Reactivity of Organic Isocyanates

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HE growing commercial importance of the organic isocyanates, particularly in the field of polymers (2, 3), emphasizes the need for more abundant information on the reactivity of isocyanates as well as for simplified techniques for obtaining kinetic data on reactions involving these materials.

Dyer and others (β) have reported on the rates of reaction of phenyl isocyanate with 1- and 2-butanol and have reviewed the literature on kinetics of reactions involving isocyanates. Brown and Dyson (4) have shown the effect of substituents on the reactivity of aryl isothiocyanates.

The present paper describes a simple spectroscopic method for obtaining kinetic data on reactions involving the isocyanate group and presents data on the effect of ring substituents on the reactivity of aromatic mono- and diisocyanates with 2-ethylhexanol. Data are also presented on the reactivity of tolylene diisocyanate and a hydroxyl-terminated adipic acid-diethylene glycol polyester of the type used for making flexible polyurethane foams and elastic polyurethanes of the Vulcollan type.

EFFECT OF SUBSTITUENTS ON REACTIVITY OF AROMATIC MONOISOCYANATES WITH 2-ETHYLHEXANOL

Materials. The monoisocyanates used for this study were prepared by reaction of the corresponding amines with phosgene according to the procedure of Siefken (?). The amine solution in toluene or monochlorobenzene was added to the phosgene solution in the same solvent and the phosgenation was completed by bubbling in phosgene during the heat-up of the reaction mixture to reflux. The excess phosgene was removed by purging with nitrogen or carbon dioxide, the solvent was stripped, and the isocyanates were isolated by vacuum distillation. Physical properties of isocyanates are shown in Table I.

Table I. Physical Properties of Monoisocyanates

	Boiling Range, ° C.	
Compound	Found	Literature (7)
Phenyl isocyanate p-Nitrophenyl isocyanate m-Chlorophenyl isocyanate o-Tolyl isocyanate p-Tolyl isocyanate	111-113/195 mm. 141-144/13-14 mm. 74-76/8.5 mm. 64-65/9 mm. 68-69/10.5 mm.	166/760 mm. 138/11 mm. 83.6/10.5 mm. 63.2-63.4/9.5 mm. 67.6-67.8/10 mm.

The purity of all isocyanates was checked by titration with dibutylamine and found to be in excess of 99.0%.

2-Ethylhexanol (Union Carbide and Carbon Corp.) was used without further purification.

Experimental Method for Determination of Isocyanates. The intense absorption of infrared radiation at the wave length of 4.5 microns caused by the isocyanate group in a molecule (δ) provides a simple method for plotting the course of a reaction. Two samples of an isocyanate of equal size are weighed out and dissolved in benzene to give 0.04N solutions. One of the solutions serves as a standard, s; 0.4 mole of 2-ethylhexanol is added to the other solution in the volumetric flask and the volume is made up to the calibration mark with benzene. This is the reaction mixture, r. After a thorough shaking, samples of both solutions are placed in approximately 0.1-mm. cells and the infrared spectrum is scanned from 4 to 5 microns using a Baird Model B spectrophotometer at slow scan with 2X slits. The absorption

band gives the transmittance, T (in per cent), of the solution by constructing a base line tangent to the shoulders of the band (Figure 1).

$$\% T = \frac{T_1}{T_0} \times 100$$
 (1)

The % T is converted to the absorbance by the expression

 $\frac{A_1}{A_2}$

$$A = 2 - \log\left(\% T\right) \tag{2}$$



absorption band of isocyanate group The absorbance, A_s , of the standard solution (equal to that of the reaction mixture at the start of reaction) constitutes the zero point. The concentration of unreacted isocyanates is determined from the absorbance A_r , of the reaction solution after the lapse of a certain time interval, and A_s , by the formula:

Concentration of unreacted isocyanate =

$$\frac{1}{2} \times 0.04 = \frac{\log \frac{(T_0)}{(T_1)_r}}{\log \frac{(T_0)}{(T_1)_s}} \times 0.04$$
 (3)

Sufficient readings at proper time intervals were taken to give adequate data for studies of reaction rate. The same pair of cells was used throughout and without removing the sample from the cell until the reaction study was completed. The cells were always

removed from the instrument between runs and kept at a constant temperature $28^{\circ} \pm 1^{\circ}$ C. As a final step, the standard solution was returned to the cell and a check result obtained on zero point absorbance. This served to verify the consistency of instrument performance when it is necessary to run the experiment over an interval of several days. Results on determination of isocyanate strength by this infrared method were compared with those obtained by titration with dibutylamine in some separate experiments. It was found that the maximum deviation was less than 2%. (Precautions were taken to eliminate moisture throughout the investigation.)

Results. To compare the reactivity of the listed isocyanates, a plot of logarithms of isocyanate concentrations (unreacted isocyanates) as calculated from Formula 3 vs. time was constructed (Figure 2).

First-order reaction rate constants were calculated for individual points of the run and averaged, from the formula $K_1 = \frac{2.303}{t} \log \frac{b}{b-x}$, where b is the initial and b-x is the equilibrium concentration of isocyanate in moles per liter, and time t is in seconds. The data are presented in Table II.

In the case of *p*-nitrophenyl isocyanate, the isocyanate was practically all consumed in 15 minutes; no data could be obtained from which a reliable rate constant could be calculated.

Table II. First-Order Reaction Rate Constants of Monoisocyanates

Compound	$K_1 \times 10^4,$ Sec. $^{-1}$
m-Chlorophenyl isocyanate Phenyl isocyanate p-Tolyl isocyanate o-Tolyl isocyanate	$7.65 \\ 1.09 \\ 0.66 \\ 0.088$

Discussion. Reactions between isocyanates and alcohols are second-order processes (6). In the present study the processes were made to assume approximately first-order kinetics by use of a substantial excess of alcohol for convenience of comparison. The data show clearly the effect of nitro- and chloro-groups in increasing reactivity, and the effect of methyl groups in inhibiting This is in agreement with the results of Baker and Holdsit. worth (1), who investigated the reaction of isocyanates with methanol in the presence of triethylamine as catalyst, and found the order of reactivity to be p-nitrophenyl isocyanate >> phenyl isocyanate > p-tolyl isocyanate. The reaction of isocyanates with alcohols is apparently of electrophylic character and a mechanism already proposed for phenyl isocyanate (1) is consistent with these results. However, there is no very great autocatalytic effect due to the urethanes formed as products of the reactions.

The steric effect of the *o*-methyl group appears unusually strong. The technical consequences of this are important, since utility for isocyanates becomes possible in applications where an uninhibited isocyanate group would be too reactive. The effect bears some similarity to so-called "blocked" isocyanates, except that the problem of disposal of the blocking molecule is not encountered.



Figure 2. Effect of substituents on reactivity of monoisocyanates with 2-ethylhexanol at 28° C.



In order to gain some understanding of the influence of the alcohol, it seems worth while to compare the present data with results obtained by Dyer (θ) on the reaction of phenyl isocyanate with 1- and 2-butanol. For data at about the same temperature (25° to 28° C.), second-order constants for three alcohols vs. phenyl isocyanate are as follows:

Alcohol	Constant \times 10 ⁴ , L. Mole ⁻¹ Sec. ⁻¹
2-Butanol 2-Ethyl-1-hexanol 1-Butanol	${1.54 \atop 2.73^a \atop 4.61}$

 a Second-order reaction rate constant was calculated for individual points of the run and averaged; from the formula

$$K_{1} = \frac{2.303}{t(a-b)} \log \frac{b}{a} \frac{(a-x)}{(b-x)}$$

where a is the initial and (a - x) is the equilibrium concentration of 2-ethylhexanol in moles per liter; other symbols are the same as stated previously.

Again steric factors apparently have important effects and the results, relatively, appear to be reasonable.

Considerable opportunity is available for control of speed of reactions of isocyanates with alcohols by variations in structure of both the alcohol and the isocyanate.

EFFECT OF SUBSTITUENTS ON REACTIVITY OF AROMATIC DIISOCYANATES WITH ALCOHOLS

Materials and Experimental Results. The diisocyanates used in this study were made from the corresponding diamines by the method described above. Because of the need for higher reaction temperatures in the phosgenation, o-dichlorobenzene was used as solvent in several cases. The low solubility of 4,4'-diaminodiphenylsulfone in common organic solvents necessitated adding this diamine to the phosgene solution in the form of a fine suspension. All diisocyanates, except 4,4'-sulfonylbis (phenyl isocy-

anate), were isolated by vacuum distillation. Physical properties are given in Table III. Analysis of the products by titration with dibutylamine showed purities of 99% or higher.

In addition to the study of reaction rates of various diisocyanates with 2-ethylhexanol, one experiment was run using tolylene diisocyanate (mixture of 80% 2,4 and 20% 2,6 isomer) and a polyester of diethylene glycol and adipic acid (hydroxyl number 57, acid number 1.6, average molecular weight 1900). The curve illustrating the kinetics of this reaction is shown in Figure 3.

All initial reaction mixtures, with the exception of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, were 0.02M with respect to diisocyanate and 0.4M with respect to 2-ethylhexanol. The concentration of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate had to be reduced to 0.002 mole per liter because of poor solubility, and the concentration of 2-ethylhexanol was reduced to 0.04 mole per liter.

As the calculated rate constants from the experimental data indicated that this reaction was of the first order, the curve representing the kinetics of that reaction has been shifted up to the higher concentration range for comparison with the other diisocyanates.

4,4'-Sulfonylbis (phenyl isocyanate) reacted so fast with 2-ethylhexanol that the reaction was almost completed in 10 minutes, and no adequate data were obtained for calculation of the reaction rate constant.

Discussion. As was the case with the monoisocyanates, diisocyanate reactions in these experiments might be expected to follow first-order kinetics, because of a substantial excess of 2-ethylhexanol. However, substantial deviations were found in the case of many of the diisocyanates (Figure 3).

		Boiling or Melting Range, ° C.	
		Found	Literature (7)
	NCO		
<i>m</i> -Phenylene diisocyanate	-NCO	108/15 mm.	104-106/12 mm.
p-Phenylene diisocyanate	OCN-NCO	107-109/10 mm.	110–112/12 mm.
1-Chloro-2,4-phenylene diisocyanate		128–129/10 mm.	122-124/11 mm.
2,4-Tolylene diisocyanate		120/10 mm.	124-126/18 mm.
2,6-Tolylene diisocyanate		101-103/6 mm.	129–133/18 mm.
Tolylene diisocyanate 60/40 ⁴	CH3 CH3	118-120/10 mm.	• • • •
3,3'-Dimethyl-4,4'-biphenylene diisocyanate	OCN	195–197/5 mm.	160-170/0.5 mm.
3,3'-Dimethoxy-4,4'-biphenylene diisocyanate	OCH_{3} OCH_{3} OCN OCH_{3} OCH_{3} OCH_{4} OCH_{3}	218-220/2.2 mm.	200–210/0.5 mm.
2,2',5,5'-Tetramethyl-4,4'-biphenylene diisocyanate	OCN-CH1 CH1	177-180/2.3 mm.	••••
4,4'-Methylenebis (phenyl isocyanate)	$0CN - CH_2 - CH_2 - NCO$	180-182/3 mm.	170/0.2 mm.
4,4'-Methylenebis (2-methylphenyl isocyanate)		200-202/3.5 mm.	• • • •
4,4'-Sulfonylbis (phenyl isocyanate)b	0CN	Melting range 153-5	154
^a Mixture of about 60% 2.4- and 40% 2.6-isomer. I. b A small sample for reaction rate studies was purifie	someric ratio was determined by infrared analysis. ed by high vacuum sublimation.		

Table III. Physical Properties of Diisocyanates

The second isocyanate group in a particular molecule evidently exerts a substantial influence on the reactivity of the first. Both phenylene diisocyanates show greater reactivity than phenyl isocyanate and both show significant decrease in slope of the rate curve, while phenyl isocyanate does not. On the basis of the data in Table IV it appears that an isocyanate group meta or para to another exerts about a sixfold increase in the (initial) rate "constant," meta being slightly more active than para. As the reaction proceeds, the urethane group presumably becomes the influencing group. It is evidently less activating than isocyanate and exerts a lesser effect in the para than in the meta position. In the case of 1-chloro-2,4-phenylene diisocyanate the isocyanate groups are further activated by the chlorine group.

Inductive effects of the isocyanate group as well as steric effects of the methyl group are apparent in the case of 2,4-tolylene diisocyanate. 2,4-Tolylene diisocyanate shows less initial reactivity than *m*-phenylene diisocyanate. In accordance with the knowledge of the reactivities of *p*- and *o*-tolyl isocyanates it is apparent that the isocyanate group in the 4 position makes a greater contribution to the rate of reaction in the early stage. After somewhat less than 50% of the 2,4-tolylene diisocyanate than that of *m*-phenylene diisocyanate, demonstrating the

steric effect of the *o*-methyl group, similar to the effect shown for *o*-tolyl isocyanate. 2,6-Tolylene diisocyanate shows decline in reactivity as reaction proceeds and the assumption is that this is due to the appearance of urethane in place of isocyanate as the activating group. The speed is higher than that of *o*-tolyl isocyanate, because of activating effects.

In the case of 4,4'-methylenebis (phenyl isocyanate) there is evidence of change in "rate constant" as isocyanate is consumed.

Table IV. First-Order Reaction Constants for Aromatic Diisocyanates at Various Degrees of Reaction Isocyanate Reacted. %

	190035	mate reace	004, 70
	10	50	90
	K	\times 10 ⁴ , Sec.	-1
p-Phenylene diisocyanate	5.7	3.7	1.6
<i>m</i> -Phenylene diisocyanate	6.0	4.4	2.5
1-Chloro-2 4-nhenvlene diisocvanate	13	9.1	4.3
4.4'-Methylenebis (2-methylphenyl isocyanate)	0.11	0.11	0.10
3.3'-Dimethoxy-4.4'-biphenylene diisocyanate	0.10	0.11	0.09
2.2',5.5'-Tetramethyl-4.4'-biphenylene			
diisocvanate	0.11	0.08	0.08
Phenyl isocyanate	1.2	1.1	1.1
2 4-Tolylene diisocyanate	2.0	1.2	0.22
2.6-Tolylana diisocyanate	0.8	0.32	0.18
3.3'-Dimethyl-4.4'-binhenylene diisocyanate	0.20	0.15	0.12
4 4'-Methylenebis (phenyl isocyanate)	1.7	1.3	0.9
x, x ======; ===========================			



Figure 3. Reactivity of aromatic diisocyanates with 2-ethylhexanol and diethylene glycol adipate polyester

- C. D.

- E.F.G.H.I.J.K.L.
- I-Chloro-2,4-phenylene diisocyanate
 m-Phenylene diisocyanate
 p-Phenylene diisocyanate
 4,4'-Methylenebis (phenyl isocyanate)
 2,4-Tolylene diisocyanate (60 % 2,4-isomer, 40 % 2,6-isomer)
 2,6-Tolylene diisocyanate
 3,3'-Dimethyl-4,4'-biphenylene diisocyanate
 4,4'-Methylenebis(2-methylphenyl isocyanate)
 3,3'-Dimethyl-4,4'-biphenylene diisocyanate
 2,2', 5,5'-Tetramethyl-4,4'-biphenylene diisocyanate
 2,0', 2,4- and 20% 2,6-isomer of tolylene diisocyanate with diethylene glycol adipate polyester

Some inductive effect is suggested for the second isocyanate group as well as for that assumed for the urethane group which is formed, which is largely offset by the deactivating influences of the p-methylene group.

Deviation from linearity in the plots of log concentration vs. time in the cases of the slow diisocyanates is only very slight.

The steric effects (which in these cases affect both isocyanate groups symmetrically) appear to outweigh any activating influence the isocyanate groups exert on each other. 4,4'-Methylenebis (2-methylphenyl isocyanate) is less reactive than 4,4'methylenebis (phenyl isocyanate) to about the same extent as is o-tolyl isocyanate compared to phenyl isocyanate. 2,2', 5,5'-tetramethyl-4,4'-biphenylene diisocyanate is about as much slower than 3,3'-dimethyl-4,4'-biphenylene diisocyanate as p-tolyl isocyanate is slower than phenyl isocyanate.

On the basis of analogies such as these, it is possible to construct from the data on mono- and diisocyanates a table of the

Table V.	Relative Effects of Substituent Groups	on
	Isocyanate Reactivity	

Substituent Group	Approximate Relative Effect
Sulfone (para)	>50
Nitro (para)	>35
Chlorine (meta)	7
Isocyanate (meta or para)	6
14,4'-Methylenebis (phenyl isocyanate) (average)]	1.3
Phenyl isocyanate	1.0
Methyl (meta or para)	0.5
Methyl (ortho)	0.08
Methoxy (ortho)	0.04

relative effects of substituents on reactivity expressed as first-order rate constants of isocyanate groups (Table V). The numerical assignments are presented as possessing tentative predictive and associative values. Simple benzene derivatives can apparently be handled reasonably accurately. Rate constants for diphenylmethane derivatives probably could not be predicted as accurately; however, good approximations should be obtained. The effects of two isocyanate groups located in separate rings of a biphenyl system on each other is not provided by the table. Nevertheless it should be possible to make some prediction of relative effects in this system by using, for example, 3,3'dimethyl-4,4'-biphenylene diisocyanate as a base.

The influence of the urethane group was not measured directly, but its effect can be deduced from the rate constants for the two phenylene diisocyanates, calculated for the final phases of the reaction (Table IV) where urethane groups predominate. It would appear that the urethane group is activating to about a twofold magnitude when meta or para to the isocyanate group, meta showing slightly greater activity. In the reaction of the polyester with tolylene diisocyanate the relative effects are consistent, although the reaction is much slower than with 2 ethylhexanol.

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Corrections

In the article entitled "Sizing Pipe for Flow of Cellulose Acetate Solutions" [F. L. Symonds, A. J. Rosenthal, E. H. Shaw, IND. ENG. CHEM. 46, 2463 (1954)], Equation 10 on page 2464 should read

$$D\Delta p/4L = 32q\mu/\pi D^3$$

In the article entitled, "Stearato Chromic Chloride" [R. K. Iler, IND. ENG. CHEM. 47, 766 (1955)]. U. S. Patent number in literature cited (5) on page 769 should be

U. S. Patent 2,307,045