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# The Kinetics of the Polyurethane-Forming Reaction between Organic Diisocyanates and Glycols. II\*

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#### SUMMARY:

With the object of clarifying the kinetics of addition reaction between organic isocyanates and alcohols, the rate of reaction between phenyl isocyanate and 1-butanol in benzene was examined in the presence of butyl phenylurethané, butyl butylurethané, and tributylamine at 20, 30, and 40 °C. by the method of differential calculi on the graph of conversion against reaction time, and the effect of these added compounds on the reaction has been investigated. The mechanism and the rate equation for the reaction of organic isocyanates with alcohols, which had been studied by BAKER et al.<sup>2)</sup> and SATO<sup>7)</sup>, were re-examined and discussed.

#### ZUSAMMENFASSUNG:

Um die Kinetik der Additionsreaktion zwischen organischen Isocyanaten und Alkoholen zu klären, wurde die Geschwindigkeit der Reaktion von Phenylisocyanat mit n-Butanol in Benzol in Gegenwart von Butylphenylurethan, Butylbutylurethan oder Tributylamin bei 20, 30 und 40 °C durch Anwendung der Differentialrechnung auf die bei Auftragung des Umsatzes als Funktion der Reaktionszeit erhaltenen Kurve untersucht; dabei wurde auch der Einfluß der zugesetzten Verbindungen auf die Reaktion geprüft. Es wurden der Mechanismus und die Geschwindigkeitsgleichung für die Reaktion der organischen Isocyanate mit Alkoholen, welche von BAKER et al.<sup>2)</sup> und SATO<sup>7)</sup> studiert wurden, neu untersucht und diskutiert.

## Introduction

The kinetics of the reaction of an isocyanate with an alcohol was first carried out by DAVIS and FARUM<sup>1</sup>). BAKER et al.<sup>2</sup>) made a detailed kinetic investigation of the spontaneous and base-catalyzed reaction of various aromatic isocyanates with alcohols and established the mechanism of these reactions. Later kinetic studies on the reaction of isosyanates with alcohols were reported by DYER<sup>3</sup>), EPHRAIM et al.<sup>4</sup>), BURKUS and ECKERT<sup>5</sup>), KOGON<sup>6</sup>), and SATO<sup>7</sup>). These investigators except SATO treated the kinetic

<sup>\*)</sup> Part I see Makromolekulare Chem. 58 (1962) 237.

results as a second order reaction. SATO treated the kinetics of the reaction of 1-alkenyl isocyanates with methanol in di-*n*-butylether by the following kinetic equation:

$$\begin{aligned} d(urethane)/dt &= k_a \text{ (isocyanate) (alcohol)}^2 \\ &+ k_p \text{ (isocyanate) (alcohol) (product)} \\ &+ k_c \text{ (isocyanate) (alcohol) (catalyst)} \end{aligned}$$

where  $k_a$ ,  $k_p$ , and  $k_c$  represent the velocity coefficients for alcohol-, product-, and catalyst-catalyzed reaction, respectively.

In a previous paper<sup>10</sup>) we have treated the kinetics of phenyl isocyanate with polymethylene glycols using the usual second order kinetics. The results apparently followed the second order kinetics with an appreciable agreement. However, the considerably effect of the product (the urethane) for the reaction has been observed, and the reaction rate equation cannot be considered in disregard of this effect.

In the present work, to obtain the fundamental evidence of the kinetics of polyaddition reaction between diisocyanates and glycols, the rate of reaction between phenyl isocyanate and 1-butanol in benzene, in the absence of, and in the presence of added compounds, was examined at 20, 30, and 40 °C. using Eq. (1) by the method of differential calculi on the graph of conversion against reaction time.

#### Experimental

## Materials

Benzene was purified by the following procedures. After shaking three times with a small amount of concd. sulfuric acid, benzene was washed with water, neutralized with sodium carbonate, and washed thoroughly with water. Calcium chloride was added to benzene, which was allowed to stand over night, distilled, and redistilled with sodium, b.p.  $80 \,^{\circ}$ C.

Phenyl isocyanate was used immediately after distillation, b.p.<sub>42</sub> 77–77.5 °C. 1-Butanol was purified by the method of CLARKE, ROBINSON, and SMITH<sup>8</sup>), b.p. 118.6–119 °C.

Tributylamine was fractionally distilled, b.p.<sub>19</sub> 98-99°C.

Butyl phenylurethane was synthesized from phenyl isocyanate and 1-butanol. Phenyl isocyanate 3.97 g. (0.030 moles) and 1-butanol 2.47 g. (0.033 moles) were mixed in an ice water bath and allowed to stand over night. The reaction product was recrystallized three times from hexane, m.p. 62.5-62.8 °C.

C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>N (193.3) Calcd. N 7.25 Found N 7.18

Butyl butylurethane was synthesized from butyl chlorocarbonate and butylamine following the method described in the literature<sup>9</sup>). 15 g. (0.2 moles) of butylamine was dissolved in 50 ml. of dry ether and to the cold solution was added a solution of 13.6 g. (0.1 mole) of butyl chlorocarbonate in an equal volume of dry ether. After the reaction was completed the amine hydrochloride was filtered off. The ether was evaporated and the urethane distilled under reduced pressure, b.p.<sub>4</sub> 101 °C.

The BEILSTEIN test for chlorine was negative.

### Procedure

The apparatus and procedure used were the same as that previously reported<sup>10</sup>). To a solution of 2 ml. of 1-butanol or 1-butanol and a urethane or a tertiary amine, a solution of 2 ml. of phenyl isocyanate was added. A check for the reaction of phenyl isocyanate (0.125 moles/l.) with butyl butylurethane (0.34 moles/l.) or with water, which enters into the reaction system despite special caution, was carried out at 40 °C. for 6 hrs. and showed that no significant reaction had occurred.

#### Calculation of Rate Constants and Results

The rate equation of reaction between organic isocyanates and alcohols is generally expressed in Eq. (2):

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x)(b-x) \tag{2}$$

where

 $k = k_a(b-x) + k_px + k_c$  (catalyst)

and a is the initial concentration of isocyanate, b is that of alcohol, and x is the amount of each reactant reacted at time t. Then k is specified in the following way by the kind of the added compounds:

None 
$$\mathbf{k} = \mathbf{k}_{\mathbf{a}}(\mathbf{b}-\mathbf{x}) + \mathbf{k}_{\mathbf{p}}\mathbf{x}$$
 (3)

$$C_{6}H_{5}NHCO_{2}C_{4}H_{9} \quad k = k_{a}(b-x) + k_{p}(d+x)$$
(4)

$$C_4H_9NHCO_2C_4H_9 \quad k = k_a(b-x) + k_px + k_c'e$$
 (5)

$$(C_4H_9)_3N$$
  $k = k_8(b-x) + k_px + k_c''f$  (6)

where d, e, and f are the amounts of the added butyl phenylurethane (BPU), butyl butylurethane (BBU), and tributylamine (TBA) respectively.

So as to obtain the rate constant in the Eqs. (3) to (6), Eq. (2) was transformed and expressed as:

$$\frac{\mathrm{dx}}{\mathrm{dt}} \frac{1}{(a-x)(b-x)} = k_a(b-x) + k_p x + k_c \text{ (catalyst)}$$

$$= (k_p-k_a)x + k_ab + k_c \text{ (catalyst)}$$
(7)

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In this equation, dx/dt is calculated graphically from the relationship between x and t for each appropriate interval of x; differential calculi on the graph were done, therefore dx/dt shown above must be written as  $\Delta x/\Delta t$  in the strict sense of the term. Plotting values of

$$\frac{\mathrm{dx}}{\mathrm{dt}} \frac{1}{(a-x)(b-x)}$$

against x, values of  $k_ab + k_c$ (catalyst) and  $k_p-k_a$  are obtained as the intercept and the slope of the plot, respectively.

The effect of the added compounds on the reaction rate of phenyl isocyanate with 1-butanol in benzene at 40 °C. is schematically shown in Fig. 1.



Fig. 1. Effect of added compounds on the reaction rate of phenyl isocyanate with 1-butanol in benzene at 40 °C. Initial concentration: 0.125 mol./l. in both.

- □ in the absence of an added compound
- in the presence of 0.1884 mol./l. of butyl phenylurethane
- in the presence of 0.00998 mol./l. of tributylamine
- in the presence of 0.1310 mol./l. of butyl butylurethane

The Reaction of phenyl isocyanate with 1-butanol was studied in the concentration range of 0.1-1.0 mole/l. in the absence of an added com-

pound and in the presence of about 0.15 mole/l. butyl phenylurethane. Representative plots of the relationship between

$$\frac{\mathrm{dx}}{\mathrm{dt}} \frac{1}{(\mathrm{a}-\mathrm{x})(\mathrm{b}-\mathrm{x})}$$

and x are shown in Fig. 2 for the spontaneous reaction at 40 °C.



Fig. 2. Representative plots of the relationship between  $\frac{dx}{dt} \frac{1}{(a-x)(b-x)}$  and x for the spontaneous reaction at 40 °C.

In the case of the reaction catalyzed by butyl butylurethane, the concentration of butyl butylurethane and the value of  $k_c'e + k_ab$  are listed in Table 1. Values of  $k_c'$  were obtained as the value of the slope from the relationship between e and  $k_c'e + k_ab$  by the method of least squares.

The results of the tributylamine-catalyzed reaction are listed in Table 2. In this case,  $k_p-k_a$  did not always coincide with that of others (see last column in Table 2) and increased with the concentration of tributylamine.

Expt. no.	React. temp. (± 0.02°C.)	Concn. of C <sub>6</sub> H <sub>5</sub> NCO (mol./l.)	Concn. of n -C <sub>4</sub> H <sub>9</sub> OH (mol./l.)	Concn. of BBU (mol./l.)	$k_{c}'e + k_{a}b \cdot 10^{4}$ (l./mol. sec.)	k <sub>e</sub> '·10 <sup>4</sup> (l. <sup>2</sup> /mol. <sup>2</sup> sec.)
<b>B-1</b>	20	0.1250	0.1250	0.1079	$3.42\pm0.50$	
B-2	20	0.1250	0.1250	0.2159	$5.70\pm0.18$	$19.7 \pm 1.1$
B-3	20	0.1250	0.1250	0.3238	$7.67\pm0.70$	
B-12	30	0.1251	0.1248	0.1132	$6.72 \pm 0.70$	
B-13	30	0.1251	0.1248	0.2263	$11.4\pm1.3$	$\textbf{37.9} \pm \textbf{1.7}$
B-14	30	0.1251	0.1248	0.3395	$15.3 \pm 1.7$	
B-18	30	0.1393	0.1257	0.1145	$11.4 \pm 0.4^{*}$	
B-19	30	0.1262	0.1248	0.3395	19.8 $\pm$ 2.0 *)	
<b>B-24</b>	40	0.1250	0.1251	0.1310	$11.6 \hspace{0.2cm} \pm \hspace{0.2cm} 1.3 \hspace{0.2cm}$	
<b>B-25</b>	40	0.1250	0.1251	0.2620	19.5 $\pm$ 4.2	$\textbf{55.8} \pm \textbf{1.7}$
B-26	40	0.1250	0.1251	0.3930	$26.2 \hspace{0.2cm} \pm \hspace{0.2cm} 3.0 \hspace{0.2cm}$	

Table 1. Relationship between concentration of butyl butylurethane (e) and values of  $k_c'e + k_ab$  and  $k_c'$  in the butyl butylurethane-catalyzed reaction of phenyl isocyanate with 1-butanol in benzene

\*) In the presence of tributylamine (0.0099 mol./l.).



Fig. 3. The temperature dependence of the apparent rate constants for k<sub>a</sub>, k<sub>p</sub>, k<sub>c</sub>', and k<sub>c</sub>''
Initial concentration of 1-butanol: 0.125 mol./l.

O Initial concentration of 1-butanol: 0.250 mol./l.

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ble 2. Relationship between concentration of tributylamine (f) and values of k <sup>c</sup> ''f + k <sub>a</sub> b, k <sub>c</sub> '', and k <sub>p</sub> -k <sub>a</sub> in the tributylamine-catalyzed	reaction of phenyl isocyanate with 1-butanol in benzene
Tabi	

	k <sub>p</sub> -k <sub>a</sub> ·10 <sup>4</sup> (l./mol. sec.)	$24.3 \pm 1.3$ $39.8 \pm 11.9$	$50.2\pm19.2$	$30.3 \pm 8.8$	$58.7\pm22.2$	$33.2\pm 4.7$	$73.2\pm 9.1$	$108 \pm 11$	$117 \pm 4$	1	
enzene	k <sub>c</sub> ''.10 <sup>4</sup> (1. <sup>2</sup> /mol. <sup>2</sup> sec.)	$324\pm87$		$375 \pm 9$			$437\pm0$				
with 1-butanol in b	$\frac{k_c''f + k_a b \cdot 10^4}{(1./mol. sec.)}$	$3.85 \pm 0.07$ $7.68 \pm 0.67$	$10.5 \pm 1.2$	$9.75 \pm 0.50$	$14.2 \pm 1.3$	$6.30\pm0.24$	$10.6 \pm 0.5$	$15.0 \pm 0.7$	${f 9.37\pm 0.21}^{*)}$	$18.0 \pm 0.5^{*}$	
henyl isocyanate	Concn. of TBA (mol./l.)	0.01028 0.02057	0.03085	0.02055	0.03083	0.00998	0.01995	0.02993	0.01105	0.02381	
reaction of p	Concn. of n-C4H90H (mol./l.)	0.1250 0.1250	0.1250	0.1240	0.1257	0.1252	0.1252	0.1252	0.1251	0.1251	(0.1884 mol./l.).
	Concn. of C <sub>6</sub> H <sub>5</sub> NCO (mol./l.)	0.1250 0.1250	0.1250	0.1203	0.1394	0.1250	0.1250	0.1250	0.1250	0.1250	l phenylurethane
	React. temp. (± 0.02°C.)	20	20	00 00 00 00	30	40	40	40	40	40	presence of buty
	Expt. no.	B-4 B-5	B-6	61-9 B-16	B-17	<b>B-</b> 27	<b>B-2</b> 8	B-29	B-30	<b>B-</b> 31	*) In the <b>J</b>

Table 3. Effect of	the added co	mpounds on t	he reaction of	phenyl isocy	anate with I	-butanol in h	oenzene	
Catalytic coefficient Initial concn. of the reactants		ka			kp		k <sub>c</sub> ′	k <sub>c</sub> ′′
(mol./l.)	0.125	0.250	0.500	0.125	0.250	0.500	0.125	0.125
Apparent rate 20°C.	1	$6.23 \pm 0.16$	$6.05 \pm 0.45$	I	$4.47\pm0.24$	$2.67 \pm 0.35$	$19.7 \pm 1.1$	$324 \pm 87$
Constant ·10 <sup>4</sup> 30 °C.	$7.59 \pm 0.20$	$7.39 \pm 0.15$	$7.43\pm0.17$	$12.1 {\pm} 0.20$	$\textbf{8.85}{\pm}\textbf{0.30}$	$6.22 \pm 0.10$	$37.9 \pm 1.7$	$375 \pm 9$
$(1.^2/mol.^2 sec.) 40 \circ C.$	Ι	$8.34{\pm}0.55$	$8.87 \pm 0.85$	$18.2\pm0.5$	$14.3 \pm 0.6$	$10.8\ \pm 0.53$	$55.8 \pm 1.7$	$437 \pm 0$
Apparent activation energy								
(kcal./mole)	I	$\textbf{2.7} \pm \textbf{0.8}$	$\textbf{3.6} \pm \textbf{1.0}$	7.8	$10.7 \pm 0.5$	$12.5 \pm 2.2$	$9.5 \pm 0.7$	$2.7\pm 0.3$
$\log A (1.^2/mol.^2 sec.)$	1	$-1.3 \pm 0.6$	$-0.56 \pm 0.75$	2.7	$4.6 \pm 0.4$	$5.8 \pm 1.6$	$4.4\pm0.5$	$0.6\pm 0.2$

## Kinetic of the Polyurethane-Forming Reaction

This same tendency was observed both in the reaction catalyzed by triethylamine and in the reaction of coexistence of butyl butylurethane and tributylamine.

The effect of the added compounds on the reaction of phenyl isocyanate with 1-butanol in benzene is summarized in Table 3. The effect of temperature on the apparent rate constants is shown in Fig. 3. Apparent energies of activation and log A were calculated from the ARRHENIUS equation,

$$\mathbf{k} = \mathbf{A}\mathbf{e}^{-\mathbf{E}/\mathbf{R}\mathbf{T}}$$

## Discussion

The kinetics of reaction of organic isocyanates and alcohols has been investigated systematically by BAKER and his co-workers<sup>2</sup>). They showed that the reaction proceeded in the following mechanism:

$$R-N=C=O + B \xrightarrow[]{k_{1}}_{k_{m}} R-N=C-O \qquad (8)$$

$$B \qquad (complex)$$

$$complex + R'-OH \xrightarrow[]{k_{n}}_{k_{m}} RNHCO_{2}R' + B \qquad (9)$$

where B are basic substances such as alcohols and tertiary amines. Assuming a steady state concentration of the complex, the following rate equation was obtained:

$$\frac{\mathrm{d}(\mathrm{RNHCO}_{2}\mathrm{R}')}{\mathrm{dt}} = \frac{k_{1}k_{n}(\mathrm{R}-\mathrm{NCO})(\mathrm{R}'-\mathrm{OH})(\mathrm{B})}{k_{m}+k_{n}(\mathrm{R}'-\mathrm{OH})}$$
(10)

The complex between the isocyanate group and basic substances, such as triethylamine, was confirmed by PESTEMER and LAUERER<sup>11</sup>). EPHRAIM et al.<sup>4</sup>) had shown that the reaction velocity for the reaction of phenyl isocyanate with methanol in various solvents is approximately connected with the hydrogen bond-forming ability of solvents. SATO<sup>7b</sup>) pointed out from the kinetics and spectroscopic results that in the reaction of isocyanates with alcohols the intermediate complex mechanism is operative, that hydrogen bonding among the reactants, the products, and the solvents is involved.

The spontaneous reaction at equal concentration is plotted in Fig. 4 according to the usual second order reaction rate equation:

$$kt = \frac{1}{a-x} - \frac{1}{a}$$

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The reaction apparently followed the simple second order kinetics. This fact shows that  $k_p$  is nearly equal to  $k_a$  in the following equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} \frac{1}{(a-x)(b-x)} = (k_p-k_a)x + k_ab$$

Table 3 and the experimental results show that the values of  $k_a$  are almost constant within the range of experimental error at the concentration range from 0.125 to 1.0 mole/l. of 1-butanol. On the other hand, the values of  $k_p$  decrease considerably with increasing the initial concentration of the reactants.



Fig. 4. Plots of the usual second order kinetics in the spontaneous reaction of phenyl isocyanate with 1-butanol in benzene at 20, 30, and 40 °C. Initial concentration: 0.500 mol./l. in both

The catalytic action of butyl butylurethane for the reaction is much greater than that of butyl phenylurethane. It seems to be suggested that the basic strength and the steric structure of the urethane act a great deal for the formation of the complex between the isocyanate group and a urethane. Therefore, Formula I is more appropriate than Formula II as the complex of an isocyanate and a urethane.

In the case of the catalyzed reaction with tributylamine, the reaction showed an accelerated rate more than the rate which had been expected from the catalyzed action with butyl phenylurethane. This seems to be explained by the formation of the ternary complex, which had been proposed in the triethylamine catalyzed reaction of organic isocyanates with primary amines by BAKER and BAILEY<sup>12</sup>). A weak basic tertiary amine acts as an electron-donor, a very weak acidic urethane as an electron-acceptor, and form the complex with the isocyanate group (Formula III). The reaction is considered to be catalyzed by this complex.

$$C_{6}H_{5}$$

$$C_{6}H_{5}-N=C-O\cdots H-NCO_{2}C_{4}H_{9}$$

$$i$$

$$N(C_{4}H_{9})_{3}$$
III

From this evidence, a tertiary amine catalyzed reaction of an isocyanate and an alcohol is expressed in the following equation:

$$\mathbf{k} = \mathbf{k}_{\mathbf{a}}(\mathbf{b}-\mathbf{x}) + \mathbf{k}_{\mathbf{p}}\mathbf{x} + \mathbf{k}_{\mathbf{c}}$$
 (tertiary amine)  
+  $\mathbf{k}_{\mathbf{c}\mathbf{p}}$  (tertiary amine)x

where  $k_{\rm cp}$  is the rate constant of the reaction catalyzed by the ternary complex.

The experimental energies of activation in the reaction of phenyl isocyanate with 1-butanol in xylene (initial concentration of phenyl isocyanate: 0.5 moles/l., of 1-butanol: 1.0 mole/l.) and with ethanol (a. large excess of ethanol) in toluene has been obtained according to the second order kinetics as  $8.1^{3}$  and  $9.5 \text{ kcal./mole}^{13}$  respectively. BAKER and GAUNT<sup>2d</sup> reported that the apparent energies of activation in the reaction of phenyl isocyanate with ethanol (initial concentration, both 0.24 moles/l.) are 10.0 kcal./mole in di-*n*-butylether and 6.7 kcal./mole in benzene. As shown in Table 3, the apparent energies of activation in this experiment are 3-4 kcal./mole for  $k_a$  and 8-13 kcal./mole for  $k_p$  in the experimental range. This fact shows that in treatment of the second order kinetics, the experimental energies of activation mainly depend upon those of the product-catalyzed reaction.

The apparent energy of activation in the triethylamine-catalyzed reaction of phenyl isocyanate with 1-butanol in toluene (initial concentration, both 0.1 mole/l.) has been calculated as 3.1 kcal./mole<sup>5</sup>). Comparing with the result of the tributylamine-catalyzed reaction in Table 3, the obtained value seems to be appropriate. Moreover, it is a noteworthy result that the apparent energy of activation for  $k_c''$  is nearly equal to that for  $k_a$ .

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