the total liquid distillate which was obtained from the vinylation of pentaerythritol in aqueous base. The mixture was heated at 137–166° for a period of 4 hr. in a magnetically stirred reactor while acetylene gas (34 g.; 1.31 moles) was pressed into the solution at a pressure of 250–470 p.s.i.g. Distillation afforded in addition to 24 g. of ethyl vinyl ether, 85 g. of a liquid product mixture and 25 g. of a brown solid residue. The liquid product mixture was separated into eleven liquid fractions (total wt. 82 g.) by distillation under reduced pressure; boiling range, 90°/0.75 mm. to 68°/0.09 mm.; n_{D}^{25}, 1.4659–1.4881. Examination of the fractions by vapor phase chromatography showed that each consisted of a mixture of three components, two in major amounts and one in trace quantities. To be certain that vinylation was complete, the fractions were combined, dissolved in 1,2-dimethoxyethane, treated with a catalytic amount of sodium methoxide and heated in the presence of acetylene for 20 hr. as described above. Again, the three compounds which could not be separated by distillation were obtained. On cooling, the tetravinyl ether of pentaerythritol (V) was precipitated from the mixture. The compound was removed by filtration and recrystallized from ethanol, m.p. 47–49°. It was demonstrated to be the major product in the mixture (estimated to be present to the extent of about 60–70%) by a vapor phase chromatographic comparison. Further precipitation of V could be induced by seeding and by the addition of ethanol to the product mixture; however, complete separation could not be effected in this manner. The infrared spectrum of V (melt) exhibited intense absorption at 1634, 1615, 1197, and 1082 cm.$^{-1}$ (vinyl ether) and did not contain absorption bands ascribable to hydroxyl or acetal functions.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39; mol. wt., 240.3; hydrolyzable aldehyde, 16.6 meq./g. Found: C, 64.72; H, 8.28; mol. wt. (ebullioscopic in acetone), 251; hydrolyzable aldehyde, 16.5 meq./g.

The tetravinyl ether V absorbed 4 moles of hydrogen quantitatively over platinum oxide at room temperature under atmospheric pressure. It absorbed bromine readily and polymerized vigorously in the presence of boron trifluoride etherate to give a solid, highly cross-linked polymer.

Hydrogenation of the products of the complete vinylation of pentaerythritol. A mixture of the products of the complete vinylation of pentaerythritol was examined by infrared spectroscopy and vapor phase chromatography. The infrared spectrum (liquid) did not exhibit hydroxyl absorption; the vapor phase chromatogram showed three components, one corresponding to about 60–70% of the mixture (previously shown to be the tetravinyl ether of pentaerythritol), one corresponding to approximately 30–40% of the mixture, and one in trace amounts.

Anal. Found: hydrolyzable aldehyde, 13.4 meq./g.; vinyl ether, 12.8 meq./g.; hydroxyl number, 25.

A portion of the mixture (52.1 g.) absorbed 0.67 mole of hydrogen over platinum oxide (0.5 g.) at room temperature under 4–30 p.s.i.g. pressure.

Hydrolysis of the saturated product mixture. The hydrogenation catalyst was removed by filtration and the filtrate was heated under gentle reflux with 200 ml. of 5.0*M* hydroxylamine hydrochloride solution for 7.25 hr. The layers were separated and the aqueous layer was washed with several portions of ether. The ether washes were combined with the organic layer and the solution was dried over anhydrous sodium sulfate. The ether was removed by distillation at atmospheric pressure, and the product mixture, which showed two VPC peaks with an approximate area ratio 7:3, was separated by distillation under reduced pressure. The tetraethyl ether of pentaerythritol (VI) boiled at 63–65° (0.3 mm.), n_{D}^{25} 1.4196, yield 27.3; reported b.p. 83° (5 mm.).[13]

Anal. Calcd. for $C_{13}H_{28}O_4$: C, 62.90; H, 11.30. Found: C, 63.11; H, 11.19.

The diethyl ether of pentaerythritol (III) had a b.p. of 92–94° (0.25 mm.), n_{D}^{25} 1.4465, yield 11.8 g.; reported b.p. 115° (5 mm.).[13] The infrared spectrum (liquid) exhibited both strong hydroxyl (3400 and 1050 cm.$^{-1}$) and ether (1090–1130 cm.$^{-1}$) absorption.

Anal. Calcd. for $C_9H_{20}O_4$: C, 56.22; H, 10.49. Found: C, 56.57; H, 10.26.

The di-3,5-dinitrobenzoate ester of III was synthesized, m.p. 123–125°. A mixture melting point with the di-3,5-dinitrobenzoate ester previously prepared from the hydrogenation product of II was undepressed. The infrared spectra of the two derivatives were superimposable.

Several experiments were necessary to establish conditions under which complete hydrolysis of the vinyl ether and acetal functions would occur. During one experiment in which only partial hydrolysis was effected by means of 5% hydrochloric acid, a small amount of pentaerythritol, m.p. *ca.* 260°, was isolated from the concentrated aqueous phase.

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[CONTRIBUTION FROM THE RESEARCH CENTER, UNITED STATES RUBBER COMPANY]

Catalysis of Isocyanate Reactions. II. Pyridine *N*-Oxide Catalysis

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Received June 12, 1961

Pyridine *N*-oxide is an effective catalyst for the reaction of phenyl isocyanate with butanol-1. The rate is directly proportional to the pyridine *N*-oxide concentration. Pyridine *N*-oxide does not catalyze the phenyl isocyanate–phenol reaction appreciably. Pyridine *N*-oxide in combination with an alkylene oxide causes the trimerization of phenyl isocyanate.

The triethylamine catalysis of the reaction of phenyl isocyanate with alcohols,[1a–] phenol,[1b] and mercaptans[2a,b] has been published. This paper reports some observations concerning the catalysis of isocyanate reactions with pyridine *N*-oxide.

EXPERIMENTAL

Conventional published procedures were used in the preparation of reactants and solvents. The kinetic method has been described previously.[3]

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Bisdiethylaminomethane catalysis of the reaction of phenyl isocyanate with 2-mercaptoethanol. A solution of 8.0 g. (0.102 mole) of 2-mercaptoethanol and 4 drops of bisdiethylaminomethane in 50 ml. of dry toluene was stirred and 11.0 g. (0.093 mole) of phenyl isocyanate was added dropwise over a ten minute period. After 24 hours the product which precipitated was collected and recrystallized from benzene. The product (yield 15.5 g., 84.2%) melted at 71–72°. The reported[2b] m.p. of 2-hydroxyethyl thiocarbanilate is 72–74°.

Trimerization of phenyl isocyanate. A solution of 5.5 g. of phenyl isocyanate in 50 ml. of dry toluene was treated with 0.25 g. of pyridine *N*-oxide. After 24 hours the precipitate was separated and recrystallized from ethanol. The product (5.0 g. yield) melted at 280–282°. The reported[4] m.p. of 1,3,5-triphenylisocyanurate is 280°.

RESULTS AND DISCUSSION

Alcohol reaction. The very strong electron donor character of amine oxides has been described previously.[5a–d] It has been shown that triethylamine *N*-oxide can displace triethylamine in the following reaction[5c]:

$$(C_2H_5)_3NO + (C_2H_5)_3NSO_3 \longrightarrow (C_2H_5)_3NOSO_3 + (C_2H_5)_3N \quad (1)$$

demonstrating the more powerful electron donor character of amine *N*-oxides. The calculations of Barnes[6] show a high charge density on the oxygen atom of pyridine *N*-oxide indicating a strong electron donor character.

The above discussion would indicate strong catalysis by amine *N*-oxides provided the mechanism of base catalysis involve the activation of the isocyanate through the formation of a base-isocyanate complex[1a–c] rather than the activation of the alcohol through a base-alcohol complex.[2b] The weaker basic character of the amine *N*-oxides would give weak base-alcohol interactions.

The calculated second order rate constants for the triethylamine, pyridine, and pyridine *N*-oxide catalyzed reactions of phenyl isocyanate with butanol-1 are listed in Table I. The pK_a's of the catalysts are included. The data demonstrate dramatically the important role the nucleophilicity[1c] plays in determining the catalytic activity. Pyridine *N*-oxide and triethylamine exhibit comparable catalytic activities, although triethylamine is 10^{10} more basic. Pyridine *N*-oxide is 6.6 times more effective than pyridine, while pyridine is 10^5 times more basic. The data clearly favor a catalytic mechanism involving activation of the isocyanate through a catalyst-isocyanate complex.

It has been shown previously[1c] that the rate of the triethylamine catalyzed reaction of phenyl isocyanate with butanol-1 in toluene is not directly proportional to the base concentration. The nonlinearity was attributed to strong alcohol-amine interactions. If the observed nonlinearity is the result of strong alcohol-amine interactions, then linearity between catalyst concentration and rate should be observed in the case of pyridine *N*-oxide catalysis. The very weak basic character of the catalyst precludes any strong interaction with alcohols even in toluene. The results of a series of phenyl isocyanate reactions with butanol-1 at varying pyridine *N*-oxide concentrations are shown in Fig. 1. Linearity between catalyst concentration and rate is apparent. These results support the mechanism of tertiary amine catalysis advanced previously.[1c]

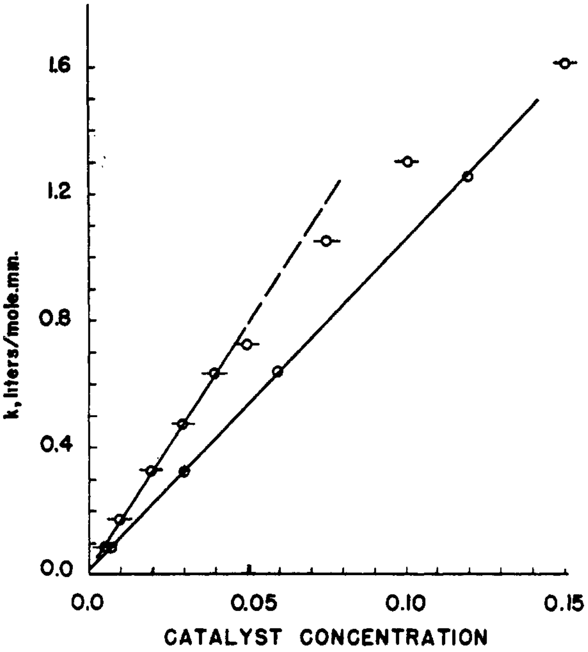

Fig. 1. Effect of catalyst concentration on the calculated second-order rate constant for the reaction of phenyl isocyanate with butanol-1 in toluene at 39.7°

-o- Triethylamine cat., phenyl isocyanate conc. = butanol-1 conc. 0.1050*M*

○ Pyridine *N*-oxide cat., phenyl isocyanate conc. = butanol-1 conc. 0.2005*M*

TABLE I

RATE CONSTANTS FOR THE CATALYZED REACTION OF PHENYL ISOCYANATE WITH BUTANOL-1 IN TOLUENE AT 39.7°
(Catalyst conc. = 0.0600*M*)

Catalyst	pK_a	k_2(l./mole^{-1}/min.$^{-1}$)
Triethylamine	10.76[a]	0.675[c]
Pyridine	5.29[c]	0.0966[d]
Pyridine *N*-oxide	0.73[b]	0.640[d]

[a] C. C. G. Calvenor, *Rev. of Pure and Appl. Chem. (Australia)*, **3**, 83 (1953). [b] H. H. Jaffe and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955). [c] Phenyl isocyanate conc. = butanol-1 conc. ≅ 0.10 M. [d] Phenyl isocyanate conc. = butanol-1 conc. ≅ 0.20 M.

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Phenol, thiophenol, and mercaptan reactions. The extreme sensitivity of the phenol[1b] and mercaptan[2a,b] reactions, relative to alcohols, toward strong tertiary amine catalysis suggests a change in catalytic mechanism. Phenol interacts very strongly with strong bases in a non-polar medium.[7a,b] It has been estimated that the phenol-trimethylamine complex possesses about 10% ionic character.[7b] Thiophenol and thio alcohols form ionic compounds with strong tertiary amines.[8]

The preceding discussion strongly suggests that in the case of the more acidic reactants—such as phenol, thiophenol, and thio alcohols—the catalysis with strong amines involves activation of the active hydrogen compound through a base complex which possesses a degree of ionic character. In support of this thesis the very weak base, pyridine *N*-oxide, does not catalyze the reaction of phenyl isocyanate with phenol in toluene, whereas the reaction is very strongly catalyzed by triethylamine (Table II). This mechanism of catalysis also is supported by the higher catalytic activity observed with pyridine relative to pyridine *N*-oxide.

TABLE II

THE CATALYZED REACTIONS OF PHENYL ISOCYANATE WITH PHENOL AND THIOPHENOL IN TOLUENE AT 39.7°

Catalyst	Cat. Conc.	k_2 (l. Mole^{-1} min.$^{-1}$) × 10^2 Phenol	Thiophenol
Pyridine *N*-oxide	0.0600 M.	0.007[a]	—
Pyridine	0.044 M.	0.13[b]	—
Triethylamine	0.045 M.	280[c]	345[c]

[a] Phenyl isocyanate conc. = phenol conc. ≅ 0.20 M.
[b] Phenyl isocyanate conc. = phenol conc. ≅ 0.06 M.
[c] Phenyl isocyanate conc. = phenol conc. = thiophenol conc. ≅ 0.10 M.

Bisdiethylaminomethane, a very strong base, does not appreciably catalyze the reaction of phenyl isocyanate with butanol-1.[1c] This strong base, however, does catalyze the reaction of phenyl isocyanate with a thio alcohol as the above-mentioned catalytic mechanism would predict. Thus, the sole product from a reaction of phenyl isocyanate with 2-mercaptoethanol catalyzed by bisdiethylaminomethane was 2-hydroxyethyl thiocarbanilate. This is the same product obtained when the reaction is catalyzed with diethylcyclohexylamine.[2b]

The paradox between relative acidity of phenol and thiophenol in water and their triethylamine catalyzed reactivities with phenyl isocyanate in toluene (Table II) deserves comment. The dissociation constant of thiophenol is more sensitive to the dielectric constant of the solvent than is that of phenol.[9] The dissociation constant of thiophenol decreases a thousandfold in going from water to 60% ethanol-water, whereas for phenol the decrease is only sixfold. In a low dielectric solvent (cyclohexane) the phenol-trimethylamine complex is more stable than the thiophenol-trimethylamine complex.[7a] Thus, the published data indicate that the degree of ionic character of the phenol-triethylamine complex is greater than is that of the thiophenol-triethylamine complex in solvents of low dielectric constant such as toluene. The observed greater reactivity of thiophenol relative to phenol in the triethylamine catalyzed reactions with phenyl isocyanate is due to the superior nucleophilicity of the thiophenoxide ion.

Trimerization of phenyl isocyanate. It has been reported[10] and independently observed in this laboratory[11] that the combination of a tertiary amine and an alkylene oxide catalyzes the trimerization of phenyl isocyanate. Pyridine *N*-oxide in combination with propylene oxide also catalyzes the trimerization of phenyl isocyanate.

Acknowledgment. The author acknowledges his indebtedness to Drs. C. F. Eckert and R. H. Ewart of this laboratory for continued advice, active interest, and encouragement. Some of the experimental work was ably performed by Mr. J. E. Wells.

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