

$B'_r = \sum_{i=0}^{i=r} A_i(T_r)^i$  where  $k = 1, 2, \dots, n - 1$  were fitted to the data by a least squares procedure. The fifth-order polynomial

$$B'_r = 12.091380 - 159.95107 T_r + 457.84870 T_r^2 - 562.84123 T_r^3 + 322.28864 T_r^4 - 70.717253 T_r^5 \quad (7)$$

where  $0.60 \leq T_r \leq 1.27$  satisfied the characteristics of the curve over the reduced temperature range  $T_r = 0.60$  up to  $T_r = 1.27$ . The average and maximum residuals, ( $B'_r$  obsd. -  $B'_r$  calcd.) are given below, and are probably well within the experimental accuracy of the data.

Average residual	0.011
Maximum residual	0.041

Table VIII gives the smoothed values of  $B'_r$  calculated from Equation 7.

$T_r$	$-B'_r$	$T_r$	$-B'_r$	$T_r$	$-B'_r$
0.60	4.36	0.85	1.87	1.10	1.03
0.65	3.68	0.90	1.62	1.15	0.91
0.70	3.09	0.95	1.43	1.20	0.81
0.75	2.59	1.00	1.28	1.25	0.73
0.80	2.18	1.05	1.15	1.27	0.72

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# Kinetics of Reaction of Certain Diisocyanates

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THE MOLECULAR structure of condensation polymers prepared from diisocyanates is substantially affected by the reactivity of the isocyanate groups and in particular by the difference in reactivity between the two isocyanate groups in an unsymmetrical diisocyanate.

In unsymmetrical diisocyanates the isocyanate groups react more independently the larger the difference in reactivity between the two groups; thus the reaction of each group can be controlled by an appropriate choice of conditions. The statistical randomness of the product which arises when symmetrical diisocyanates are used can thus be avoided.

As part of an experimental program on polyurethanes the reactivity of certain unsymmetrical diisocyanates with alcohol was determined.

## EXPERIMENTAL

**Rate Measurements.** The method used to determine the reactivities of the isocyanate groups was very similar to the one described previously by Bailey and coworkers (1). Chlorobenzene was used as the solvent, however, and a 10-fold excess of isoamyl alcohol was used to react with the

diisocyanate. In this method the rate of disappearance of the NCO-band at 4.5 microns in the infrared spectrum of the reaction mixture is measured. The infrared spectra were run in an air-conditioned room, which was maintained at about 21-3° C., but the reaction mixture itself in the absorption cell was not thermostated. Many spectral determinations were made, and the smooth curve drawn through the data was used in determining the pseudo first-order rate constants after the reaction had proceeded to the extent of about 10 to 20% and after approximately 70 to 80% reaction had occurred. Because the diisocyanates frequently were used as distilled from the reaction mixture without further purification, and because of the other inaccuracies of the procedure used, the rate constants were determined to only one significant figure.

The third column of Table I lists the half lives of the reaction estimated from data after 10 to 20% reaction had taken place. In the fourth column the half lives of the reaction estimated from data after 70 to 80% of the reaction had been completed are given. The last column lists the ratio of the two half lives. This ratio may be taken as a measure of the difference in reactivity of the two isocyanate groups of the unsymmetrical diisocyanate. Although the half lives are reported to only one significant figure,

Table 1. Relative Reactivities of Unsymmetrical Diisocyanates

Isocyanate	Isocyanate Concn., <i>M</i>	$\lambda^{1/2}$ , Min. 10-20% Reaction	$\lambda'^{1/2}$ , Min. 70-80% Reaction	$\frac{\lambda'^{1/2}}{\lambda^{1/2}}$
1-Phenoxy-2,4-phenylene diisocyanate	0.01	90	700	7
1-Phenoxy-2,4-phenylene diisocyanate	0.02	20	200	9
2,6-Dichloro-1,4-phenylene diisocyanate	0.01	10	300	24
2,6-Dichloro-1,4-phenylene diisocyanate	0.02	4	100	31
2-Nitro-1,4-phenylene diisocyanate	0.01	4	30	8
1- <i>tert</i> -Butyl-2,4-phenylene diisocyanate	0.02	20	200	9
$\beta$ -( <i>p</i> -Phenylisocyanato)ethyl isocyanate	0.02	20 <sup>a</sup>	70	4 <sup>a</sup>
$\beta$ -( <i>p</i> -Phenylisocyanato)butyl isocyanate	0.02	80	600	7
$\beta$ -Methyl- $\beta$ -( <i>p</i> -phenylisocyanato)propyl isocyanate	0.02	2 hr.	300 hr.	150

<sup>a</sup>Doubtful value because of experimental uncertainties.

the ratios of the half lives are reported to somewhat greater precision, because these ratios should be more reliable than the absolute values.

**Preparation of Diisocyanates.** All diisocyanates were prepared by phosgenation of the corresponding diamine hydrochlorides. The phosgene was obtained from the Matheson Co. 1,2,4-trichlorobenzene (Dow Chemical Co.), a generally useful solvent medium for the phosgenation of amine hydrochlorides, was used in most cases. The general success of the trichlorobenzene is probably due to its high boiling point. In some of the phosgenations *p*-chlorotoluene (Eastman White Label) was used as the solvent.

**Preparation of Diamines. 1-PHENOXY-2,4-DIAMINO BENZENE.** The compound was prepared by condensing 2,4-dinitrochlorobenzene (Matheson, Coleman, and Bell) with potassium phenolate (2), and reducing the dinitro compound with iron and hydrochloric acid.

**2,6-DICHLORO-1,4-DIAMINO BENZENE.** 2,6-Dichloro-4-nitroaniline (Antara Chemical Co.) was reduced with zinc and ammonium chloride (5).

**1-*tert*-BUTYL-2,4-DIAMINO BENZENE.** *tert*-Butylbenzene (Eastman White Label) was nitrated with mixed acid (6), and the resulting dinitro compound was reduced with iron and hydrochloric acid.

**1-AMINO-2-(*p*-AMINOPHENYL)-ETHANE (4).**  $\beta$ -Phenylethylamine (Fisher Scientific Co.) was acetylated with acetic anhydride. The amide was nitrated with mixed acid in the cold. The nitro amide was hydrolyzed with boiling hydrochloric acid solution and the free nitro amine was then reduced with hydrogen and Raney nickel to the diamine.

**1-AMINO-2-(*p*-AMINOPHENYL)-BUTANE (3).** *p*-Nitrobenzyl chloride (Eastman White Label) was condensed with the sodium salt of 1-nitropropane (Commercial Solvents) in absolute ethyl alcohol. The resultant dinitro compound was reduced with Raney nickel and hydrogen.

**1-AMINO-2-METHYL-2-(*p*-AMINOPHENYL)PROPANE.** This compound (3) was prepared by the procedure described above using 2-nitropropane as the reactant.

## DISCUSSION

Bailey, Kirss, and Spaunburgh (1) found the ratio of reactivities of the isocyanate groups in 1-chloro-2,4-phenylene diisocyanate to be about 3 to 1 and the ratio in 1-methyl-2,4-phenylene diisocyanate to be about 7 to 1. The ratio of reactivities of the isocyanate groups in 1-substituted-2,4-diisocyanates was expected to vary with the size of the ortho substituent. However, the reactivity

ratios for 2-nitro-1,4-phenylene diisocyanate, and 1-phenoxy- and 1-*tert*-butyl-2,4-phenylene diisocyanates were all in the range of 7-9 to 1. These data suggest a definite limit to the effectiveness of a single ortho substituent.

Of course, the electronegativity of the ortho substituent affects the rate of isocyanate reaction, but this effect is approximately the same for both isocyanate groups on the benzene ring. Thus, the ratio of reaction rates is primarily a function of the steric effect of the substituent group on the closer isocyanate radical.

Two ortho groups, as in 2,6-dichlorophenylene 1,4-diisocyanate, exert a large deactivating influence. Two larger ortho groups might exert an even larger influence.

In two cases, duplicate runs at two concentrations are given. The ratios of reactivities are nearly unchanged with concentration, but the half lives are not precisely related inversely to concentration as they should be for a true second-order reaction.

Because alkyl isocyanates are much less reactive than aryl isocyanates,  $\beta$ -(*p*-phenylisocyanato)ethyl isocyanate was expected to exhibit a large difference in reactivity, but surprisingly, did not.

Apparently the methylene groups exert only a small deactivating influence. By substituting alkyl groups on the  $\beta$ -carbon, the unsymmetry was greatly increased. Also, the reactivity of the *p*-NCO group was appreciably affected by the substitution. The half lives for the reactions of the primary, secondary, and tertiary alkyl isocyanate groups of the substituted  $\beta$ ,*p*-phenethyl isocyanates are seen to be 70 minutes, 600 minutes, and 300 hours, respectively. These are approximately in the ratios 1:10:300.

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