benzene,  $E_2 \gg E_3$  is again in harmony with the large integral values of  $k_3/k_2$  which show that  $k_3 \gg k_2$  for both alcohols. Whilst the importance of alcohol solvation of the intermediate polar complex in the less polar solvent cannot be ignored, this suggests that the main factor responsible for the increased reaction velocity in benzene is the presence of *monomeric* alcohol molecules which have a much greater facility to attack the intermediate complex than have the alcohol-ether solvated (or associated alcohol) molecules exclusively present in the di-*n*-butyl ether. Such greater facility could arise from either or both of two causes: (1) the great diminution in any compression energy in the necessary close approach to the intermediate complex when the attacking entity is a single alcohol molecule in comparison with the bulky solvated or associated alcohol molecules; (2) the fact that no energy is now required to break hydrogen bonds in a solvated molecule before reaction is completed.\* In other words, it is probable that the large negative values of  $E_3 - E_2$  are due to a great decrease in  $E_3$  rather than to any significant increase in  $E_2$ , when the solvent is changed from butyl ether to benzene.

Another striking feature is the effect of solvent change on the sign and magnitude of the values of the concentration-dependent energy term  $\epsilon$ . In butyl ether these are very small and negative, but in benzene they are large and positive. In so far as this term may be regarded as a measure of deviation from true second-order kinetics, this indicates a much greater divergence in benzene than in butyl ether.

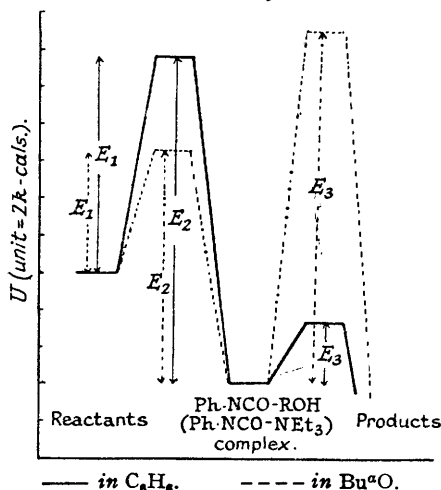
Thus the general picture of the mechanism of the uncatalysed reaction in benzene is that the difficult stage is the initial formation of the intermediate, polar, alcohol-isocyanate complex but that, once this is formed, the whole reaction has a very great tendency to "run downhill" by reaction with a second molecule of alcohol to give the uncharged, urethane product, as indicated diagrammatically by the full lines in the figure. In butyl ether the two possibilities, *viz.*, the dissociation of the intermediate complex into isocyanate and alcohol or its further

\* If the increase in the value of  $k_3/k_2$  when benzene replaces the ether as solvent is ascribed essentially to a resulting increase in  $k_3$ , it is not without significance that the calculated value of  $E_3(Bu^{\alpha}_2O) - E_2(C_6H_6)$  for the ~14-fold increase at 20° (MeOH) is  $\ln 14RT = 1.36$  kcal., and that for the 30-fold increase in the corresponding catalysed reaction is 2.4 kcal., values which are of the correct order of magnitude for O-H . . . O bonding (*cf.* Davies, *Ann. Reports*, 1946, **43**, 7).

reaction with alcohol to give the urethane, would seem to be much more evenly balanced, as indicated, diagrammatically by the broken lines in the figure.

(B) *Catalysed Reaction*.—The catalysed reaction in benzene was studied with 0.01M-triethylamine as the catalyst and so, for comparative purposes, the values of  $k_{bi}$  in butyl ether, obtained with 0.03M-triethylamine, have been divided by 3. This procedure is justified by the direct proportionality between the velocity coefficients and the concentration of the base catalyst which was established in Part II.

*Diagrammatic representation of energy levels in the reaction between Ph·NCO and MeOH in benzene and in di-n-butyl ether solutions.*



Kinetically, the catalysed reaction in benzene is of the same type as that in butyl ether, the plot of  $1/k_o$  against  $[ROH]$  again giving the straight line required by the relationship  $[NEt_3]/k_{bi} = 1/k_c = k_2/k_1k_3 + [ROH]/k_1$ . The various terms have the same significance as the corresponding ones in Part II.

The data for benzene solution are given in Table II (*italics*), those in butyl ether being included for comparison.

*Discussion*.—As was the case with the uncatalysed reaction, and for similar reasons, the velocity of the catalysed reaction is faster in benzene than in butyl ether and the increase is more marked with methyl than with ethyl alcohol. Contrary to the findings with the uncatalysed reaction, however, it will be noticed that, in the catalysed reaction, the effect of varying  $[ROH]$  on the magnitude of  $k_{bi}$  is much greater in benzene than it is in the ether. Thus at 20°, the ratios of the values of  $k_{bi}$  at 0.24 and 2.4M-alcohol concentration are, for methyl alcohol,  $27.6/2.71 = 10$  in benzene, and  $6.78/1.82 = 3.5$  in the ether, whilst, for ethyl alcohol, the corresponding values are  $7.54/1.08 = 7$  and  $2.45/0.57 = 4.3$ , respectively. Such differences may arise from the greater importance of solvation, both of the amine, as revealed by the infra-red data (Part IV, *loc. cit.*), and of the polar complex  $Ph \cdot N^+C(NR_3) \cdot \overset{-}{O}$ , by the alcohol in the less polar hydrocarbon solvent. The greater interaction in the case of methyl alcohol is reflected in the greater difference in the ratios in the two solvents for this alcohol (10, 3.5) than in those for ethyl alcohol (7, 4.3).

The values of  $E_1$  and  $k_1$  are of the same order of magnitude in both solvents although  $E_1$  is somewhat smaller (and  $k_1$  slightly larger) in benzene than in butyl ether. Since both these entities are likely to be even more influenced by solvation in benzene than in the ether (owing to greater solvation of the amine and of the intermediate complex by alcohol in the former solvent) any deduction of a quantitative character could have little value.

The main cause of the increased velocity of reaction in benzene evidently lies in the much greater value of  $k_3/k_2$  in this solvent, the increase in which, for the catalysed reaction, is even greater than it is for the spontaneous reactions. Thus, with methyl alcohol at 20°, there is a 30-fold increase in the value of  $k_3/k_2$  when benzene replaces butyl ether as the reaction solvent (*cf.* footnote, p. 29). In harmony with this, the negative values of  $E_3 - E_2$  are very much larger in benzene than in the ether, indicating that, in the former solvent  $E_2 \gg E_3$ . It is

TABLE II.

Reaction between varying concentrations of ROH with phenyl isocyanate (0.24M) catalysed by 0.01M-NEt<sub>3</sub> in (a) di-n-butyl ether and (b) benzene, at 20° and 30°.

(I) Methyl alcohol, g.-mols./l.

	2.4.		1.92.		0.96.		0.48.		0.24.		0.12.	
	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.
10 <sup>2</sup> k <sub>bl</sub> <sup>30°</sup> .....	3.56	4.38	4.24	5.39	65.7	10.33	8.32	19.84	9.2	34.0	—	(35.0)
10 <sup>2</sup> k <sub>bl</sub> <sup>20°</sup> .....	1.82	2.71	2.22	3.62	3.63	7.30	5.39	16.82	6.76	27.60	7.86	34.2
k <sub>bl</sub> <sup>30°</sup> /k <sub>bl</sub> <sup>20°</sup> .....	1.96	1.61	1.91	1.49	1.81	1.43	1.54	1.18	1.36	1.23	—	(1.02)
E <sub>bl</sub> , kcals. ...	11.9	8.5	11.4	7.1	10.5	6.4	7.6	2.9	5.4	3.7	—	(0.4)
ε, kcals. ....	7.0	24.8	6.6	24.7	5.2	24.1	3.6	23.0	2.2	21.2	1.3	18.5
E <sub>bl</sub> - ε, kcals.	4.9	-16.3	4.8	-17.6	5.3	-17.7	4.0	-20.1	3.2	-17.5	—	-18.1
	k <sub>1</sub> <sup>30°</sup> .	k <sub>1</sub> <sup>20°</sup> .	k <sub>1</sub> <sup>30°</sup> /k <sub>1</sub> <sup>20°</sup> .		E <sub>1</sub> , kcals.	(PZ) <sub>1</sub> .	(k <sub>3</sub> /k <sub>2</sub> ) <sup>30°</sup> = γ.	(k <sub>3</sub> /k <sub>2</sub> ) <sup>20°</sup> = x.	γ/x.	E <sub>3</sub> - E <sub>2</sub> , kcals.		
In Bu <sup>a</sup> <sub>3</sub> O .....	12.05	5.45	2.19		14.0	1.5 × 10 <sup>11</sup>	1.01	1.60	0.63	—	9.4	
In C <sub>6</sub> H <sub>6</sub> .....	10.87	6.97	1.56		7.9	5.0 × 10 <sup>6</sup>	11.5	47.8	0.24	—	-25.2	

(II) Ethyl alcohol, g.-mols./l.

	2.4.		1.92.		0.96.		0.48.		0.24.		0.12.	
	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.
10 <sup>2</sup> k <sub>bl</sub> <sup>30°</sup> .....	1.14	1.66	1.32	2.04	1.86	3.52	2.88	6.52	3.83	9.32	4.52	11.84
10 <sup>2</sup> k <sub>bl</sub> <sup>20°</sup> .....	0.57	1.08	0.69	1.31	1.14	2.57	1.80	4.77	2.45	7.54	2.85	9.29
k <sub>bl</sub> <sup>30°</sup> /k <sub>bl</sub> <sup>20°</sup> .....	1.98	1.54	1.91	1.56	1.63	1.37	1.60	1.37	1.56	1.24	1.59	1.28
E <sub>bl</sub> , kcals. ...	12.1	7.7	11.4	7.9	8.6	5.6	8.3	5.6	7.8	3.8	8.2	4.2
ε, kcals. ....	6.9	17.4	6.5	15.5	5.3	14.2	3.9	12.7	2.5	10.2	1.5	7.6
E <sub>bl</sub> - ε, kcals.	5.2	-9.7	4.9	-7.6	3.3	-8.6	4.4	-7.1	5.3	-6.4	6.7	-3.4
	k <sub>1</sub> <sup>30°</sup> .	k <sub>1</sub> <sup>20°</sup> .	k <sub>1</sub> <sup>30°</sup> /k <sub>1</sub> <sup>20°</sup> .		E <sub>1</sub> , kcals.	(PZ) <sub>1</sub> .	(k <sub>3</sub> /k <sub>2</sub> ) <sup>30°</sup> = γ.	(k <sub>3</sub> /k <sub>2</sub> ) <sup>20°</sup> = x.	γ/x.	E <sub>3</sub> - E <sub>2</sub> , kcals.		
In Bu <sup>a</sup> <sub>3</sub> O .....	3.45	1.60	2.16		13.7	1.6 × 10 <sup>10</sup>	1.41	2.27	0.62	—	8.5	
In C <sub>6</sub> H <sub>6</sub> .....	4.40	2.66	1.65		8.8	8.8 × 10 <sup>6</sup>	4.20	10.77	0.39	—	-18.4	

considered probable that this may again be ascribed to a large decrease in E<sub>3</sub> rather than to any significant change in E<sub>2</sub>, and thus arises from the much greater facility of attack by monomeric alcohol molecules on the amine-isocyanate intermediate complex. The general character of the difference between the reactions in benzene and in butyl ether is thus of the same type as that exhibited by the spontaneous reaction, which is indicated diagrammatically in the figure. The much larger value of the k<sub>3</sub>/k<sub>2</sub> ratios in benzene is reflected in the increase in the values of the concentration-dependent energy term ε in this solvent, thus indicating a greater divergence from true second-order kinetics in benzene than in butyl ether. Finally, the important rôle of alcohol solvation of the amine is also indicated by the parallelism between the values of E<sub>1</sub> and (PZ)<sub>1</sub>, an increase in E<sub>1</sub> always being accompanied by a corresponding increase in (PZ)<sub>1</sub> (cf. Part II, p. 14).

Summarising the whole field covered by the experimental data collected in Parts II—V of this series, it seems justifiable to conclude that the mechanisms for both the spontaneous and the base-catalysed reactions of phenyl isocyanate with alcohols which have been advanced are essentially correct, but that serious complications are introduced as a result of association and solvation. These latter factors, whilst capable of qualitative interpretation in the light of the experimental data, are not amenable to quantitative treatment on the basis of kinetic studies alone.

EXPERIMENTAL.

*Purification of Materials.*—The "AnalaR" benzene was purified and dried as described in Part IV, and all other materials were the purified specimens used in earlier parts of this series.

*Velocity Determinations.*—These were carried out exactly as described in the previous parts of this series. The micro-technique, described in Part II, for the determination of phenyl isocyanate was checked in the new solvent and found to be equally satisfactory in this medium. A suitable calibration curve in the presence of only 0.01M-triethylamine was constructed and used for the determinations in the base-catalysed reaction. The values of k<sub>exp</sub> were derived, as before, from the good straight lines obtained (with 6—8 individual readings) on the basis of the usual second-order kinetic relationship.

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