ously do not occur on the surface of the selenium as they do in the case of platinum and palladium because reducing the amount of selenium did not affect the yield. In fact in the last experiment in Table II all the selenium was in "solution" and the reaction mixture was homogeneous.

Although these studies are not far enough advanced as yet to warrant speculation regarding mechanism, it does appear probable that in many respects selenium attack is analogous to oxygen attack. Reactions involving formation of hydroperselenides and diselenides and cleavage of these to form radical intermediates appear to be important steps.

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[CONTRIBUTION FROM THE HOUDRY LABORATORIES, HOUDRY PROCESS CORP.]

The Catalytic Effects of 1,4-Diaza[2.2.2]bicyclooöctane for Isocyanate Reactions

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The reaction of phenyl isocyanate with either water or 2-ethylhexanol is of the first order with respect to the catalyst concentration, the isocyanate concentration and the water or alcohol concentration. When the 2-ethylhexanol is present in large excess over the phenyl isocyanate, the catalytic effect of triethylenediamine decreases with increasing alcohol concentration while the rate of the uncatalyzed reaction increases. In a solvent-free system the catalytic effect disappears entirely. When either dioxane or benzene is used as a solvent, the reaction of phenyl isocyanate with 2-ethylhexanol is about three times greater than with water. The kinetics of the catalyzed reaction is compatible with the mechanism postulated by Baker and co-workers, but there are other possible mechanisms that cannot be excluded. Comparison of the catalytic activity of triethylenediamine with triethylamine, N,N'-dimethylpiperazine and N-ethylmorpholine shows that it is, respectively, 4.3, 5.3 and 17.3 times greater for the reaction between phenyl isocyanate and 2-ethylhexanol in benzene and 2.7, 2.8 and 5.5 times greater for the reaction between phenyl isocyanate and water in 1,4-dioxane.

The two main reactions of isocyanate group involved in the production of polyurethan foams are the reactions of the isocyanate groups with organic hydroxyl groups and water. The first of these reactions is responsible for chain growth, while the second causes chain extension and provides the carbon dioxide necessary for the foaming.

The kinetics of the reaction with hydroxyl group in the presence of a variety of tertiary amine catalysts has been studied by Baker, Bailey, Dyer, Ephraim and others.[1-7] However, there is very little information on the reaction of isocyanates with water.

In practical tests, it was found that 1,4-diaza-(2.2.2)bicyclooöctane, also called triethylenediamine, is an excellent catalyst in the preparation of polyurethan foams[8,9] and therefore it appeared of interest to collect quantitative data on the activity of this tertiary amine for catalyzing isocyanate reactions in the model system phenyl isocyanate–2-ethylhexanol–water.

The purpose of this paper is to show that triethylenediamine has an unusually high catalytic effect on the reactions in this system.

Experimental

Materials.—Phenyl isocyanate (Fisher certified reagents) and 2-ethylhexanol-1 (Eastman Kodak Co., practical) were fractionally distilled under reduced pressure prior to use. Spectro grade benzene (Eastman Kodak Co.) was refluxed, distilled and stored over calcium hydride. 1,4-Dioxane (Union Carbide Chemicals Co.) was refluxed with sodium until the metal became shiny, doubly distilled from sodium and stored over calcium hydride. A peroxide test on the pure material proved to be negative. DABCO-grade diazabicyclooöctane of the Houdry Process Corp. was purified by sublimation. The product used was of 99.8% purity. The other tertiary bases used, triethylamine (Pennsalt Chemical Corp.), N,N'-dimethylpiperazine and N-ethylmorpholine (Union Carbide Chemicals Co.) were fractionally distilled prior to use.

Procedure.—Stock solutions were prepared by weighing out the correct amount of material and diluting to the proper level using volumetric flasks. Whenever possible, a dry-box was used in effecting transfers.

Reaction mixtures were prepared by adding the desired amount of tertiary base and alcohol to a flask, diluting with solvent short of the calibration mark and adding the proper amount of phenyl isocyanate solution to make up to the mark.

The reaction flasks were stoppered with rubber caps so that samples could be withdrawn at the proper time interval with a hypodermic syringe. The reaction flasks were thermostated with a water-bath at 23°. A few experiments were also carried out at 47°.

A Perkin-Elmer, model 12, infrared spectrometer was used to measure the optical density of the isocyanate peak. Samples withdrawn from the reaction flask were placed in a cell, and the spectrum was scanned in the 4.5 μ region.[5] When the isocyanate peak was reached the time was noted.

Calibration data showed an almost linear correlation between optical density at 4.33 μ and isocyanate concentration. None of the solvents or reaction products was found to interfere with isocyanate analysis.

Calculation of the Rate Constants.—The rate constants (k_0 and k_2 for the catalyzed and uncatalyzed reactions, respectively) were calculated on the basis of simple second-order kinetics. In the case of the reaction with water, it was assumed that the rate is controlled by the reaction of phenyl isocyanate with one mole of water to form phenyl-

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(1) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 9, 19, **27** (1949).

(2) J. W. Baker and J. B. Holdsworth, *ibid.*, 713 (1947).

(3) J. Burkus and C. F. Eckert, THIS JOURNAL, **80**, 5948 (1958).

(4) J. W. Baker, M. M. Davies and J. Gaunt, *J. Chem. Soc.*, 24 (1949).

(5) M. E. Bailey, V. Kirss and R. G. Spaunburgh, *Ind. Eng. Chem.*, **8**, 794 (1956).

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

(7) S. Ephraim, A. E. Woodward and R. B. Mesrobian, *ibid.*, **80**, 1326 (1958).

(8) W. E. Erner, A. Farkas and P. W. Hill, in the course of publication.

(9) R. D. Aylesworth, R. H. Boehringer, D. T. Moore and M. H. Smith, *Modern Plastics*, 145 May (1958).

carbamic acid which after rapid decarboxylation to aniline reacts with a second mole of phenyl isocyanate.

Results

Reaction of Phenyl Isocyanate with 2-Ethylhexanol.—This reaction was followed in benzene and dioxane and found to correspond to second-order kinetics in both solvents in accordance with the theory of Baker and co-workers.[1,2] Figure 1 shows the effect of the triethylenediamine concentration in benzene. Similar data were obtained also in dioxane. The rate constants calculated for various catalyst concentrations are summarized in Table I which also includes the catalytic constant k_c calculated from the relation

$$k_2 = k_0 + k_c(C) \qquad (1)$$

where (C) is the catalyst concentration and k_0 the rate constant for the uncatalyzed reaction.

TABLE I

REACTION BETWEEN PHENYL ISOCYANATE AND 2-ETHYLHEXANOL

Temp., °C.	Solvent	Reactant concn., mole/l. TED.[a] (C)	C_6H_5·NCO	C_8H_{17}-OH	k_2, l./mole hour	$\frac{k_2 - k_0}{(C)}$
23	Benzene	0.00	0.073	0.073	0.144	..
23	Benzene	.0014	.073	.073	7.8	5480
23	Benzene	.0035	.073	.073	19.2	5450
23	Benzene	.0070	.073	.073	39.0	5580
23	Dioxane	.00	.073	.073	0.02	..
23	Dioxane	.0014	.073	.073	2.16	1530
23	Dioxane	.0035	.073	.073	4.9	1400
23	Dioxane	.0070	.073	.073	10.3	1470
47	Benzene	.0	.073	.073	0.60	..
47	Benzene	.0014	.073	.073	15.8	10900
23	Benzene	.0014	.036	.036	10.8	..
23	Benzene	.0014	.072	.072	9.1	..
23	Benzene	.0014	.144	.144	8.2	..
23	Benzene	.00	.073	.62	1.35	..
23	Benzene	.0014	.073	.62	2.70	970
23	Benzene	.00	.073	.70	1.34	..
23	Benzene	.0014	.073	.70	2.54	860
23	Benzene	.00	.073	1.96	3.00	..
23	Benzene	.0014	.073	1.96	2.80	..
23	None	.00	.073	5.74	3.6	..
23	None	.0014	.073	5.74	3.45	..

[a] TED = triethylenediamine.

The rate constants for the uncatalyzed and catalyzed triethylenediamine reactions at 47° are also given in Table I. The temperature dependence corresponds to an activation energy of 11.1 and 5.5 kcal./mole for the uncatalyzed and catalyzed reactions, respectively.

At 23°, additional runs were also carried out with equimolar concentrations of the alcohol and the isocyanate at 0.036 and 0.144 molar concentration. Again, the second-order kinetics was found to be valid. The corresponding rate constants are summarized in Table I. While the constants decrease somewhat with increasing reactant concentration, they are compatible with the second-order mechanism as expected from the theory developed by Baker and co-workers.[1,2]

The effect of increasing excess alcohol concentration on the triethylenediamine-catalyzed reaction is shown by the second-order velocity constants listed in Table I together with the corresponding rate constants for the uncatalyzed reaction. The striking decrease in the rate constant of the catalyzed reaction and increase in the rate constant of the uncatalyzed reaction by increasing alcohol concentration is worth noting. Since the difference of these two types of rate constants is characteristic of the rate constant due to the catalyst alone, it is readily seen that 0.0014 *M* triethylenediamine has no effect at alcohol concentrations exceeding one molar.

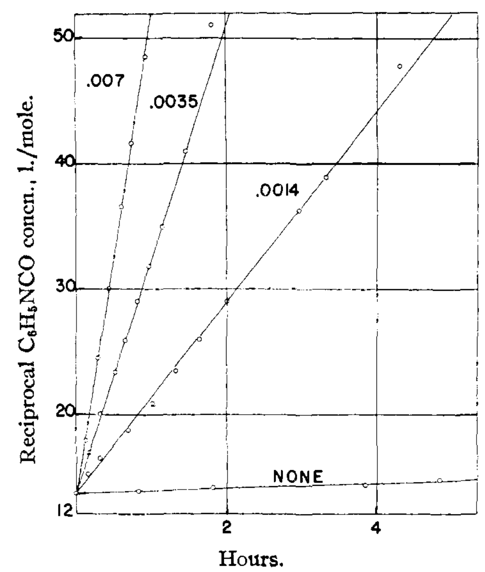

Fig. 1.—Reaction of phenyl isocyanate (0.073 *M*) with ethylhexanol (0.073 *M*) in benzene at 23° in the presence of diazabicycloöctane. The numbers indicate the concentration of diazabicycloöctane in moles/liter.

Since data on other amines were required for sake of comparison, rate constants for the reaction between phenyl isocyanate and ethylhexanol were also measured in the presence of 0.0014 *M* triethylamine, 1,4-dimethylpiperazine and N-ethylmorpholine. These amines were chosen since they resemble structurally triethylenediamine and have basicities covering pK_B from 3.3 to 6.5. From the data summarized in Table II, it will be seen that the catalytic activity of triethylenediamine is, respectively, 4.3, 5.3 and 17.3 times that of the mentioned amines. The higher activity of triethylenediamine is of particular significance in view of the fact that the amines tested included amines of basicity higher and lower than that of triethylenediamine.

TABLE II

REACTION BETWEEN C_6H_5NCO (0.073 *M*) AND $C_8H_{17}OH$ (0.073 *M*) AT 23° IN BENZENE

	Effect of the amine catalyst pKb	k_2, l./mole hour	(0.0014 *M*) $\frac{k_2 - k_c}{(C)}$
Triethylenediamine	5.40	7.8	5480
Triethylamine	3.36	1.9	1260
1,4-Dimethylpiperazine	5.71	1.56	1020
N-Ethylmorpholine	6.49	0.58	315

Reaction of Phenyl Isocyanate with Water.—Since no kinetics data were available on the amine-catalyzed reaction between isocyanates and water, the order of the reaction had to be first established. Figure 2 shows the progress of this reaction

Table III

Reaction of Phenyl Isocyanate with Water at 23°

Solvent	C_6H_5NCO, mole/l.	H_2O, mole/l.	Catalyst	Concn. (C) mole/liter	k_2, l./mole hr.	$\frac{k_2 - k_0}{(C)}$
Benzene	0.059	0.029	Triethylenediamine	0.0000	0.23	..
Benzene	.059	.029	Triethylenediamine	.0014	2.16	1380
Benzene	.059	.029	Triethylamine	.0014	0.78	390
Dioxane	.072	.036	Triethylenediamine	.0000	.006	..
Dioxane	.072	.036	Triethylenediamine	.0014	.64	4500
Dioxane	.072	.036	Triethylenediamine	.0035	2.2	6280
Dioxane	.072	.036	Triethylenediamine	.0070	4.3	6180
Dioxane	.072	.036	Triethylamine	.0014	0.24	1670
Dioxane	.072	.036	N,N'-Dimethylpiperazine	.0014	.23	1600
Dioxane	.072	.036	N-Ethylmorpholine	.0014	.12	820
Dioxane	.036	.018	Triethylenediamine	.0014	.72	..
Dioxane	.144	.072	Triethylenediamine	.0014	.64	..
Dioxane	.073	.072	Triethylenediamine	.0014	.86	..
Dioxane	.073	.144	Triethylenediamine	.0014	.62	..

in dioxane at 23° in the absence and presence of triethylenediamine. It will be noted that after half of the isocyanate has reacted, the reaction tends to proceed faster than compatible with second-order kinetics. The possible reason for this acceleration will be discussed below.

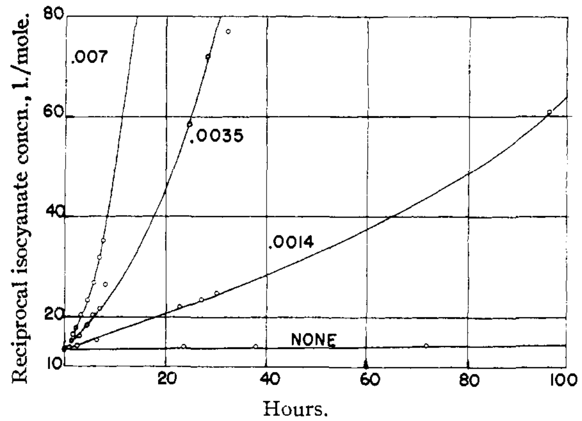

Fig. 2.—Reaction of phenyl isocyanate (0.0726 *M*) with water (0.036 *M*) in dioxane at 23°. The numbers indicate the concentration of diazabicyclooctane in moles/liter.

The initial rate constants for these runs and the corresponding catalytic constants are summarized in Table III. Again, it will be noted that the triethylenediamine-catalyzed reaction is about four times faster in benzene than in dioxane and that the catalytic constant for triethylenediamine is four to seven times larger than that for the other amines.

In order to ascertain the true order of the reaction, rate measurements for the triethylenediamine-catalyzed reaction were extended to lower and higher initial reactant concentrations and to reaction mixtures containing two and four times the equivalent water concentration. These runs yielded the initial rate constants summarized in Table III. The relatively small variation of these constants is taken as indication that the reaction progress between phenyl isocyanate and water is in satisfactory agreement, at least in its initial stages, with second-order kinetics.

A comparison of the rate constants for the two reactions studied in the two solvents used shows that the rate for the water reaction is about one-third of that for ethylhexanol for the triethylenediamine-catalyzed system in both solvents and for the uncatalyzed system in dioxane.

Discussion

The most striking point in this study is the relatively high activity of triethylenediamine for the isocyanate reaction when compared with the activity of other amines. In order to find an explanation for this observation, it will have to be considered in the light of the mechanism applicable to these reactions. Since on the basis of the present experiments and experiments of others it is not possible to decide the true nature of the isocyanate catalysis, we shall assume tentatively for the sake of this discussion that Baker's mechanism is valid.

According to Baker's mechanism, the rate of the catalyzed reaction will depend on the concentration of the amine complex and on the specific velocity constant for the reaction which involves this complex and the alcohol (or water in the case of the second reaction studied). Since triethylenediamine is free from steric hindrance and the nitrogen atoms are readily accessible to the reactants, it is very readily seen that the complex formation between this molecule and an isocyanate molecule takes place more readily than with an amine having carbon–nitrogen bonds capable of free rotation around the nitrogen atom, thereby sterically hindering the close approach of another molecule. Related to the postulate of the higher stability of the triethylenediamine–isocyanate complex as compared with a similar complex of other tertiary amines is the observation of Brown and Eldred[10] on the formation of quaternary alkyl derivatives of quinuclidine, $CH(C_2H_4)_3N$, a compound similar to triethylenediamine, but containing only one bridgehead nitrogen atom. The authors found that certain quaternary salts of quinuclidine formed fifty to seven hundred times faster than the corresponding derivatives of triethylamine.

It is significant that the affinity of an amine for a proton is not necessarily a measure of that amine's ability to complex with a molecule such as phenyl isocyanate because the proton, being much smaller than the isocyanate, is not greatly influenced by

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[10] H. C. Brown and N. R. Eldred, This Journal, **71**, 445 (1949).

steric factors. Thus, the higher stability of unhindered amine–isocyanate complexes will not be shown by measurement of the basicity of the amine toward a proton.

An increased catalytic activity of the sterically unhindered triethylenediamine could also be expected even if the concentration of its complex were not larger than the concentration of the hindered amine complex, provided the velocity constant for the reaction involving this complex is larger than that involving the complex formed from the hindered amines.

As far as the mechanism of the water–isocyanate reaction is concerned, there is no reason to assume that this reaction occurs according to a mechanism different from the one operative in the reaction with the alcohol. The observed increase in the second-order rate constant during the reaction might be due to a catalytic effect of the ureides formed in this reaction; it is planned to check into this point.

Acknowledgment.—The authors are indebted to Dr. G. A. Mills and Mr. J. B. Maerker for their interest in this work. The infrared measurements were carried out by A. E. Creamer.

MARCUS HOOK, PENNA.

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Abnormal Beckmann Rearrangement of Spiroketoximes in Polyphosphoric Acid

BY RICHARD K. HILL AND ROBERT T. CONLEY[1]

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The Beckmann rearrangement of spiroketoximes having the spiro atom alpha to the oxime carbon has been carried out under various conditions. Using thionyl chloride or phosphorus pentachloride, most yielded mixtures of the normal lactam product and the product of a "second-order" cleavage, an unsaturated nitrile. The rearrangement of spirocyclopentanone oximes in polyphosphoric acid led in high yield to bicyclic α,β-unsaturated ketones, which were shown to result from acid-catalyzed cyclization of the unsaturated nitriles. Under these conditions, spirocyclohexanone oximes yielded, besides α,β-unsaturated ketones, small amounts of lactams and larger quantities of saturated amides. Spiro-[cyclopentane-1,2′-pseudo-indoxyl] oxime was cleaved by polyphosphoric acid to cyclopentanone and anthranilamide.

Among the classes of ketoximes which undergo "abnormal" reactions when subjected to Beckmann rearrangement conditions are those completely substituted at an α-carbon atom; these oximes often cleave to unsaturated nitriles or to mixtures of olefin and nitrile.[2,3] A striking feature of the reaction is the dependence of its course upon the particular reagent employed. α-Phenylisobutyrophenone oxime, for example, rearranges to dimethyl phenylacetanilide with hydrogen chloride in acetic acid, but is cleaved by thionyl chloride to benzonitrile and α-methylstyrene.[2j] Pivalophenone oxime yields three different products,[2b,4] depending on the reagent: hydrogen chloride in acetic acid yields pivanilide, benzenesulfonyl chloride in alkali produces *t*-butylbenzamide, and phosphorus pentachloride cleaves the molecule to benzonitrile. The situation is complicated, of course, by the geometrical isomerization of many oximes in either acidic or alkaline media.[5] Brown and co-workers[4] have explained the results with pivalophenone oxime by showing that a preliminary isomerization of the oxime is likely in the hydrogen chloride reaction, while the propensity of phosphorus pentachloride to cause scission is probably due to the very rapid dissociation of the oxime chlorophosphate. In general, aryl sulfonyl chlorides in alkali or pyridine have been the preferred reagents for effecting the normal rearrangement of these oximes.[3a,b] Whether polyphosphoric acid (PPA), which was shown to suppress many of the other abnormal reactions of oximes,[6] also brings about normal rearrangement of oximes of this type is not known, except for one case recently reported by Bruson and co-workers.[3d]

An interest in the preparation of some simple spiroamines led us to investigate the rearrangement of the oxime of spiro[4,5]decanone-1 (Ic) with different reagents in the hope of finding conditions which might lead to the lactam IIb.[7] The results obtained were interesting enough that several related ketones (Ia–e) were prepared and their oximes rearranged.[8]

Synthesis of the spiroketones followed standard routes. Compounds Ia and Id were prepared by pinacol rearrangement of 1,1′-dihydroxybicyclobutyl and 1,1′-dihydroxybicyclopentyl, respectively. Contraction of the ketone ring in Id by

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[1] Taken, in part, from the Ph.D. thesis of R. T. Conley, Princeton University, 1956.

[2] (a) R. Leuckart and E. Bach, *Ber.*, **20**, 104 (1887); (b) G. Schroeter, *ibid.*, **44**, 1201 (1911); (c) O. Wallach, *Ann.*, **259**, 309 (1890); (d) W. H. Perkin, Jr., and A. F. Titley, *J. Chem. Soc.* **119**, 1089 (1921); (e) W. H. Glover, *ibid.*, **93**, 1285 (1908); (f) C. C. Price and G. P. Mueller, THIS JOURNAL, **66**, 634 (1944); (g) P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2806 (1955); (h) M. J. Hatch and D. J. Cram, *ibid.*, **75**, 38 (1953); (i) W. L. Bencze and M. J. Allen, *J. Org. Chem.*, **22**, 352 (1957); (j) R. E. Lyle and G. G. Lyle, *ibid.*, **18**, 1058 (1953); (k) R. E. Lyle, H. L. Fielding, G. Canquil and J. Rouzand, *ibid.*, **20**, 623 (1955).

[3] For exceptions, see (a) B. M. Regan and F. N. Hayes, THIS JOURNAL, **78**, 639 (1956); (b) S. Kaufmann, *ibid.*, **73**, 1779 (1951); (c) W. D. Burrows and R. H. Eastman, *ibid.*, **79**, 3756 (1957); (d) H. A. Bruson, F. W. Grant and E. Bobko, *ibid.*, **80**, 3633 (1958).

[4] R. F. Brown, N. M. van Gulick and G. H. Schmid, *ibid.*, **77**, 1094 (1955).

[5] (a) P. W. Neber, K. Hartung and W. Ruopp, *Ber.*, **58**, 1234 (1925); (b) R. S. Montgomery and G. Dougherty, *J. Org. Chem.*, **17**, 823 (1952).

[6] E. C. Horning, V. L. Stromberg and H. A. Lloyd, THIS JOURNAL, **74**, 5153 (1952).

[7] A better synthetic route to these spirolactams was subsequently developed, starting with nitrocycloalkanes; see R. K. Hill, *J. Org. Chem.*, **22**, 830 (1957).

[8] A preliminary account of this work was reported by R. K. Hill and R. T. Conley, *Chemistry & Industry*, 1314 (1956).