[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

Preparation, Properties, and Polymerization of *N*-Vinyl-2-oxazolidinone

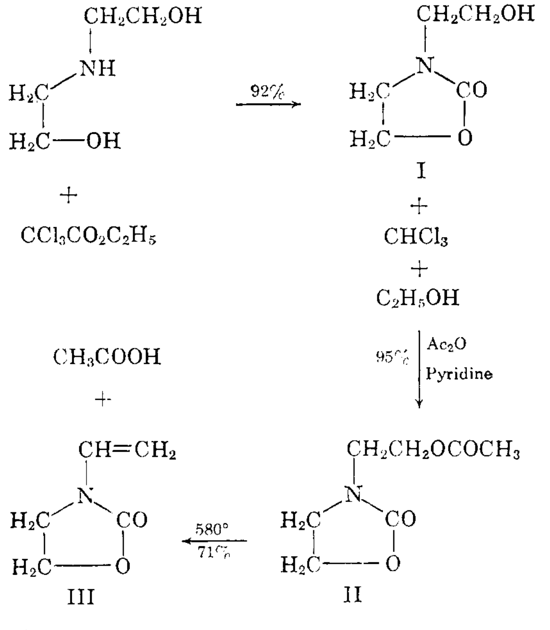
ABRAHAM KUTNER

Received January 20, 1961

N-Vinyl-2-oxazolidinone (III) has been prepared by deacetylation of *N*-(2-acetoxyethyl)-2-oxazolidinone at 580°. III is sensitive to mineral acids, hydrolyzing to 2-oxazolidinone (IV) and acetaldehyde. III readily adds IV to form *N*,*N'*-ethylidenebis(2-oxazolidinone) (V). Pyrolysis of V *in vacuo* gave a low yield of IV, and a resin, presumably poly(*N*-vinyl-2-oxazolidinone). Attempts to prepare III by treatment of IV with vinyl acetate in the presence of mercuric ion also resulted in the formation of V. This reaction was also shown to apply to amides, *N*,*N'*-ethylidenebis(acrylamide) being formed from acrylamide and vinyl acetate under the same conditions. III is readily polymerized by radical catalysts to a white solid which decomposes at about 300° without melting. The polymer is swollen by, but insoluble in, water. It is soluble, however, in such diverse solvents as formamide, aqueous formaldehyde, and in mineral and organic acids. Treatment of the polymer with refluxing hydrochloric acid in an effort to prepare poly[*N*-(2-hydroxyethyl)vinylamine] was partly successful. The resulting polyelectrolyte was irreversibly insolubilized by alkali..

Considerable interest has been expressed recently[1] in the new monomer, *N*-vinyl-2-oxazolidinone (III). The potential of the polymer as a competitor for poly(*N*-vinyl-2-pyrrolidinone) has been cited, and its use as a plasticizer for poly(acrylonitrile) has been claimed.[2] In light of recent disclosures[3-5] dealing with the preparation of III by dehydrohalogenation of *N*-(2-chloroethyl)-2-oxazolidinone, we are prompted to report our experience with this compound.

In this laboratory, III was prepared by the reaction sequence shown. Formation of *N*-(2-hydroxyethyl)-2-oxazolidinone (I) by reaction of diethanolamine and ethyl trichloroacetate is an adaptation of an oxazolidinone ring closure method developed by Lesher and Surrey.[6] Acetylation, followed by pyrolysis of the acetate (II) at 580° affords III. Over-all yield of monomer from the alcohol is somewhat better and the reagents less costly for this reaction sequence than for the chlorination-dehydrochlorination route,[5] and a saving of several days of reaction time is realized. Physical properties of the alcohol and monomer agree well with those reported. For the alcohol, Drechsel[4] gives a boiling point of 162° at 1.0 mm., n_D^{25} 1.482, and for the vinyl compound, a b.p. of 70° at 0.1 mm., n_D^{25} 1.494. Our values are, respectively, b.p. 150–155° at 0.25 mm., n_D^{25} 1.4840, and b.p. 70.5–72° at 0.25 mm., n_D^{20} 1.4964. III is soluble in the common organic solvents, and only slightly soluble in water. Like vinyl ethers and esters, it is sensitive to mineral acid, hydrolyzing readily to acetaldehyde and 2-oxazolidinone (IV). An alternative synthesis of I by the reaction of diethanolamine with diethyl carbonate in the presence of a sodium methoxide catalyst[7] also gave nearly quantitative yields. When made this way, however, the alcohol (I) would not distill readily without decomposition, and, for this reason, the former synthesis was preferred.



We were unable to vinylate IV with acetylene. At 150°, and 220 p.s.i. of a 2:1 acetylene-nitrogen mixture, there was no observable pressure drop after fifteen hours. We also tried to vinylate IV with vinyl acetate, according to Adelman's procedure for preparing vinyl esters[8] and vinyl ethers.[9] Although no reaction was apparent at 0°, a slightly exothermic reaction occurred at room temperature. The product isolated was *N*,*N'*-ethylidenebis(2-oxazolidinone) (V). Its identity was confirmed by elementary analysis and by hydrolysis and conversion of the aldehyde fragment to its 2,4-dinitrophenylhydrazone. Apparently, III, which is

---

(1) *Chem. Week*, **81**, No. 7, 57 (1957).

(2) W. Schuller and E. Kerle, U. S. Pat. **2,786,043** (1957).

(3) W. Arend and H-G. Trieschmann, German Patent Application **B34032** IV b/12 p. (1956).

(4) E. K. Drechsel. *J. Org. Chem.*, **22**, 849 (1957).

(5) E. K. Drechsel, U. S. Pat. **2,818,362** (1957).

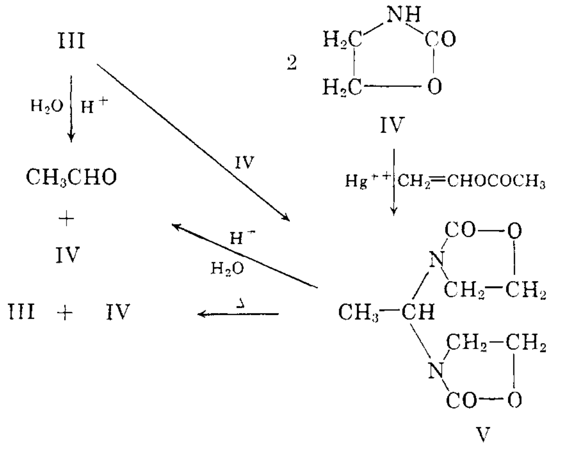
(6) G. Y. Lesher and A. R. Surrey, *J. Am. Chem. Soc.*, **77**, 636 (1955).

(7) A. H. Homeyer, U. S. Pat. **2,399,118** (1946).

(8) R. L. Adelman, *J. Org. Chem.* **14**, 1057 (1949).

(9) R. L. Adelman, *J. Am. Chem. ,Soc.*, **75**, 2678 (1935).

formed first, rapidly adds a molecule of IV. In a separate experiment, the identical product was formed by adding IV to III in a slightly acid medium. In seeking to extend the scope of this reaction to amides, acrylamide was readily converted to *N,N'*-ethylidenebis(acrylamide) (VI) under essentially the same conditions. Undoubtedly, other examples of this reaction will be found. The chemistry of *N*-vinyl-2-oxazolidinone and its ethylidene compound closely parallels that of *N*-vinylpyrrolidinone and its ethylidene compound.[10] A single attempt to decompose V to III and IV by heating *in vacuo* in the presence of an inhibitor was only partly successful. None of the vinyl compound was isolated, although about a 20% yield of IV was realized. The residue was resinous, III apparently having polymerized.



III polymerized readily in the presence of radical catalysts in bulk, in solution, or in suspension. Azobisisobutyronitrile was the most effective catalyst tried, giving quantitative conversions in twenty hours when the monomer was polymerized at 65° in the presence of water. Peroxide catalysts such as *tert*-butyl hydroperoxide and benzoyl peroxide, used at elevated temperatures, were ineffective in this system, whereas a redox catalyst consisting of equivalents of *p*-menthane hydroperoxide and sodium sulfite gave a 42% conversion at 5°. Bulk polymerizations catalyzed by benzoyl peroxide generally gave conversions of less than 50%; solution polymerizations in benzene were somewhat better.

The polymer isolated is a white solid, decomposing at about 300° without melting. It is swollen by, but insoluble in water, although similar homopolymers of molecular weights up to 100,000 are reported[4] to be water-soluble. Inasmuch as this polymer is soluble in such diverse solvents as formamide, 37% aqueous formaldehyde, and mineral and organic acids, it is unlikely that it is cross-linked.[11] Anomalous water-solubility behavior has been noted in polymers prepared from 5-methyl-*N*-vinyl-2-oxazolidinone.[12]

An attempt to polymerize the monomer with a titanium trichloride–hydroxylamine hydrochloride catalyst gave a crystalline nonpolymeric product. It was identified as V, undoubtedly formed as described before. Acid hydrolysis of III apparently occurs more rapidly than polymerization under these conditions.

The possibility of hydrolyzing poly(*N*-vinyl-2-oxazolidinone) to poly[*N*-(2-hydroxyethyl)vinylamine] was briefly studied. After refluxing a 10% solution of polymer in 10% hydrochloric acid for several hours, the polymer was recovered essentially unchanged. Similar treatment in constant boiling or concentrated hydrochloric acid, however, resulted in the evolution of carbon dioxide, and afforded products which were water-soluble. The high viscosity of these solutions in water in comparison with the greatly reduced viscosity in 0.1*N* sodium chloride suggests that the hydrolyzed polymer is polyelectrolytic. Upon treatment of the hydrolyzate with periodic acid, 0.21 g. of acid (as H_5IO_6) was consumed per gram of polymer. Under the same conditions, poly(*N*-vinyl-2-oxazolidinone) consumed no periodate. The observations that α-amino alcohols can be cleaved by periodic acid,[13] whereas the corresponding *N*-acylated amino alcohols are not attacked,[14] support the conclusion that the hydrolyzed polymer contained the $—NHCH_2CH_2OH$ group. When a solution of hydrolyzed polymer was made alkaline, the polymer became irreversibly insolubilized. Attempts to saponify poly(*N*-vinyl-2-oxazolidinone) by heating in a 10% sodium hydroxide solution also resulted in irreversible insolubilization.

EXPERIMENTAL[15]

N-(2-Hydroxyethyl)-2-oxazolidinone (I). A flask equipped with a stirrer, dropping funnel, and reflux condenser fitted with an adapting for distillation was charged with 105 g. (1 mole) of diethanolamine. The flask was warmed on a steam bath, and to it with stirring was added 200 g. (1.05 moles) of ethyl trichloroacetate during 1 hr. Chloroform and

---

[10] J. W. Breitenbach, *J. Polymer Sci.*, **23**, 949 (1957).

[11] In a private communication, E. K. Drechsel suggested that water insolubility may be caused by traces of a cross-linking agent, or by complexing of polymer with polyvalent cations. Although an infrared spectrum of the polymer does not reveal any unexpected absorptions, the former possibility cannot be entirely ruled out. As little as 0.1% of an undetected cross-linking agent could have a marked effect on solubility properties of the polymer. A further possibility is that these polymers are higher in molecular weight than those heretofore reported.

[12] W. E. Walles, W. F. Tousignant, and T. Houtman, Jr., 137th Meeting American Chemical Society, Cleveland, Ohio, April, 1960, Abstracts p. 4S.

[13] B. H. Nicolet and L. A. Shinn, *J. Am. Chem. Soc.*, **61**, 1615 (1939).

[14] B. H. Nicolet and L. A. Shinn, *J. Biol. Chem.*, **142**, 139 (1942).

[15] Melting points are uncorrected.

ethanol distilled to almost the calculated volume. The last traces of chloroform and ethanol were removed *in vacuo*. The product was isolated by distillation, 120 g. (92%) boiling at 150–155° at 0.25 mm. (n_D^{20} 1.4840) being collected.

Anal. Calcd. for $C_5H_9NO_3$: C, 45.8; H, 6.87; N, 10.68. Found: C, 45.8, 45.4; H, 7.03, 6.89; N, 10.38, 10.67.

N-(2-Acetoxyethyl)-2-oxazolidinone (II). Compound I (38.9 g.) was mixed with 32.0 g. of acetic anhydride, and 100 ml. of pyridine. After the initial exothermic reaction had subsided, the mixture was heated on a steam bath for 0.5 hr. Acetic acid and pyridine were removed *in vacuo* leaving 53.8 g. of a pale yellow liquid. This crude acetate is soluble in water and in benzene, and insoluble in ether. It was isolated by distillation at 139–141° at 0.75 mm. to give 48.8 g. (95%) of a mobile, colorless liquid which crystallized on standing. An analytical sample was recrystallized by solution in benzene and addition of ether to incipient turbidity; m.p. 52–54° (hexagonal prisms).

Anal. Calcd. for $C_7H_{11}NO_4$: C, 48.6; H, 6.36. Found: C, 48.6, 48.7; H, 6.64, 6.49.

N-Vinyl-2-oxazolidinone (III). II was pyrolyzed in a vertical Pyrex tube 25 mm. in diameter and 50 cm. long, equipped with standard taper joints and thermocouple well sealed into its center. II was added from an electrically heated dropping funnel supported on one branch of a Y-tube, the other branch being used to admit nitrogen. The tube, packed to a few inches from the top with $^1/_4$-in. Pyrex beads, was externally heated over about 12 in. of its length. Pyrolyzate was condensed at the bottom of the tube and collected in an ice cooled, side-neck flask.

With nitrogen passing in slowly, the tube was heated to 565–580°. To the top of the tube, 50.6 g. (0.29 mole) of II was added at the rate of 1.9 g. per min. Titration of an aliquot of the condensed pyrolyzate (47.8 g.) indicated the evolution of 44% of the theoretical quantity of acetic acid. 2,6-Di-*tert*-butyl-*p*-cresol (0.4 g.) was added as an inhibitor, and the acid was stripped on a steam bath at reduced pressure. The residue was fractionated to give 15.9 g. (71% based on unrecovered II) of III, b.p. 70.5–72° at 0.25 mm. (n_D^{20} 1.4964; d_{25}^{25} 1.1697) and 16.4 g. (32.4%) of the original acetate (b.p. 125–127° at 0.35 mm.). III absorbed the theoretical volume of hydrogen over a 5% palladium-charcoal catalyst.

Anal. Calcd. for $C_5H_7NO_2$: C, 53.1; H, 6.24; N, 12.38. Found: C, 52.7, 53.2; H, 6.11, 6.38; N, 12.22, 11.92.

N,N'-Ethylidenebis(2-oxazolidinone) V. (*A*) *By reaction of vinyl acetate with 2-oxazolidinone* (IV). A three neck, round bottom flask equipped with a stirrer, dropping funnel, and drying tube was charged with 172 g. (2 moles) of redistilled vinyl acetate, 28.4 g. (0.33 mole) of IV, and 1 drop of 80% copper naphthenate as an inhibitor. The flask was cooled in an ice-water bath, and with stirring, 0.63 g. of mercuric acetate, followed within a few minutes by 0.03 ml. of concd. sulfuric acid, were added. During the reaction 2.0-ml. aliquots were taken from the reaction mixture, mixed with 25 g. of ice and water, and promptly titrated for acetic acid with standard base. After the mixture was stirred for 4 hr. at 0–5°, acetic acid evolution was less than 8% of the theoretical. Additional mercuric acetate and sulfuric acid were added and the reaction temperature was allowed to rise to 28°. During the next several hours, the original solid dissolved, and a voluminous, white, crystalline precipitate formed. After 24 hr., the reaction was complete.

The solid was collected, washed with ether, and air-dried to give 27.4 g. (84%) of crude V, m.p. 115–117°. A sample thrice recrystallized from 95% ethanol melted at 149–150°

Anal. Calcd. for $C_8H_{12}N_2O_4$: C, 48.0; H, 6.00; N, 14.0. Found: C, 48.2, 48.1; H, 5.98, 6.18; N, 13.65, 14.03.

Hydrolysis and formation of a 2,4-dinitrophenylhydrazone from the ethylidene compound were accomplished in one operation. A solution of 0.2 g. of V in 2 ml. of water and 5 ml. of alcohol was mixed with 0.4 g. of 2,4-dinitrophenylhydrazine in sulfuric acid according to Shriner and Fuson,[16] and then heated on a steam bath for 10 min. The yellow-orange crystals which formed on cooling were collected, washed with 80% alcohol, and dried (0.21 g.). They melted at 146–147° without further purification. A mixture of this product with authentic acetaldehyde-2,4-dinitrophenylhydrazone gave the same melting point.

(*B*) *By addition of 2-oxazolidinone* (IV) *to vinyloxazolidinone* (III). To a solution of 0.87 g. of IV in 5.0 ml. of water was added 1.13 g. of III. A few drops of 10% hydrochloric acid was added, and the somewhat cloudy solution was warmed to about 75° on a hot plate. The odor of acetaldehyde was noted. The mixture stood overnight, and the solvent was then removed in a current of air. The solid residue was triturated with ether, washed on a funnel with ether, and dried. Yield: 1.53 g., m.p., 122–125°. Recrystallization from methanol-ether afforded 1.15 g. of V, m.p., and m.p. of a mixture with the product prepared by method A, 148–152°.

Pyrolysis of N,N'-ethylidenebis(2-oxazolidinone) (V). V (12.0 g.) was mixed with 0.2 g. of 2,6-di-*tert*-butyl-*p*-cresol and heated to 140–160° at 0.6 mm. The distillate (1.1 g.) crystallized on cooling, m.p. 80–86°. Recrystallization from ethanol-ether raised the m.p. to 87–89°. A mixture with an authentic sample of IV gave the same melting point.

N,N'-Ethylidenebis(acrylamide) (VI). To 158 ml. of vinyl acetate, 0.4 g. of hydroquinone, and 28.4 g. (0.4 mole) of acrylamide there was added, with stirring, 0.8 g. of mercuric acetate and 2 drops (*ca.* 0.04 ml.) of concd. sulfuric acid. After several hours, a solid deposited. Stirring was continued to a total of 68 hr. (or until the titer of the aqueous extract of an aliquot became constant). The crystalline solid was collected, washed with 10 ml. of vinyl acetate, and then with 10 ml. of ether. The air-dried product (27.6 g., 82% calculated as VI) melted at 155–160°. Recrystallization from acetone-ethanol (6:1) afforded glistening, colorless clusters of broad needles, m.p. 153–155°.

Anal. Calcd. for $C_8H_{12}N_2O_2$: C, 57.2; H, 7.15; N, 16.7. Found: C, 57.7, 57.7; H, 7.32, 7.19; N, 16.2, 16.6.

Attempts at further purification frequently gave needles melting above 300°. When the same reaction was run at −15° in an effort to obtain the *N*-vinyl compound, only the starting material was recovered after 24 hr. Hydrolysis as before, and treatment of the hydrolyzate with 2,4-dinitrophenylhydrazine, again showed the presence of acetaldehyde.

Upon being heated to 180°, VI polymerized to an orange-brown solid which was infusible and insoluble in the common solvents. Condensation of acrylamide with acetaldehyde in the presence of hydrochloric acid[17] gave a product whose physical and chemical properties were identical with those of VI.

Poly(N-vinyl-2-oxazolidinone). (*1*) *Polymerization in water.* Into a pressure bottle were charged 25.0 g. of III and 63 ml. of distilled water which had been adjusted to *p*H 7.2 with a drop of 0.1*N* sodium hydroxide. Nitrogen gas was bubbled through this suspension for 20 min., 0.1 g. of azobisisobutyronitrile was added, and the bottle was closed with a cap equipped with a self-sealing rubber liner. Through a hypodermic needle, the air above the reaction mixture was replaced with nitrogen. The bottle was jacketed in a brass can, and placed on a rotating rack in a constant temperature bath at 65° for 20 hr. Polymer separated as a very viscous oil. The water layer was decanted, and the polymer layer was dissolved in 100 ml. of formamide. To isolate the polymer, this solution was poured with stirring into 800 ml. of methanol. The white, granular product was redissolved in formamide and reprecipitated with methanol. It was dried *in vacuo* at 80° to yield 24.5 g. (98%) of poly(*N*-vinyl-2-oxazolidinone), η_{rel} (1% in formamide) 2.45.

---

[16] R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, 3rd ed., John Wiley and Sons, Inc., New York, 1948, p. 171.

[17] L. A. Lundberg, U. S. Pat. 2,475,846 (1949).

Anal. Calcd. for $C_5H_7NO_2$: C, 53.1; H, 6.24; N, 12.38. Found: C, 52.7, 53.0; H, 6.22, 6.42; N, 11.76, 11.82.

The polymer was insoluble in, but swollen by, water. It was soluble in formamide, mineral and organic acids, and 37% aqueous formaldehyde. The polymer was insoluble in the common organic solvents such as alcohols, esters, ethers, hydrocarbons.

(*2*) *Polymerization in bulk.* A thick-walled, Pyrex, cappable tube was charged with 2.16 g. of monomer and 0.022 g. of azobisisobutyronitrile. The tube was capped, and polymerization carried out under nitrogen as before. After 48 hr., the contents of the tube had gelled. Isolation afforded 1.04 g. (46%) of polymer, η_{rel} (1% in formamide) 1.44.

(*3*) *Polymerization in an organic solvent.* A solution of 3.0 g. of III in 2.0 ml. of anhydrous benzene was polymerized at 70 over a 36-hr. period, with 0.03 g. of benzoyl peroxide as catalyst. Yield: 1.71 g. (57%) of polymer, η_{rel} (1% in formamide) 1.23.

Attempted polymerization of III *with titanium trichloride-hydroxylamine hydrochloride.* To 2.0 g. of III in 25 ml. of hexane, at 22°, were added, with stirring, 0.02 g. of hydroxylamine hydrochloride and 0.2 ml. of 20% titanium chloride solution (Lamotte Chemical Co.). In a few minutes, the temperature rose to 26°, and an oily product deposited on the sides of the flask. The product hardened in 15 min. to a solid, soluble in water and in methanol. It was purified by solution in methanol, and precipitation in excess ether. The product (0.85 g.), after recrystallization from methanol ether, melted at 146–148°. Elementary analysis (C, 47.95, 47.92; H, 5.86, 6.05; N, 14.09, 14.18) and a mixed melting point with V confirmed the identity of this product as V.

Hydrolysis of poly(N-vinyl-2-oxazolidinone). Poly(*N*-vinyl-2-oxazolidinone) 2.0 g., η_{rel} (1% in formamide) 2.5, was dissolved in 25 ml. of concd. hydrochloric acid. The solution was refluxed for 3 hr., while carbon dioxide evolved. The cooled, viscous solution, added slowly with stirring to 150 ml. of methanol, deposited a white, granular precipitate. After being filtered and washed with methanol, the hydrolyzate was redissolved in 25 ml. of water and reprecipitated in methanol. The specific viscosity of the hydrolyzed polymer in water was 15.7. Its intrinsic viscosity $[\eta]$ at 25° in 0.1*N* sodium chloride was 0.185.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE AMERICAN UNIVERSITY OF BEIRUT]

Kinetics of the Reaction of Phenyl Isocyanate with Aniline[1]

KENNETH SAUER[2] AND MARIE H. KASPARIAN

Received December 5, 1960

The kinetics of the reaction between phenyl isocyanate and aniline at 25° in benzene and chlorobenzene as solvents has been studied as a function of the initial concentrations of the reactants. When the initial concentrations of the two reagents are approximately equal the rate expression is given by Rate = $k_3(C_6H_5NH_2)^2(C_6H_5NCO)$. The rate constant, k_3, depends on the initial concentrations. When aniline is initially in substantial excess, the rate expression is the same and $k_3 = 0.021 \pm 0.001$ l.²/mole²-sec. When phenyl isocyanate is in substantial excess the rate law becomes Rate = $k_4(C_6H_5NH_2)^2(C_6H_5NCO)^2$, where $k_4 = 1.0 \pm 0.2$ l.³/mole³-sec. The measurements were made on solutions saturated with the product, diphenylurea. A mechanism is proposed which involves two intermediate complexes of the reagents.

The reaction of isocyanates with amines has been studied previously by several investigators.[3-5] Reviews of the early work on this reaction and also of that on related reactions of isocyanates, especially with alcohols, have been published.[6,7] The results of Naegeli *et al.*[4] showed that an increase in the rate of reaction occurs when electron-attracting substituents are present on the isocyanate molecule or when electron-donating groups are attached to the amine. They further observed that carboxylic acids and tertiary bases, such as pyridine, are catalysts for the reaction.

Studies of the kinetics of the reaction between isocyanates and alcohols have led to the proposal that the first step in the mechanism is the formation of a complex between the isocyanate and the alcohol (or a base catalyst, if present) followed by the reaction of the complex with the alcohol to give the urethane product.[8] The kinetics of this reaction are between second and third order. Arnold *et al.*[7] suggested that the reaction between isocyanates and amines follows an analogous mechanism with the amine taking the place of the alcohol. They report some unpublished experiments of Craven which show that the amine-isocyanate reaction is not simply first-order in each reactant, as had been previously assumed.[3] The order with respect to amine was seen to vary from first to second, depending on the particular amine used.[7]

Baker and Bailey,[5] as a result of their extensive kinetic studies, conclude that the mechanism of the isocyanate-amine reaction is analogous to that for the isocyanate-alcohol reaction. As expected, the

---

(1) Abstracted from the thesis of Marie H. Kasparian, submitted in partial fulfillment of the requirements for the Master of Science degree at the American University of Beirut, June 1960.

(2) Chemistry Department, University of California, Berkeley, Calif.

(3) T. L. Davis and F. Ebersole, *J. Am. Chem. Soc.*, **56**, 885 (1934).

(4) C. Naegli, A. Tyabji, and L. Conrad, *Helv. Chim. Acta*, 21, 1127 (1938).

(5)(a) J. W. Baker and D. N. Bailey, *J. Chem. Soc.*, 4649 (1957); (b) 4652 (1957); (c) 4663 (1957).

(6) J. H. Saunders and R. J. Slocombe, *Chem. Revs.*, **43**, 203 (1948).

(7) R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Revs.*, **57**, 47 (1957).

(8)(a) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947); (b) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 9 (1949); (c) 19 (1949); (d) J. W. Baker, M. W. Davies and J. Gaunt, *J. Chem. Soc.*, 24 (1949); (e) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 27 (1949).