

### 758. *Kinetics of Some Alcohol-Isocyanate Reactions.*

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The kinetics of the reactions of phenyl isocyanate with ethanol, 2-ethoxyethanol, polymethylene glycols, and polyethylene glycols in dioxan and other solvents have been studied. The results cannot be explained on the basis of mechanisms previously suggested. Effects believed to be due to hydrogen bonding have been observed, but are not fully understood.

DESPITE considerable study in recent years, the mechanism of the spontaneous reaction, in solution, of alcohols with isocyanates is not well understood. It appears that the mechanism is dependent upon the nature of the reactants and the reaction medium. Baker and Gaunt<sup>1</sup> suggested that the reaction proceeds through an intermediate alcohol-isocyanate complex which reacts further with the alcohol to form the urethane. This mechanism accounts for the behaviour observed in some cases,<sup>2-4</sup> but in others,<sup>5-7</sup> alternative mechanisms have been suggested.

We have studied the reaction of phenyl isocyanate, in dioxan solution, with ethanol, 2-ethoxyethanol, ethylene glycol, and some polymethylene and polyethylene glycols, and have found that none of the kinetic expressions advanced so far can account for the observed behaviour.

#### EXPERIMENTAL

*Solvents.*—AnalaR benzene was dried by means of three applications of freshly extruded sodium wire; an isatin test for thiophene gave a negative result, and the water content (Karl Fischer) was 0.002%. Dioxan was refluxed with hydrochloric acid, neutralised with solid potassium hydroxide, dried by refluxing over sodium, and then distilled from sodium; it had b. p. 100.6—101.0°, and its water content (Karl Fischer) was 0.0015%. Other solvents were fractionally distilled; tetrahydrofuran had b. p. 66.2—66.4°, and 1,2-dimethoxyethane had b. p. 84.7—85.0°. All the solvents were stored in contact with sodium wire.

*Reactants.*—Phenyl isocyanate was distilled under reduced pressure immediately before each

<sup>1</sup> Baker and Gaunt, *J.*, 1949, 19.

<sup>2</sup> Baker and Gaunt, *J.*, 1949, 27.

<sup>3</sup> Dyer, Taylor, Mason, and Samson, *J. Amer. Chem. Soc.*, 1949, **71**, 4106.

<sup>4</sup> Iwakura, Okada, and Yamashiro, *Makromol. Chem.*, 1962, **58**, 237.

<sup>5</sup> Ephraim, Woodward, and Mesrobian, *J. Amer. Chem. Soc.*, 1958, **80**, 1326.

<sup>6</sup> Sato, *J. Amer. Chem. Soc.*, 1960, **82**, 3893.

<sup>7</sup> Sato, *J. Org. Chem.*, 1962, **27**, 819.

kinetic run; it had b. p. 66—68°/25 mm. Ethanol was dried by the sodium-diethyl phthalate method and then distilled, both the first and the last 20% being rejected. 2-Ethoxyethanol and the glycols were treated with anhydrous sodium sulphate, to remove any gross water-contamination, and were finally dried and purified by slow fractionation through a 30-cm. Vigreux column, the first 20% being rejected {2-ethoxyethanol, b. p. 134—135°; ethylene glycol, b. p. 123—124°/20 mm. [water (Karl Fischer), 0.025%]; trimethylene glycol, b. p. 132°/22 mm.; tetramethylene glycol, b. p. 140°/22 mm.; hexamethylene glycol, b. p. 151—153°/20—23 mm.; diethylene glycol, b. p. 149°/28 mm.; triethylene glycol, b. p. 155—158°/8—9 mm. [water (Karl Fischer), 0.004%]}. Tetraethylene glycol was prepared by reaction of the monosodium derivative of ethylene glycol (2 mol.) with bis-(2-chloroethyl) ether (1 mol.), and was fractionated (b. p. 118—119°/0.1 mm.).

*Kinetic Procedure.* Kinetic measurements were carried out at  $30 \pm 0.05^\circ$  in oven-dried "Quickfit" glassware (cooled in desiccators), using greased stoppers and moisture-absorption tubes and keeping the time of exposure to the atmosphere to a minimum. A number of blank runs was carried out with only the solvent and the isocyanate. Over the periods that the actual runs were followed, the blank runs showed no detectable decrease in isocyanate concentration, and a decrease of only 1% was observed after three weeks.

Phenyl isocyanate was used throughout at a concentration of 0.20M, and the ratio [ROH]:[Ph·NCO] was varied from 1.0 to 22.5. The consumption of isocyanate during the course of the reaction was followed by using the method of Stagg.<sup>8</sup> The reactions were followed up to 40—80% conversion, and the observed second-order rate constants ( $k_{\text{obs}}$ ) were obtained from the slopes of the straight-line plots of  $\log_{10} b(a-x)/(b-x)$  against time; the values of  $k_{\text{obs}}$  thus obtained are listed in the Table.

Values <sup>a</sup> of  $10^3 k_{\text{obs}}$  (l. g.-equiv.<sup>-1</sup>, min.<sup>-1</sup>). [Ph·NCO] = 0.20M; temperature, 30°; solvent, dioxan, unless otherwise stated.

Alcohol or glycol	[ROH] (g.-equiv. l. <sup>-1</sup> )									
	0.20	0.50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	4.50
C <sub>2</sub> H <sub>5</sub> OH			0.774	1.40	2.05	2.87	3.81	4.77	5.56	6.54
" <sup>b</sup>			0.984	1.68	2.45	3.28				
" <sup>c</sup>		0.636	1.16	1.75	2.47	3.29				
" <sup>d</sup>	8.70	21.0	31.1	32.6	34.1					
C <sub>2</sub> H <sub>5</sub> O·CH <sub>2</sub> ·CH <sub>2</sub> ·OH ...			0.294	0.438	0.606	0.791				
HO·CH <sub>2</sub> ·CH <sub>2</sub> ·OH	0.102		0.378	0.642	1.04	1.51	1.97	2.41	2.83	3.40
H·[O·CH <sub>2</sub> ·CH <sub>2</sub> ] <sub>2</sub> ·OH ...	0.156		0.432	0.624	0.918	1.13				
H·[O·CH <sub>2</sub> ·CH <sub>2</sub> ] <sub>3</sub> ·OH ...	0.192		0.366	0.504	0.684	0.810				
"	2.34		3.00		3.24					
H·[O·CH <sub>2</sub> ·CH <sub>2</sub> ] <sub>4</sub> ·OH ...	0.284		0.486	0.582	0.624	0.696				
HO·[CH <sub>2</sub> ] <sub>3</sub> ·OH			2.21	3.71	3.96	5.99				
HO·[CH <sub>2</sub> ] <sub>4</sub> ·OH			1.92	2.84	3.79	4.82				
HO·[CH <sub>2</sub> ] <sub>6</sub> ·OH			0.984	1.80	2.63					

<sup>a</sup> Estimated precision  $\pm 3\%$ , or better. <sup>b</sup> In tetrahydrofuran. In 1,2-dimethoxyethane. <sup>d</sup> In benzene.

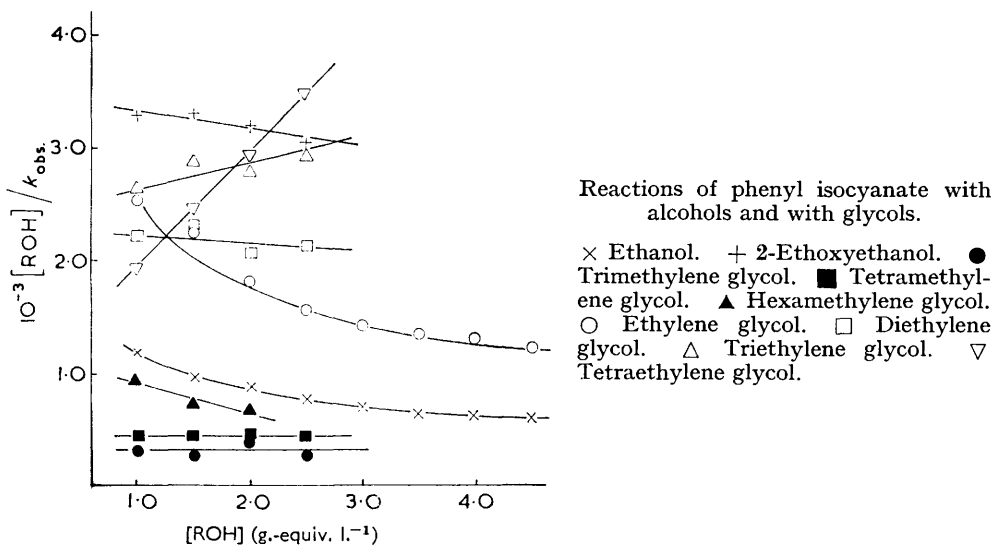
## RESULTS AND DISCUSSION

No significant deviations from second-order kinetics were found, the second-order rate plots being quite linear. Regression analysis of the data obtained for ethanol in benzene and in dioxan, ethylene glycol in dioxan, and tetraethylene glycol in dioxan (at [ROH]:[Ph·NCO] ratios of 10) gave, in each case, a correlation coefficient of 1.00.

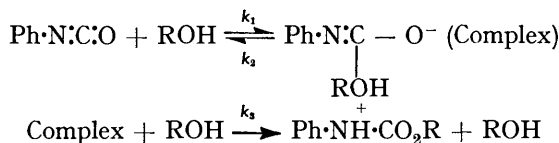
For the reaction of polyethylene glycols with phenyl isocyanate in dioxan at 30°, the second-order rate constants varied according to the ratio [ROH]:[Ph·NCO]. With equivalent amounts of reactants, the values of  $k_{\text{obs}}$  were in the order tetraethylene glycol > triethylene glycol > diethylene glycol > ethylene glycol; however, when [ROH]:[Ph·NCO] was increased to 10.0 or more, this order was reversed. The relative reactivities of the polymethylene glycol were far less dependent on the ratio [ROH]:[Ph·NCO], and the

<sup>8</sup> Stagg, *Analyst*, 1946, **71**, 557.

order of reactivity was always trimethylene glycol > tetramethylene glycol > hexamethylene glycol > ethylene glycol. The lower rate of reaction of ethylene glycol compared with trimethylene glycol may possibly be due to steric effects, as suggested by Baker and Gaunt for the case of methanol and ethanol. The rates of reaction of ethanol with phenyl isocyanate in dioxan, tetrahydrofuran, and 1,2-dimethoxyethane all increased markedly with increasing ethanol concentration, but the reactions were much slower than in benzene. Similarly, the rate of reaction of triethylene glycol in dioxan was less than in benzene, but the decrease was less than that found for ethanol.



The validity of Baker and Gaunt's mechanism was tested for the reaction, in dioxan, of phenyl isocyanate with ethanol, 2-ethoxyethanol, and the glycols by plotting  $[ROH]k_{obs}$  against  $[ROH]$  (see the Figure). Baker and Gaunt's mechanism



requires that this plot should be linear with a positive slope ( $1/k_1$ ) and a positive intercept ( $k_2/k_1k_3$ ). With ethylene glycol in dioxan, it was found that the plot of  $[ROH]/k_{obs}$  against  $[ROH]$  was a curve of negative slope approaching a limiting value of  $[ROH]/k_{obs}$ . In the case of diethylene glycol, the slope was also negative, but for triethylene and tetraethylene glycols, positive slopes were found and the plots appeared to be linear. Trimethylene, tetramethylene, and hexamethylene glycols gave straight-line plots in which  $[ROH]/k_{obs}$  remained virtually constant as  $[ROH]$  was increased. It is inferred from these observations that Baker and Gaunt's mechanism is incomplete for reactions conducted in polar solvents, since it does not allow a negative slope for the plot of  $[ROH]/k_{obs}$  against  $[ROH]$ .

It appears that the reactions are not sufficiently sensitive to water to necessitate the taking of extreme precautions to eliminate it, for the present purpose. The presence of up to 2% of water in the glycols caused increases (of up to 25%) in rate coefficients, but did not alter the pattern of behaviour noted in the  $[ROH]/k_{obs}$  vs.  $[ROH]$  relationships.

Regarding a urethane-catalysis term as insignificant during the initial stages of the reaction, the mechanism of Ephraim, Woodward, and Mesrobian<sup>5</sup> requires a non-linear dependence of  $[\text{ROH}]/k_{\text{obs}}$  on  $[\text{ROH}]$  of the form

$$[\text{ROH}]/k_{\text{obs}} = [\text{ROH}]/(A[\text{ROH}] + B)$$

which does not allow a negative slope. Similarly, neglect of the urethane-catalysis term in Sato's kinetic expression<sup>6</sup> leads to the requirement that  $[\text{ROH}]/k_{\text{obs}}$  remain constant.

Both the lower rate of reaction in polar solvents and the lower reactivities of polyethylene glycols compared with polymethylene glycols are undoubtedly due to hydrogen bonding. Studies of polyethylene glycols in carbon tetrachloride<sup>9</sup> have shown that there is a transition from intermolecular hydrogen bonding with ethylene glycol to exclusively intramolecular hydrogen bonding with tetraethylene and higher glycols. Appreciable intramolecular hydrogen bonding has been found in trimethylene and tetramethylene glycols, but none has been found in hexamethylene glycol.<sup>10</sup>

It is noteworthy that the non-linearity and negative slope in the plot of  $[\text{ROH}]/k_{\text{obs}}$  against  $[\text{ROH}]$  are most pronounced when intermolecular hydrogen bonding with solvent is greatest, as is particularly evident from the reactions of ethanol and of ethylene glycol with phenyl isocyanate in dioxan. For the polyethylene glycols in dioxan, as the chain-length of the glycol is increased, the change from intermolecular (with solvent) to intramolecular hydrogen bonding is accompanied by a change in the slope (from negative to positive) of the plot of  $[\text{ROH}]/k_{\text{obs}}$  against  $[\text{ROH}]$ . Thus, tetraethylene glycol, which has ample ability for intramolecular hydrogen bonding, owing to the presence of internal ether-oxygen, shows an ideal plot of  $[\text{ROH}]/k_{\text{obs}}$  against  $[\text{ROH}]$  as required by Baker and Gaunt's mechanism.

It is obvious that hydrogen bonding can play an important and complex role in the mechanism of alcohol-isocyanate reactions. Previous attempts to account for hydrogen-bonding effects<sup>5,7,11</sup> in alcohol-alcohol and alcohol-solvent complexes appear to be inadequate. The present results bring to light a marked difference between the effects of hydrogen bonding involving self-association of the alcohol (or glycol), intermolecularly or intramolecularly (cf. ethanol in benzene and tetraethylene glycol in dioxan), and those involving association with solvent (cf. ethanol and ethylene glycol in dioxan). The problem of a comprehensive mechanism which accounts satisfactorily for hydrogen-bonding effects is still to be resolved.

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<sup>9</sup> Uchida, Kurita, Koizumi, and Kubo, *J. Polymer Sci.*, 1956, **21**, 313.

<sup>10</sup> Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

<sup>11</sup> Baker, Davies, and Gaunt, *J.*, 1949, 24.