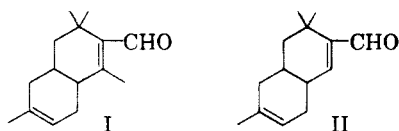


there is evidence that sometimes the *cis*-isomer absorbs at longer wave length in spite of steric interactions. For example, in ethanol, angelic acid has λ_{\max} 215.5 μ , whereas tiglic acid has λ_{\max} 212.5 μ .⁸ In *n*-heptane, *cis*-piperylene has λ_{\max} 226 μ , whereas *trans*-piperylene has λ_{\max} 223 μ , and the same order is found in the vapor phase.⁹

In contrast to our observations, the wave length displacement between compounds I and II is only



5 μ ,¹⁰ and the displacement between 1-vinylcyclohexene (λ_{\max} 230 μ) and 2-methyl-1-vinylcyclohexene (λ_{\max} 233 μ) is only 3 μ .¹¹ In the former set of data, the structures have, however, been assigned only tentatively, and both sets of data are not recent. We, therefore, consider it probable that some of these spectral data are in error.

EXPERIMENTAL

Spectra were determined by standard methods on a Unicam SP 500 or Beckman DU spectrophotometer. The purification of the compounds, the absorption intensity values, and the spectral curves will be described separately in a fuller discussion of the relevant compounds.

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Near Infrared Studies. Rate Constants for the Alcohol/Aryl Isocyanate Reaction

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In the near infrared spectrum (14,300–4000 cm^{-1}) are found the overtone and combination frequencies of the OH, NH, CH, and SH fundamental stretching vibration. In a recent paper, we have shown that this region can be used to reveal the presence of an intramolecular hydrogen bond in aryl allophanates and biurets.¹ Similarly, the ki-

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netics of the alcohol/isocyanate reaction can be studied by using the near infrared spectrum to follow the course of the reaction.

Davis and McC. Farnum² were the first to study the relative reactivity of phenyl isocyanate with lower aliphatic alcohols. The kinetics of the tertiary amine catalyzed reaction of aromatic mono-isocyanates with methanol were studied by Baker and Holdsworth.³ They showed that the reaction of an alcohol with phenyl isocyanate follows second order kinetics. Baker and Gaunt⁴ studied both the base-catalyzed and uncatalyzed reactions of phenyl isocyanate with lower alcohols in di-*n*-butyl ether and in benzene and have obtained kinetic evidence for the mechanism of this reaction.

EXPERIMENTAL

Materials. Every effort was made to exclude water from the solvent and reactants in order to keep hydrolysis to a minimum. Ethyl alcohol was dried by the method of Fieser.⁵ Eastman Kodak phenyl, *p*-tolyl, and *o*-tolyl isocyanate and Du Pont toluene-2,4-diisocyanate and toluene-2,6-diisocyanate were carefully redistilled into preflamed 10-ml. glass ampoules and sealed under dry nitrogen. A reagent grade of carbon tetrachloride was used without further purification. Triethylamine was purified by distillation over lithium aluminum hydride into ampoules and sealed under dry nitrogen.

Spectrophotometric method. The intense absorption of near infrared radiation at a wave length of approximately 6750 cm^{-1} caused by the NH group of a carbanilate provides an excellent method for following the rate of reaction between ethyl alcohol and an aryl isocyanate. The rate of increase of carbanilate formed from the alcohol/isocyanate reaction was noted by the increase in absorption at 6750 cm^{-1} at regularly timed intervals. Measurements were made in a 10.0-cm. quartz cell using the Cary Spectrophotometer model No. 14. The instrument was provided with a thermostatically controlled cell holder and was held at $28 \pm 0.2^\circ$.

The concentration of carbanilate at time t was determined from the absorption $\log I_0/I$ by the Beer-Lambert formula where $\log I_0/I$ is the intensity of absorption, L is the length of the cell in centimeters, c is the concentration of carbanilate in moles per liter, and e is the molar absorptivity.

$$\log I_0/I = eLc \quad (1)$$

The molar absorptivity for ethyl carbanilate (I), ethyl-4-methylcarbanilate (II), ethyl-2-methylcarbanilate (III), ethyl-3-isocyanato-4-methylcarbanilate (IV), and ethyl-3-isocyanato-2-methylcarbanilate (V) was obtained from the slope of the straight line by plotting $\log I_0/I$ against concentration of carbanilate. A typical plot is shown in Fig. 1. The strong polar effect of ethyl alcohol upon the absorption of radiation by the NH group and, therefore, upon the molar absorptivity for the carbanilates was taken into consideration in the following manner. A sufficient quantity of ethyl alcohol was present in each solution of carbon tetrachloride and carbanilate (representing a point on the straight

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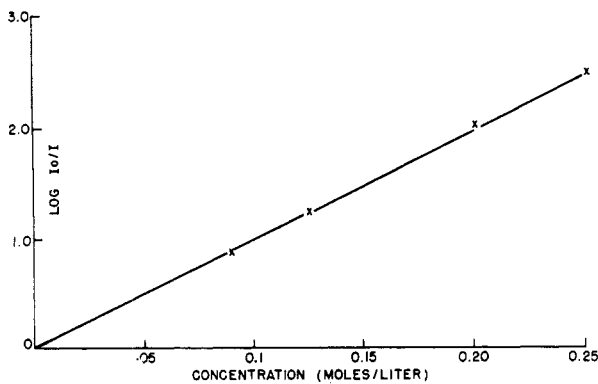


Fig. 1. Plot of $\log I_0/I$ vs. the concn. of ethyl carbanilate in CCl_4 and ethyl alcohol at $28 \pm 0.2^\circ$

line) to maintain a total molarity of 0.250. The values of e were found to be 0.985, 1.116, 0.820, 1.109, and 0.809 for I-V, respectively.

The rate constants were calculated from the customary second order rate expression (2 and 3) for equal and unequal reactant concentrations, where a is equal to the initial concentration of ethyl alcohol, b is equal to the initial concentration of isocyanate, and x is the concentration of carbanilate at time t .

$$k = 1/t \frac{x}{b(b-x)} \quad (2)$$

$$k = 1/t \frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)} \quad (3)$$

The second order rate constants are listed in Table I and Table II and Figs. 2, 3, and 4.

TABLE I

RATE CONSTANTS FOR THE BASE CATALYZED REACTION OF AN AROMATIC ISOCYANATE WITH ETHYL ALCOHOL IN CARBON TETRACHLORIDE AT $28 \pm 0.2^\circ$

No.	R	Reaction		Relative Reactivity
		$(\text{C}_2\text{H}_5)_3\text{N} \times 10^2$ Moles/Liter	$\text{K} \times 10^4$ Liter, Mole $^{-1}$ Sec. $^{-1}$	
1	H	7.2	43.30	1.0
2	<i>p</i> -CH ₃	7.2	18.42	0.47
3	<i>o</i> -CH ₃	7.2	5.16	0.118

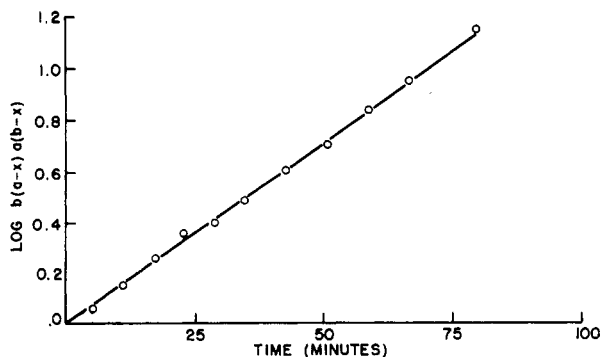


Fig. 2. Second order rate plot for phenyl isocyanate with ethyl alcohol in CCl_4 catalyzed by triethylamine at $28 \pm 0.2^\circ$.

TABLE II

RATE CONSTANTS FOR THE UNCATALYZED REACTION OF AROMATIC ISOCYANATES WITH ETHYL ALCOHOL IN CARBON TETRACHLORIDE AT $28 \pm 0.2^\circ$

No.	R	R'	Reaction	
			$\text{K} \times 10^4$ Liter, Mole $^{-1}$ Sec. $^{-1}$	Relative Reactivity
1	H	H	2.50	1.0
2	2-CH ₃	5-NCO	10.70	4.0
3	2-CH ₃	3-NCO	2.46	0.98

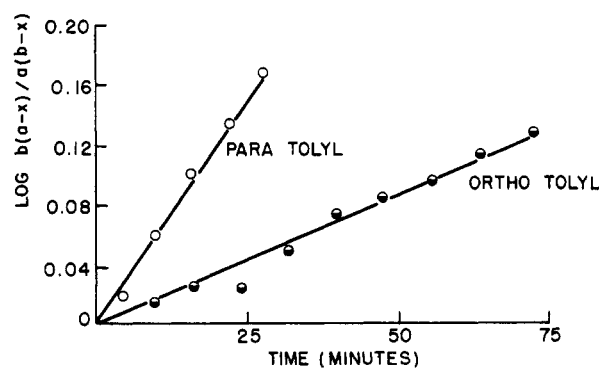


Fig. 3. Second order rate plot for *o*- and *p*-tolylisocyanate with ethyl alcohol in CCl_4 catalyzed with triethylamine at $28 \pm 0.2^\circ$.

The second order plot for the triethylamine catalyzed reaction of phenyl, *p*-tolyl, and *o*-tolyl isocyanate was good up to 70–96% completion of the reaction, *e.g.*, Fig. 2. The second order plot for the uncatalyzed reaction of toluene-2,4-diisocyanate with ethyl alcohol resulted in a straight line up to approximately 60% of reaction. Several workers^{6,7} have shown that the two isocyanato groups of toluene-2,4-diisocyanate differ in reactivity by a factor of ten. Isolation studies by Arnold and Simons⁸ have unequivocally shown that the 4-isocyanato group of toluene-2,4-diisocyanate reacts faster toward aniline than the 2-isocyanato group. Therefore we have assumed that the 2-isocyanato group does not react in sufficiently high rate to interfere with our calculations for obtaining a rate constant for the 4-isocyanato group.

On the other hand the two isocyanato groups of toluene-2,6-diisocyanate are equivalent in reactivity and this was taken into consideration in the calculation of the rate constant. A linear rate plot was obtained only up to 30% of reaction. This is due to the fact that ethyl-3-isocyanato-2-methyl carbanilate is five times less reactive than toluene-2,6-diisocyanate.⁹

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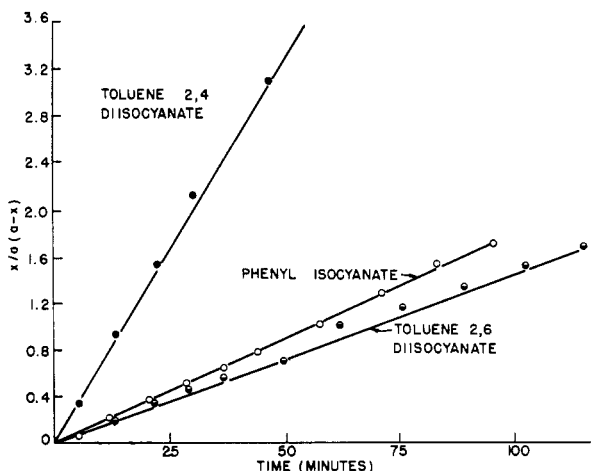


Fig. 4. Second order rate plot for phenyl isocyanate, toluene-2,4, and 2,6-diisocyanate with ethyl alcohol in CCl_4 at $28 \pm 0.2^\circ$.

Solutions. For a kinetic run involving triethylamine as the catalyst (a) 100 ml. of 0.5 molar absolute ethyl alcohol and 0.072 molar triethylamine in carbon tetrachloride and (b) 100 ml. of 0.250 molar of phenyl, *o*-, or *p*-tolyl isocyanate in carbon tetrachloride were prepared at $28 \pm 0.2^\circ$. For an uncatalyzed run (c) 100 ml. of 0.250 molar absolute ethyl alcohol in carbon tetrachloride and (d) 100 ml. of 0.250 molar toluene-2,4- or 2,6-diisocyanate or phenyl isocyanate in carbon tetrachloride were made up at $28 \pm 0.2^\circ$.

For a typical kinetic measurement 50 ml. of solution (a) or (c) and 50 ml. of (b) or (d) were mixed at 28° and this mixture used to fill a 10.0-cm. quartz cell. The time at which the two solutions were mixed was taken as t_0 .

DISCUSSION

The order of reactivity of the second order rate constants for the triethylamine-catalyzed reaction of phenyl, *p*-tolyl, and *o*-tolylisocyanate with ethyl alcohol is 1.0:0.47:0.118 (Table I). Thus the presence of a methyl group para or ortho to an isocyanato group, decreases the rate to one half and one eighth, respectively, of the value obtained for the unsubstituted phenyl isocyanate.

The deactivating influence of a methyl group upon an isocyanato group is also revealed by the results in Table II. The second order rate constant for the first isocyanato group of toluene-2,6-diisocyanate is less than the second order rate constant for the 4-isocyanato group of toluene-2,4-diisocyanate by a factor of approximately 4.8.

The influence of an isocyanato group meta to another was not measured directly, but its effect can be deduced from the rate constant data in Tables I and II, assuming that triethylamine has the same accelerating effect on each of the alcohol/aryl isocyanate reactions. The electron releasing methyl group para to an isocyanato group (*e.g.*, *p*-tolylisocyanate) decreases the rate of reaction by a factor of approximately 2 (Table I, Nos. 1 and 2). The introduction of an isocyanato group into the 2-position of 4-isocyanato-toluene (to give toluene-2,4-diisocyanate) leads to a fourfold increase in the rate of reaction of the 4-isocyanato group when compared to phenyl isocyanate (Table II, Nos. 1 and 2). Therefore, the electron activating effect of a meta-isocyanato group (toluene-2,4-diisocyanate *vs.* *p*-tolylisocyanate) increases the rate of reaction of an isocyanato group (para NCO) with ethyl alcohol by a factor of 8. The same results are obtained when the relative reactivity of *o*-tolylisocyanate and toluene-2,6-diisocyanate are compared (Table I, Nos. 1 and 3 and Table II, Nos. 1 and 3). Recently, Burkus and Eckert obtained a factor of 7 for the electron activating effect of a meta-isocyanato group.¹⁰

CONTRIBUTION No. 246

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