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The Kinetics of the Triethylamine-catalyzed Reaction of Diisocyanates with 1-Butanol in Toluene

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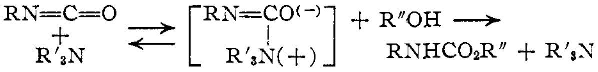
The kinetics of the triethylamine-catalyzed reactions of diisocyanates with 1-butanol were studied by a volumetric method. The data were treated by a method developed by Frost and Schwemer[5] for competitive consecutive second-order reactions. The rates of reaction of *m*-phenylene, *p*-phenylene, 2,4-tolylene, 2,6-tolylene, durene, 4,4′-diphenylmethane, 3,3′-dimethyl-4,4′-diphenylmethane and 1,6-hexamethylene diisocyanates and phenyl, *o*-tolyl and *p*-tolyl isocyanates were determined. Some experimental energies and entropies of activation were calculated. The relative effects of various substituent groups on the reactivity of an aromatic isocyanate function were determined from the rate data.

Introduction

Baker, *et al.*,[1] were the first to report a thorough investigation of the uncatalyzed and tertiary amine-catalyzed reactions of aromatic isocyanates with the hydroxyl function. The experimental results of the uncatalyzed reactions were verified by Dyer, *et al.*[2] The recent industrial interest in polyisocyanate modified polymers has resulted in the publication of many investigations concerning the reactions of the isocyanate function.[3]

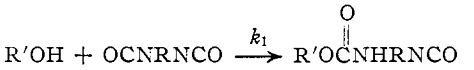
The mechanism of the tertiary amine-catalyzed reactions of aromatic isocyanates with alcohols proposed by Baker and Gaunt[1] follows the scheme



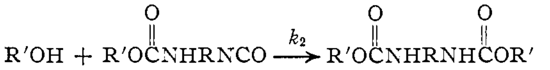
$$\begin{matrix} RN{=}C{=}O \\ + \\ R'_3N \end{matrix} \rightleftarrows \left[\begin{matrix} RN{=}CO^{(-)} \\ | \\ R'_3N(+) \end{matrix}\right] + R''OH \longrightarrow RNHCO_2R'' + R'_3N$$

The reaction was shown to be kinetically second order; first order with respect to each reactant. The magnitude of the over-all rate constant was reported to be directly proportional to the concentration of the tertiary amine catalyst.

It is assumed that the reaction of a diisocyanate with an alcohol proceeds by competitive consecutive second-order reactions through an intermediate urethano-isocyanate, as



$$R'OH + OCNRNCO \xrightarrow{k_1} R'O\overset{\overset{O}{\|}}{C}NHRNCO \quad (1)$$



$$R'OH + R'O\overset{\overset{O}{\|}}{C}NHRNCO \xrightarrow{k_2} R'O\overset{\overset{O}{\|}}{C}NHRNH\overset{\overset{O}{\|}}{C}OR' \quad (2)$$

The problem of competitive consecutive second-order reactions has been considered by several investigators.[4] Frost and Schwemer[5] were the first to integrate this kinetic system in terms of general variables for the special case of stoichiometrically equivalent amounts of the reactants A and B. The method of Frost and Schwemer is used in this paper to treat the data obtained from the reactions of the diisocyanates with 1-butanol.

Experimental Details

Materials and Purification.—The diisocyanates, with the exception of 2,6-tolylene diisocyanate,[6] were obtained from commercial sources and were distilled prior to use. Reagent grade 1-butanol was treated with sodium (10% by weight) and distilled. The triethylamine catalyst was refluxed over phthalic anhydride, distilled, refluxed over sodium and distilled from sodium prior to use. Reagent grade toluene, which was used as a solvent, was refluxed over sodium and distilled, and the dioxane which was used in the preparation of the non-aqueous titration reagents, was purified by the standard Fieser procedure.

Kinetic Method.—In a 100-ml. volumetric flask a solution of diisocyanate in toluene was prepared which was approximately 0.100 *M* with respect to the diisocyanate. The exact molarity of the solution was determined by withdrawing a 5-ml. aliquot of the diisocyanate solution and adding it to 10 ml. of di-*n*-butylamine–dioxane solution which was about 0.1500 *M* with respect to the di-*n*-butylamine. The excess di-*n*-butylamine was determined by titration with a perchloric acid–dioxane solution, which was about 0.0750 *M* with respect to perchloric acid, to a methyl red end-point.

In a second 100-ml. volumetric flask a 1-butanol–triethylamine–toluene solution was prepared. The molarity of the 1-butanol was exactly twice the molarity of the diisocyanate solution and the molarity with respect to triethylamine was approximately 0.0600 *M*. The exact molarity of the solution with respect to triethylamine was determined by titration of an aliquot with standard perchloric acid–dioxane solution to a methyl red end-point.

A kinetic run was initiated by adding 25 ml. of the diisocyanate solution to 25 ml. of the 1-butanol–triethylamine solution contained in a 100-ml. volumetric flask. The reaction mixture was thoroughly shaken and the time when half of the diisocyanate solution had been added was recorded as the start of the reaction. The reaction was followed by pipetting 5-ml. aliquots of the reaction mixture at recorded time intervals, adding them to 5-ml. portions of standard di-*n*-butylamine solution contained in 125-ml. erlenmeyer flasks, washing down the sides of the flasks with 20-ml. portions of dioxane and titrating the excess di-*n*-butylamine with a standard perchloric acid–dioxane solution to a methyl red end-point.

Mathematical Treatment of Kinetic Data.—The treatment of competitive consecutive second-order reactions developed by Frost and Schwemer for equivalent amounts of reactants *A* and *B* has been applied, as follows, to the reaction of certain diisocyanates with 1-butanol.

$$A + B \xrightarrow{k_1} C \qquad (3)$$

$$A + C \xrightarrow{k_2} D \qquad (4)$$

From equations 3 and 4 it follows that the differentials of *A* and *B* with respect to time are given by equations 5 and 6

$$dA/dt = -k_1AB - k_2AC \qquad (5)$$

$$dB/dt = -k_1AB \qquad (6)$$

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[1] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947); J. W. Baker and J. Gaunt, *ibid.*, 18, 27 (1949).

[2] E. Dyer, H. A. Taylor, S. J. Mason and J. Samson, THIS JOURNAL, **71**, 4106 (1949).

[3] Ferstandig and Scherrer, Paper presented before the Division of Petroleum Chemistry, American Chemical Society Meeting, April 12, 1956, in Dallas, Texas; M. E. Bailey, V. Kirss, R. G. Spaunburg, *Ind. Eng. Chem.*, **48**, 794 (1956); Symposium on Isocyanate Polymers, held by the Division of Paint, Plastics, and Printing Ink Chemistry, American Chemical Society Meeting, September, 1956, in Atlantic City, N. J.

[4] C. K. Ingold, *J. Chem. Soc.*, 2170 (1931); M. Ritchie, *ibid.*, 3112 (1931); F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942); D. French, THIS JOURNAL, **72**, 4806 (1950); S. Widequist, *Arkiv Kemi*, **8**, 325 (1955); W. G. McMillan, THIS JOURNAL, **79**, 4838 (1957).

[5] A. A. Frost and W. C. Schwemer, *ibid.*, **74**, 1268 (1952).

[6] A sample of pure 2,6-tolylene diisocyanate was generously supplied by Professor H. Kwart, University of Delaware.

where A, B and C represent the molar concentrations of the alcohol, the diisocyanate and the urethano-isocyanate, respectively. The dimensionless parameters in equation 7 are introduced to simplify the mathematics.

$$\alpha = A/A_0 \qquad \beta = B/B_0$$
$$\tau = B_0k_1t \qquad \kappa = k_2/k_1 \qquad (7)$$

where A_0 and B_0 are the initial concentrations of alcohol and diisocyanate, respectively.

Frost and Schwemer showed that the solution of the kinetic problem involves the evaluation of the integral in equation 8 for various values of the limit β and the parameter κ. In their paper[5] they presented two tables which

$$\tau = \frac{1 - \kappa}{1 - 2\kappa}\int_{\beta}^{1} \frac{d\beta}{\beta^2[1 + (1/1 - 2\kappa)\beta^{\kappa - 1}]} \qquad (8)$$

we have used to analyze our experimental data for values of κ and τ and from the relationships given in equation 7 we have calculated k_1 and k_2. One table contains values for τ as a function of κ and α, and the other table relates κ to the time ratio, the time ratio being the ratio of the times for certain fractions of a reactant to disappear.

Results

The experimental time ratios, used for the determination of κ, were obtained from a large scale plot of time *vs.* percentage reaction where the total percentage reaction was carried beyond 60. Figure 1 shows the plot obtained for the triethylamine-catalyzed reaction of 2,6-tolylene diisocyanate with 1-butanol in toluene at 39.69°. The data and calculations involved in a typical kinetic run are summarized in Table I.

TABLE I

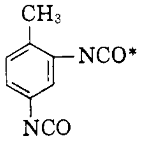
CALCULATION OF RATE CONSTANTS FOR THE TRIETHYLAMINE-CATALYZED REACTION OF 2,6-TOLYLENE DIISOCYANATE WITH 1-BUTANOL IN TOLUENE AT 39.69°

k_2 = 0.852/6.1 = 0.140 l.mole^{-1}min.$^{-1}$, A_0 = 0.1064 M, B_0 = 0.0532 M, [triethylamine] = 0.0313 M

Reacn., %	t, min.	Percentages compared	t ratio	$1/\kappa$	τ	k_1, l. moles^{-1} min.$^{-1}$
20	6.00	60/20	9.12	6.10	0.272	0.852
30	10.95	60/30	5.00	6.20	.497	.852
40	18.60	60/40	2.94	6.07	.839	.850
50	31.10	60/50	1.76	6.20	1.41	.854
60	54.70	50/20	5.18	6.10	2.47	.852
		50/30	2.84	6.10		
					Av.	0.852
			Av.	6.11		

By using identical conditions of reactant and catalyst concentrations and temperature, the results listed in Table II were obtained for several diisocyanates and a few monoisocyanates. Some of the reactions were carried out at 24.41° and the calculated energies and entropies of activation are also listed in Table II.

With the exception of 2,4-tolylene diisocyanate, the diisocyanates reported in Table II are structurally symmetrical, possessing two isocyanate groups of equal reactivity, so that treating their reactions with 1-butanol as competitive consecutive reactions is straightforward. However, the mathematical treatment of an unsymmetrical diisocyanate, such as 2,4-tolylene diisocyanate, is complicated by the diversity of molecular structures. In the case of 2,4-tolylene diisocyanate a thorough analysis would involve the reactivities of four different groups.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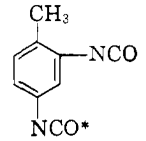
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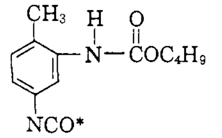
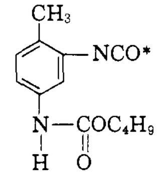

III


IV

The rate constants reported for 2,4-tolylene diisocyanate are approximations in that it was assumed that structures I and II have equal reactivities and that III and IV are equivalent.

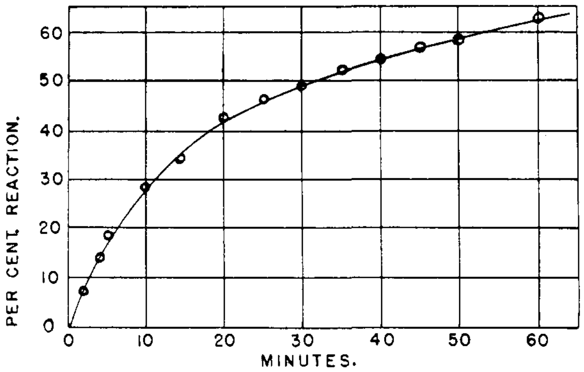


Fig. 1.—A percentage reaction *vs.* time (minutes) plot for the triethylamine-catalyzed reaction of 2,6-tolylene diisocyanate with 1-butanol in toluene at 39.69°.

Table II shows that with the exception of the aliphatic diisocyanate, 1,6-hexamethylene diisocyanate, one isocyanate function possesses an activating influence upon the other isocyanate function. With the exception of durene diisocyanate, where the steric requirements of the four methyl groups inhibit the normal interaction of the isocyanate groups, two isocyanate groups attached to the same benzene nucleus have a large activating influence on the reactivity of each other. The effect is so large that an ordinary second-order plot of the data shows a pronounced discontinuity around 50% reaction. The first and last parts of such a plot may be used to obtain approximate values of the two rate constants. The second-order plot of the hexamethylene diisocyanate reaction shown in Fig. 2 does not show any discontinuity around the point of 50% reaction, whereas other second-order plots in Fig. 2 show a very distinct break in continuity for 2,6-tolylene diisocyanate and a less pronounced break for durene diisocyanate.

The ratios of the rate constants, k_1/k_2, for 4,4′-diphenylmethane diisocyanate and 3,3′-dimethyl-4,4′-diphenylmethane diisocyanate are 2.91 and 2.36, respectively. These data show that a methylene bridge effectively isolates the two isocyanate functions and the introduction of an *o*-methyl group further reduces the influence of one

TABLE II

REACTION RATE CONSTANTS AND ENERGIES AND ENTROPIES OF ACTIVATION

Diisocyanate	k_1/k_2 39.69°	k_1, l. mole^{-1} min.$^{-1}$ 39.69°	k_1, l. mole^{-1} min.$^{-1}$ 24.41°	k_2, l. mole^{-1} min.$^{-1}$ 39.69°	k_2, l. mole^{-1} min.$^{-1}$ 24.41°	$\Delta E^{\ddagger}$, kcal.		$-\Delta S^{\ddagger}$, e.u.	
m-Phenylene	8.40	4.34	3.58	0.517	0.389	2.4	3.4	58.1	59.1
p-Phenylene	9.18	3.15	2.35	.343	.235	3.5	4.6	55.2	56.3
2,6-Tolylene	6.11	0.884	0.732	.143	.108	2.3	3.4	61.8	61.8
Durene	2.63	.0219		.0083					
4,4′-Diphenylmethane	2.91	.960		.33					
3,3′-Dimethyl-4,4′-diphenylmethane	2.36	.165		.070					
2,4-Tolylene	11.9	1.98	1.53	.166	0.123	3.1	3.6	57.4	60.7
1,6-Hexamethylene	2.00	0.0050		.0025					
Monoisocyanate									
Phenyl		0.406	0.315			3.1		60.7	
p-Tolyl		.210	.158			3.4		60.9	
o-Tolyl		.0655	.0458			4.3		61.4	

isocyanate group on the reactivity of the other isocyanate function.

Table III summarizes the effects which various substituents have on the reactivity of an isocyanate function attached to the same phenylene ring.

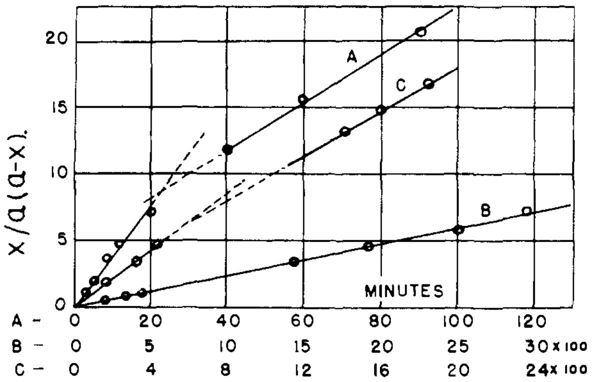


Fig. 2.—Second-order plots for the triethylamine-catalyzed reactions of 1-butanol with 2,6-tolylene diisocyanate (A), 1,6-hexamethylene diisocyanate (B) and durene diisocyanate (C) in toluene at 39.69°.

Since the diisocyanates have two groups of equal reactivity, one must make allowance for a statistical factor of two in comparing rates of the diisocyanates with rates of the monoisocyanates. It should be kept in mind that the effects reported here do not necessarily apply to conditions different from those used in the rate measurements.

TABLE III

EFFECTS OF VARIOUS SUBSTITUENTS ON THE REACTIVITY OF A PHENYLENE ISOCYANATE FUNCTION

Substituent group	Relative reactivity
m-Isocyanato	6–7
p-Isocyanato	4
o-Methyl	$^1/_4$–$^1/_6$
p-Methyl	$^1/_2$
m-Urethano	2
p-Urethano	1
Phenyl isocyanate reactivity = 1.0	

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[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Hydrogen Bond. III. The Effect of the Size of Substituents upon the Length of the Hydrogen Bond in Various Substituted 1,2-Diols

BY LESTER P. KUHN

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The bands due to free and internally bonded OH groups have been measured for various substituted ethylene glycols having the structures R_2COHCH_2OH, *meso* and racemic $(RCHOH)_2$, and $(R_2COH)_2$ where R is methyl, ethyl, isopropyl and *t*-butyl. In the racemic series of 1,2-disubstituted ethylene glycols, all of the compounds exist in the conformation which allows the OH groups to be *cis*. In the *meso* series, when R is a normal alkyl group the OH groups are again *cis* but when R is isopropyl the predominant conformation has the OH groups *trans*, and when R is *t*-butyl the conformation is exclusively *trans*. In each series of compounds increasing the steric requirements of R decreases the distance between the OH groups as indicated by an increase in $\Delta\nu$. Tetra-*t*-butylethylene glycol with a $\Delta\nu$ of 170 cm.$^{-1}$ has the strongest hydrogen bond of any diol thus far reported. It is suggested that the repulsion between the alkyl groups on the adjacent carbon atoms of the substituted glycol produces a deformation of the molecule which allows these groups to be farther apart and at the same time causes the OH groups to be brought closer together. The deformation may be either a decreasing of the O–C–C bond angles or a bending of the central C–C bond.

In previous papers[1] it was shown that diols which contain an intramolecular hydrogen bond show two OH bands when measured in dilute carbon tetrachloride solution, the higher frequency band being due to the free OH group and the lower frequency band to the bonded OH group. It was

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[1] (a) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952); (b) **76**, 4323 (1954).