KINETICS

OF THE REACTION BETWEEN

PHENYL ISOCYANATE AND ANILINE

BY

MARIE H. KASPARIAN
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(iv)
Kinetic studies have been undertaken to elucidate the mechanism of the reaction of phenyl isocyanate with aniline in chlorobenzene and benzene as solvents. The reaction was found to be third order overall when the initial reactant concentrations were almost the same. The order of the reaction in benzene was also found to be third order, approximately second order in aniline and first order in isocyanate, when excess aniline was used. The experimental rate constant for the latter reaction was found to be $8.80 \times 10^{-3} \pm 0.10 \times 10^{-3}$ $l/m^3$-sec. However, when excess isocyanate was used, the reaction changed to fourth order, second order in isocyanate and second order in aniline, the experimental rate constant for the reaction being $1.13 \ l/m^3$-sec at 25°C.

To explain these findings, it was necessary to modify the previously suggested mechanism for amino-isocyanate reactions. The new mechanism postulates the formation of two intermediate complexes made up of phenyl isocyanate and aniline molecules.
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INTRODUCTION

I-1 History of the Kinetics of Isocyanate-Amine Reactions

The formation of substituted ureas from primary and secondary amines is one of the earliest known and important reactions of isocyanates\(^1\). Due to the lack of suitable quantitative methods for the determination of either reactants or product, insufficient rate data have been published to establish the kinetic order of this reaction. It is hoped that the results obtained from the experiments described herein will clarify the mechanism of the isocyanate-amine reactions in some respects.

The reaction has generally been assumed to follow simple second order kinetics.

\[
\begin{align*}
\text{isocyanate} & \quad \text{amine} \\
\text{(R)Ar-N=O} & \quad + \quad \text{(R)Ar-NH}_2 \\
\text{---} & \quad \text{---} \\
\text{urea} & \quad \text{(R)Ar-NH-C-NH-Ar(R)}
\end{align*}
\]

The rate of the reaction has been thought to depend on the first power of the concentration of each reactant.

The first attempts at quantitative rate determinations for reactions involving phenyl isocyanate and different primary aliphatic and aromatic amines were reported by Davis and Ebersole\(^2\) in 1954. It was then\(^2\) agreed that (1) the reaction of amines with isocyanates goes to completion if an excess of the amine is present (2) the reaction is not reversible at ordinary temperatures. The relative reaction velocities of various aliphatic amines with phenyl iso-
cyanate were determined. The velocities were found to be of the same order of magnitude, but were not identical for the different aliphatic amines. Aromatic amines were shown to be less reactive.

Later, in 1938, Naegeli et al. studied the effect of nuclear substituents on the reactivity of aryl isocyanates with aryl amines. The isocyanate reactivity was shown to increase with increase in the electron-attracting power of the substituents. The amine activity was found to increase with increase in the electron-donating power of the substituents. The reaction was proved to be catalyzed by pyridine, a tertiary base, and by some carboxylic acids. It was reported to be unaffected by water or inorganic acids, salts and bases. In all these studies however, the method used to follow the reaction with time was based on the determination of yields of isolated products through mixed melting point technique.

An accurate chemical method of quantitative analysis of isocyanates was developed by Stagg in 1946. This volumetric method consists of the reaction of isocyanates with excess standard amine followed by the back titration of the excess amine. This method made possible a detailed study of the analogous urethane formation.
1-2 Kinetics and Mechanism

A. Alcohol-Isoxyrate Reactions.

A number of kinetic studies have been made on alcohol-isocyanate reactions \(^2b\), \(^5\)\(^-\)\(^11\). A review of these and related topics has been published by Arnold, Nelson and Verbanck \(^5\) in 1957.

The earliest work on the kinetics of the action of isocyanates on alcohols was that of Davis and Parnum \(^2b\) who studied the relative reactivities of the lower aliphatic alcohols with phenyl isocyanate by using the freezing point of the product urethane mixtures obtained from the reaction of two different alcohols with a known but limited quantity of phenyl isocyanate as a criterion for determining the ratio of the two products. Taking methanol as the standard, the relative rates of ethyl, \(n\)-propyl, \(n\)-butyl, 1-butyl and \(n\)-amyl alcohols have been found to lie between 0.7 and 1.0, those of sec-propyl and butyl alcohols being about one third and of the tert-butyl and amyl alcohols being about one per cent.

A clarification of the mechanism of the alcohol-isocyanate reactions was provided by Baker and his co-workers. In a series of papers, they gave a detailed study of the kinetics of the "spontaneous" as well as the base-catalyzed reaction of alcohols with isocyanates. By using a modification of the Stagem \(^3\) method of analysis for isocyanates Baker
and Holdsworth indicated that (1) the second order coefficients obtained for the phenyl isocyanate-methanol system remained approximately constant with a tendency to drift upward in the later stages of the reaction, (2) the reaction was base-catalyzed, supporting earlier evidence given by Tarbell, Wallat and Wilson, (3) the rate of the reaction was directly proportional to the concentration of the base-catalyst.

By studying the reaction in the presence of a constant concentration of a base catalyst and varying the initial isocyanate-alcohol concentration ratios, Baker and Holdsworth concluded that the alcohol addition to the carbonyl carbon of the isocyanate group follows second order kinetics. In the absence of a base catalyst experimental data revealed autocatalysis of the "spontaneous" reaction by the weakly basic product urethane.

To account for these facts, the authors proposed a mechanism for the base-catalyzed reactions of alcohols with isocyanates which has the following scheme:

\[
\begin{align*}
\text{Ar-N=C=O} + \text{R}_3\text{N} & \xrightarrow{k_2} \text{Ar-N=C=O-R}_3\text{N} \\
\text{Complex} & \xrightarrow{k_3} \text{NH}_2\text{ArCO}_2\text{Me} + \text{R}_3\text{N}
\end{align*}
\]

\[
\begin{align*}
\text{Ar-N=C=O} + \text{MeOH} & \xrightarrow{k_0} \text{NH}_2\text{ArCO}_2\text{Me}
\end{align*}
\]
With this mechanism at hand repulsion energies between adjacent substituent groups in the complex were calculated for the different bases and isocyanates used. Higher repulsion energies were obtained for the dialkyl anilines. This confirmed the suggestion of explaining in terms of steric effects the absence of catalytic activity in the dialkylanilines.

The "spontaneous" reaction \(^7b,c\) also appeared to follow second order kinetics with the complication that the rate constant obtained was dependent on the ratio of the initial alcohol-isocyanate concentrations. Baker and Gaunt\(^7d,e\) explained this by saying that alcohol acts both as a reactant and as a catalyst by forming a complex with the isocyanate through a reversible reaction:

\[
\begin{align*}
\text{Ar-NC}=O & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Ar-NC}=O\cdot\overset{\Theta}{\text{ROH}} \\
\overset{\Theta}{\text{Complex}} & \\
\text{Complex} + \text{ROH} & \underset{k_3}{\rightarrow} \text{Ar,NCOCOR} + \text{ROH}
\end{align*}
\]

The experimental results obtained from the uncatalyzed reactions were verified by Dyer et al.\(^6\) who used dilatometric methods for studying the rates of n-butyl and sec-butyl alcohols with phenyl isocyanate and confirmed their results by chemical analysis.

A rate expression was derived\(^7a\) by assuming a steady
state concentration of the complex. The resulting expression after rearrangement was:

\[
\frac{[\text{RON}]}{k_0} = \frac{k_2}{k_1 k_3} \cdot \frac{[\text{ROH}]}{k_0}
\]

where \(k_0\) is the specific rate constant of the "spontaneous" reaction which is subject to alcohol and water catalysis only. The straight lines obtained by plotting \(\frac{[\text{ROH}]}{k_0}\) against ROH showed that the experimental data account for the proposed mechanism.

A study \(^{7b,c}\) of the base-catalyzed reaction in dimethyl ether and benzene as solvents, at two different temperatures made possible the evaluation of \(k_1\) and \(k_3\), activation energy associated with \(k_4\), both of which proved to be a function of only the nature, and not the concentration, of the alcohol. Baker and Gaunt \(^{7b,c}\) explained this fact by postulating the formation of an alcohol-base hydrogen-bonded complex which, according to the authors, should react with the isocyanate to form the same transition isocyanate-base complex as the free base itself. The formation of an alcohol-base complex was later verified by spectroscopic studies \(^7d\). The second point gives as another possible explanation for the above mentioned fact was the alcohol solvation of the polar intermediate complex. Although the alcohol-complex interaction was still present in experiments involving benzene as solvent, a tremendous increase in the
rate of the reaction was observed under identical conditions indicating a greater concentration of monomeric alcohol in benzene. Decrease in the value of k_3 with decreasing initial alcohol concentration was found to be smaller in benzene than it is in ether, another evidence for the absence of alcohol-solvent association in benzene.

Recently, Ephraim, Woodward and Neohbian investigated the "spontaneous" reaction of alcohols with phenyl isocyanate in a variety of solvents. Their results indicate that the rate is dependent chiefly on the dielectric constant of the solvent — a point which has not been brought up earlier — and to some extent on the hydrogen-bonding character of the solvent. The reaction order was found to be a function only of the hydrogen-bonding character of the solvent. In view of the new findings, the mechanism postulated by Baker and co-workers2bc,d for the uncatalyzed reaction was modified.

(i) ROH $\rightleftharpoons_{k_3}$ Complex 1

(ii) ROH + solvent $\rightleftharpoons_{k_{1b}}$ Complex 2

(iii) ROH + urethane $\rightleftharpoons_{k_{1c}}$ Complex 3

Complex 1 + R-N=O $\rightleftharpoons_{k_{2a}}$ urethane + ROH

Complex 2 + R-N=O $\rightleftharpoons_{k_{2b}}$ urethane + solvent

Complex 3 + R-N=O $\rightleftharpoons_{k_{2c}}$ 2 urethane
where $k_1$'s are the equilibrium constants and $k_2$'s are the rate constants. Reactions (i) and (iii) were found to predominate in non-hydrogen bonding solvents whereas (ii) and (iii) were so in hydrogen-bonding ones.

B. Amine-Isocyanate Reactions.

It was only after such a detailed study of the isocyanate-alcohol reaction kinetics that the simple picture of isocyanate-amine reactions became suspect. Recently, a review article by Arnold, Nelson and Verbano mentioned some kinetic experiments involving the reaction of different aromatic isocyanates with aromatic amines in dioxane as solvent. The study was done by Graven who had presented the report at an American Chemical Society Symposium on isocyanates. The rates were found to be affected more by changes in amine concentration than in isocyanate concentration; the reactions were observed to be catalyzed by the product itself to different extents, depending on the basic strength of the product. Carboxylic acids and tertiary amines proved to be catalysts for the reactions, the former being more effective. Most of this interpretation was based on studies of initial rates. The expression relating the initial rate to the initial concentrations was found to be $R_0 = k_1 c_0^n$, where $c_0$ is the initial concentration of isocyanate and amine, respectively; $R_0$ is the initial slope of the plot of isocyanate concentration versus time and $n$
is the initial reaction order in amine – constant for a given isocyanate–amine pair. Calculated values of \( n \) and \( k \) based on initial rates have been reported for various amine–isocyanate combinations. For the aniline–isocyanate system, \( n \) was found to be 1.7 when initial rates were considered. However, with rates at the half-time of the reaction the order was found to be in the range of 1.2 and 1.3. It is apparent that the reaction order in isocyanate was assumed to be one. No experiments verifying this have been reported. The value of \( n \) was shown to remain approximately constant for a given isocyanate concentration over a wide range of initial amine concentrations. The ratio of the initial concentrations of the reactants did not exceed two in the reported experiments.

By analogy with the alcohol–isocyanate reaction mechanism and relying on the observations from experiments, Graven has proposed two competing reactions for amine–isocyanate systems:

1. **Uncatalyzed Step**, which presumably is important at the initial stages of the reaction,

   \[
   \begin{align*}
   \text{1. } & \text{Ar-N=O} + \text{Ar-NH}_3 \quad \xrightarrow{k_2} \quad \text{Ar-N=O} \cdot \text{Ar-NH}_3 \\
   & \quad \xrightarrow{k_1} \quad \text{Ar-NH}_2 \\
   & \quad \xrightarrow{} \quad \text{Complex}
   \end{align*}
   \]

2. **Complex + Ar-NH}_3 \quad \xrightarrow{k_3} \quad (\text{ArNH})_n\text{C}=\text{O} + \text{Ar-NH}_3
II. Catalyzed Step, which is important later in the course of the reaction,

1. Ar-N=O + Ar-N=O $\xrightarrow{k_3 k_4} \text{Complex}$

2. Complex + (ArNH)$_2$O $\xrightarrow{k_5}$ 2(ArNH)$_2$O

Using the uncatalyzed path, the initial rate expression was found to be,

$$R_o = \frac{k_3 k_4 [O]_o^{\frac{3}{2}}}{k_4 + k_3 [O]_o}$$

which agrees with the observed initial rate expression at the initial stages of the reaction.

I-3 Methods of Analysis

The technique/titration in non-aqueous solvents is now recognized to be a powerful tool for the analysis of organic amines. Many aliphatic and aromatic amines cannot be titrated in aqueous solutions because they are either insoluble in water or they act as only very weak bases in the presence of the basic solvent water. During the past thirty five years a simple, rapid and accurate analytical method has been developed for the quantitative determination of amines. It is based on the experimental fact that certain non-aqueous media accentuate the basic properties of amines.
Very sharp end points were obtained through the use of very slightly basic solvents. The first titrations of organic amines were done in glacial acetic acid solvent using a mineral acid in glacial acetic acid as the titrant. Sharper end points were observed in the titration of aromatic amines when perchloric acid in acetic acid was used instead of hydrochloric or sulfuric acid; the order of acidity in glacial acetic acid, found by Kolthoff and Willman was HClO₄ > HBr > H₂SO₄ > HCl > HNO₃. Aniline and other bases were titrated in benzene and chloroform the titrant being hydrogen chloride dissolved in benzene. p-Toluenesulfonic acid in benzene was tried as a titrant by Dietzel and Paul, but it proved to be too weak to give good results.

Fritz has indicated that several inert solvents, such as benzene and chlorobenzene, can serve as convenient media for titrations of weak and strong bases with perchloric acid in acetic acid as titrant. In fact, in most of these solvents cited by Fritz, the methyl violet end point was found to be sharper than in acetic acid alone. Crystal violet is another indicator recommended for use in acetic acid medium.

Titrations in non-aqueous media were found to be particularly useful in the quantitative determination of aliphatic and aromatic primary, secondary and tertiary amines in amine mixtures.

The method has been applied to a variety of substances
using both visual indicators and potentiometric procedures.
II-1 Introduction

The experimental procedure involves the preparation of different solutions of n- and di-n-butylanine, aniline, ethyl and phenyl isocyanates in benzene and in chloro-benzene, and of perchloric acid in glacial acetic acid. Standardization of these solutions was done mostly by titration using methyl violet as indicator and sometimes by infrared spectrophotometry.

The mixing of reactants when a reaction is started, sampling and analysis at proper intervals of time complete the scheme of the procedure used in the course of this study.

II-2 Reagents

a. Perchloric acid in glacial acetic acid: The titrant acid used for the determination of concentrations of aniline and other amines was prepared by dissolving 70% perchloric acid (Merck, extra pure grade) in glacial acetic acid (Merck, extra pure i.e. 99-100% pure) to make up about 0.0500 molar solution. Perchloric acid was preferred to other mineral acids, like sulfuric or hydrochloric acid, because perchloric acid is the strongest acid in non-aqueous media, and also because of complications arising from the facts that sulfuric acid is diotropic and hydrogen
chloride is volatile.\textsuperscript{19}

The titrant solution was prepared according to the directions specified by Fritz.\textsuperscript{12} Water was found to decrease the sharpness of the end points of titrations when present in amounts larger than 3\% of the original solution.\textsuperscript{15a} In this particular case, water is undesirable because it reacts with the isocyanate to form the corresponding amine. The water that was introduced by the perchloric acid and in the glacial acetic acid was allowed to react with the calculated amount of acetic anhydride (actually 90\% of the theoretical amount).\textsuperscript{12} The solution was then standardized against potassium acid phthalate dissolved in glacial acetic acid to a methyl violet end point.\textsuperscript{12,19} No drying of the primary standard was necessary because of its low hygroscopicity.

b. Amine and isocyanate solutions in benzene:

Stock solutions of the distilled aniline (Merek, extra pure), n-butylamine (Eastman Kodak, white label) di-n-butylamine (Eastman Kodak, white label) and phenyl isocyanate (Eastman Kodak, white label) were prepared only a few hours before starting a run. The amine solutions in benzene (Eastman Kodak spectro grade) were standardized with standard perchloric acid in acetic acid using methyl violet as the indicator. The violet to blue color change of the indicator was taken as the end point of the titration.
The end point color was determined potentiometrically by using a Radiometer-Universal-pH-Meter Model 32 with a glass indicator electrode and silver-silver chloride reference electrode. The end point color does not agree with the end point reported by Pritz. 16a.

A sample of the solution of amine in benzene was pipetted into an Erlenmeyer flask and was diluted to a final volume of 50 ml. with glacial acetic acid to reduce dilution effects on the end point.

The initial concentration of phenyl and ethyl isocyanate solutions was determined by a slight modification of the Stegg method of analysis. 3 A known volume of the isocyanate solution in benzene was allowed to react with an excess of either standard n-butylamine 4 or di-n-butylamine 11 for a few minutes. The reaction was proved to be very rapid. After dilution with acetic acid, the excess amine was back titrated with perchloric acid. Di-n-butylamine was found to be more convenient for this purpose because the addition of acetic acid in the dilution step caused white fumes to be liberated which remained in the titration flask all through the process, making the end point detection very difficult. The results obtained from both amines agreed within experimental error (deviations less than 1% were observed).

II-3 Rate Studies

a. Temperature Control: A water bath, fitted with an electric thermoregulator (Fenwal expanding shell type),
heating device and a stirrer was used for controlling the temperature of reaction mixtures. The thermometer used read accurately five hundredths of a degree. Its zero point was checked in an equilibrium mixture of ice and water. The thermostat temperature fluctuations amounted to \( \pm 0.20^\circ C \), so that the uncertainty involved in the temperature readings is of the order of 0.20 to 0.3 \( ^\circ C \).

b. Preliminary Investigations: Experiments were conducted to prove that (i) the isocyanate does not react with the solvent or with the product under the conditions of the experiment, (ii) the presence of isocyanate does not interfere with the titration of the amine with standard perchloric acid in glacial acetic acid.

(i) Twenty-five milliliters of a benzene solution of phenyl isocyanate was placed in the thermostat at 25\(^\circ\)C. At intervals, samples were analyzed by titration. The isocyanate concentration was found to be unchanged, within 1\% deviation, over a period of one week.

(ii) Similar trials involving the isocyanate together with product carbonilide (Eastman Kodak, white label) indicated less than 1\% change for the different determinations done in the course of four days.

c. Analytical Procedure:

(i) Runs involving the determination of aniline during the progress of the reaction. The large number of separate rate determinations makes it impracticable to
record the details of all the runs individually. In general 6-15 separate concentration determinations were done at proper time intervals and the value of the velocity coefficient was calculated from the slopes of the curves of appropriate concentration terms versus time.

To prevent the reaction of the isocyanate with atmospheric moisture, all the glass apparatus was dried at 125°C in an electric oven before use; the sampling pipets were thoroughly cleaned, rinsed with acetone and were left overnight to dry in the oven at 50°C to minimize changes in the volume of the pipets. All the solutions were handled in glass stoppered apparatus. The solutions were exposed to the atmospheric moisture as little as possible.

A typical run is described below: The concentration of the stock solutions of phenyl isocyanate and aniline were determined as described and the solutions were allowed to stand in the thermostat at 25.0 ± 0.2°C for about thirty minutes to attain temperature equilibrium. Known volumes of the stock solutions were pipetted one at a time, and were transferred to the reaction flask in such proportions that, when mixed, the desired initial reactant concentrations were obtained. The zero time was taken as that time when half the volume of the second solution (amine or isocyanate) had drained into the reaction flask. The total volume of the resulting solution was between 50 and 100 ml. The solution was mixed well by shaking immediately afterwards.
samples ranging in volume between 1 and 10 ml. were withdrawn at appropriate intervals and were run directly into a previously chilled (near 10-15°C) sample of glacial acetic acid such that the final volume of the solution was 50 ml. Five to six drops of the methyl violet indicator solution were added and the anilines was titrated to the first disappearance of the violet color using a 5,000 ml. semi-micro buret. The immediate cooling of the sample to nearly 10-15°C and the dilution with acetic acid slowed down the reaction with phenyl isocyanate so much that no appreciable reaction occurred during the 100 sec. titration period. A magnetic stirrer was used for stirring the sample during titration.

Due to the fact that the product was slightly soluble in benzene (about 12.7 mg in 100 gm of benzene at 18°C.) pipetting difficulties were encountered, especially the start of the reaction where the crystals or sometimes heavy gelatinous precipitates had not enough time to settle. However, the product did not interfere with the titration. A small error was introduced in the reading of the volume of the pipetted sample but this seemed to be insignificant.

(11) Runs involving the determination of isocyanate during the progress of the reaction.- The experimental method used for the determination of the isocyanate concentration was infrared analysis.
In runs where the reactant aniline was in excess, the rate of the reaction was followed with time by following the concentration of the phenyl isocyanate in the solution with time. The intense absorption of infrared radiation at 2267 cm\(^{-1}\) (4.43 \(\mu\)) of the isocyanate group was utilized for plotting the course of the reaction\(^{20,21}\).

**Calibration Curve for Phenyl Isocyanate in Benzene Saturated with Carbonitride.**

Eleven solutions of phenyl isocyanate were prepared and standardized as described earlier by titrimetric method using di-n-butylamine as the standard base. Samples of each of the solutions were placed in a cell with sodium chloride windows. The pathlength used all through was 0.1000 cm. The infrared spectrum was scanned from 4 to 4.7 \(\mu\) using a Perkin Elmer Infracord Spectrophotometer Model 157, with no reference cell in the reference beam; this could be done because the solvent benzene did not absorb infrared radiation in the region where the isocyanate band occurred. The carbon dioxide absorption peak (4.2 \(\mu\)) occurred in the scanned region, very close to the wavelength studied. This was no problem because the isocyanate peak in question was sharp and well resolved from other bands.

To have a standard reference point the instrument was set at 100% transmittance at 4 \(\mu\) every time a spectrum
was taken. The absorbance was read directly from the graph paper and was plotted against concentration in moles per liter. The concentration range chosen was between \(7.66 \times 10^{-2}\) and \(0.64 \times 10^{-2}\) m/l. The curve thus obtained (Fig. 1) showed a negative deviation from Beer's law, the apparent molar absorption coefficient being 530 at the beginning and 697 at the end of the curve.

The runs with excess amine were carried out similarly to those with excess isocyante as described above. The reaction vessel was kept in the thermostat. Small samples were taken at intervals and placed in the 0.1005 cm. cell. The spectrum was scanned between 4 and 4.7 \(\mu\) and the sample was discarded. The reaction was not carried in the cell itself, in order to prevent urea deposition on the walls of the cell and to have a better temperature control than would be obtained if the cell were kept at room temperature. However, another difficulty was encountered. The time elapsed between sampling and measurement was quite important (about 50 sec.) especially when the initial points were considered. On the average, the first reading was taken after 130 to 200 secs. from zero time. In this way the sample remained outside the thermostat, at room temperature which usually differed from the thermostat temperature by a few degrees; this meant that the reaction occurred at room temperature 50\% of the time before the initial absorbance reading was taken for measurements at 100 secs., and 25\% of the time for
Fig. 1 Calibration curve: phenyl isocyanate concentration (m/l) versus absorbance
initial measurements at 200 secs. This might explain the scatter obtained in the initial points of some plots.

The noted time for all the absorbance readings taken throughout the reaction was that time when the instrument went through the peak at 4.43 μ.
EXPERIMENTAL RESULTS

III-1 Introduction

Preliminary kinetic investigations involving the systems ethyl isocyanate-aniline and phenyl isocyanate-aniline in benzene and chlorobenzene were carried out at initial concentrations between 0.02 and 0.07 m/l. In all cases the initial concentrations of the two reagents were about the same (maximum difference was about 10%). These reactions were treated as second order processes for which the following expression holds true as long as the initial concentrations are not exactly the same.

\[
\frac{1}{B_0-A_0} \ln \frac{A_0B}{B_0A} = k_2 t
\]

where \( A_0 \) and \( B_0 \) are the initial concentrations of the reactants whereas \( A \) and \( B \) are the reactant concentrations at time \( t \) and \( k_2 \) is the second order rate constant of the reaction. The term \( \ln \frac{A_0B}{B_0A} \) was plotted against time for the different runs. None of the curves exhibited the linear relations expected from a second order process. All the plots and curvature which indicated change in the apparent order of the reaction as it proceeds. The second order plots of the concentration terms against time have in general shown less scattering of the points in the case of ethyl isocyanate-aniline system. This reaction was found to be much slower than the reaction of phenyl isocyanate with aniline, as expected. To find the second order rate
constants of these reactions tangents were drawn to points at the initial stages of the reaction and the slopes were taken. The values of $k_3$ obtained were not constant for different initial reactant concentrations. They seemed to depend on the initial concentrations of both reactants. The values for $k_3$ increased with increase in the initial reactant concentrations. The initial rate was found to be more affected by changes in the initial amine concentration than of the isocyanate. In general, the slope of the curves was observed to increase at the later stages of the reaction.

These preliminary results indicated a complex rather than a simple bimolecular mechanism for the reaction in question. The rest of this work was devoted to the study of the complex kinetic behavior of the isocyanate-amine reactions.

III-2 Rate Studies in Chlorobenzene

The preliminary data obtained for the phenyl isocyanate-aniline system in chlorobenzene were treated using the expression for a third order reaction,

$$\frac{1}{2} \left( \frac{1}{c_0^2} - \frac{1}{c_0^2} \right) = k_3 t$$

(2)

where $c_0$ is the initial concentration of either reactant, $c$ is the concentration of the chosen reactant at time $t$ and $k_3$ is the third order rate constant of the overall
reaction. For a reaction of the type

\[ A + B \rightarrow \text{products} \]

the use of equation (2) requires that the initial concentra-
tions of A and B be the same or nearly the same. If the
reaction is third order, a plot of \(1/c^2\) against time will
give a straight line with \(2k_3\) as its slope. Such a treat-
ment of the data is summarized in Table 1.

<table>
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<th>(c_0) (aniline), m/l</th>
<th>(c_0) (PhHCO), m/l</th>
<th>(k_3), (1^2/\text{m}^2\text{-sec})</th>
</tr>
</thead>
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<tr>
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<td>(1.4 \times 10^{-1})</td>
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<td>0.0318</td>
<td>0.0488</td>
<td>(1.24 \times 10^{-1})</td>
</tr>
<tr>
<td>0.0211</td>
<td>0.0157</td>
<td>(1.38 \times 10^{-1})</td>
</tr>
</tbody>
</table>

In some cases, a downward drift of the points was
observed after 75-90% reaction in the third order plot; \(k_3\)  
was determined from the slope of the best straight line
drawn through most of the points. The results show an  
increase in \(k_3\) as the initial concentration of the aniline  
decreases.

III-3 Rate Studies in Benzene

The data obtained from these studies were treated  
in the same manner as above. Third order rate constants
listed in Table 2 were calculated by plotting the square of  
the reciprocal of the aniline concentration versus time.
The plots obtained were linear in most cases. In some of the runs, however, large scatter of the very last points was observed. The results obtained are listed in Table 2.

Table 2

<table>
<thead>
<tr>
<th>$c_a$(aniline), m/l</th>
<th>$c_a$(HNO3), m/l</th>
<th>$k_2$, $1^2$/m²·sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0707</td>
<td>0.0562</td>
<td>7.70 x 10⁻²</td>
</tr>
<tr>
<td>0.0560</td>
<td>0.0332</td>
<td>6.00 x 10⁻³</td>
</tr>
<tr>
<td>0.0353</td>
<td>0.3331</td>
<td>7.65 x 10⁻²</td>
</tr>
<tr>
<td>0.0240</td>
<td>0.0616</td>
<td>3.10 x 10⁻³</td>
</tr>
<tr>
<td>0.0235</td>
<td>0.0221</td>
<td>0.194</td>
</tr>
</tbody>
</table>

There does not seem to be a consistency in the $k_2$ values obtained.

Some experiments were done using acetic solvent chlorobenzene and benzene mixtures of predetermined concentration and a known dielectric constant, prepared by changing the proportions of pure liquids. These experiments were performed in order to study the effect of the dielectric constant of the solvent on the rate of the isocyanate-amine reactions. It was hoped in this manner to test the expression given by Kirkwood⁡ that relates the dielectric constant of the solvent to the rate constant of a simple bimolecular reaction. The fact that the reactions did not follow second order kinetics, however, ruled out the possibility of making this test.
III-4 Rate Studies in Benzene - Saturated with Carbonilide

To reduce the effect of autocatalysis by the product urea to its minimum all the runs to follow were

-carried in benzene saturated with carbonilide. Values of
the coefficient $k_0/k_1$ for the system phenyl isocyanate-

-aniline reported by Craven on his communication indicate
that catalysis by the urea produced during the reaction is

-

-very small. In this special case, for benzene as solvent,
-
the effect will be much smaller because of the low solu-
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For the special case where isocyanate remains constant throughout the reaction, the above rate expression reduces to

$$\text{Rate} = k' \left[ A \right]^a$$

(4)

where $k'$, the apparent rate constant of the reaction, is the product of $k$ and $\left[ I \right]^b$.

$$k' = k \left[ I \right]^b$$

(5)

The reaction would then be pseudo $'a'$ th order in aniline concentration. $k'$ can be determined from the curves obtained when appropriate concentration terms for the amine are plotted against time. The correct order in amine was determined by trial and error. Different values were given to $'a'$; log (aniline) was plotted against time to test for $a = 1$, i.e. first order, and $\frac{1}{(\text{aniline})^{a-1}}$ was plotted versus time to test for $'a'$ th order, for $a > 1$. The value of $'a'$ that gave the best straight line for the experimental points was considered to be the correct order in aniline (Fig. 2).

From equation (5),

$$\log k' = \log k + b \log \left[ I \right]$$

(6)

Using equation (6) it can be calculated from the slope of a plot of log $k'$ versus log $\left[ I \right]^b$. Log $k$ then would be the intercept of the plot.

Considering the second order plots in aniline concentration, $k'$ values were obtained for the runs involving excess isocyanate. The apparent rate constants were
Fig. 2 \( \frac{1}{(A)^{n-1}} \) (1/m) versus time in sec for experiments with excess isocyanate.

Curve 1. \( a = 2.5 \)
Curve 2. \( a = 1.7 \)
Curve 3. \( a = 2.0 \)

where \( a = n \) in the figure
determined for several runs with different initial isocyanate concentrations (Table 3).

<table>
<thead>
<tr>
<th>c₀(PhNCO), m/l</th>
<th>c₀(PhNCO)/c₀(aniline)</th>
<th>kᵦ, 1/m sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1342</td>
<td>3.77</td>
<td>1.29x10⁻²</td>
</tr>
<tr>
<td>0.1496</td>
<td>4.10</td>
<td>1.76x10⁻²-1.85x10⁻²</td>
</tr>
<tr>
<td>0.2222</td>
<td>6.28</td>
<td>4.23x10⁻²-4.43x10⁻²</td>
</tr>
<tr>
<td>0.2795</td>
<td>7.85</td>
<td>6.74x10⁻²-6.84x10⁻²</td>
</tr>
<tr>
<td>0.3746</td>
<td>10.34</td>
<td>6.47x10⁻²-7.92x10⁻²</td>
</tr>
</tbody>
</table>

* Range of kᵦ values determined from the slopes of the different possible straight lines that could be drawn through the points.

Log kᵦ was plotted against log[I] (Fig. 3). The slope of the best straight line passing through the points was found to be between 2.0 and 2.2. In equation (8) this is '1', the order in isocyanate. The value of k was calculated from the intercept to be 1.13 $1^\circ/m^2$-sec. Values other than 2.0 were given to 'a'; the curves obtained by plotting log kᵦ values against log[I] showed wide scattering of the points and it was impossible to assume any reasonable curve for the plot.

B. Experiments with Excess Aniline

To provide an experimental basis for the order of the reaction in isocyanate concentration, kinetic investigations were undertaken where the aniline concentration was kept in appreciable excess all through the reaction. This is the reverse of the situation described in section A.
Fig. 3  Plot of $\log k'$ versus $\log [I]$, where $[I]$ is the initial isocyanate concentration for the different runs with excess isocyanate.
above. This resulted in a pseudo \(i\)th order reaction in isocyanate where \(i\) could be determined from the experimental data by trial and error again.

The change in isocyanate concentration with time was followed by infrared analysis (see page 18). For the present reaction,

\[ k'' = k [1]^i \]  

and therefore,

\[ \log k'' = \log k + a \log [A] \]  

where \([A]\) is the concentration of aniline (excess reagent) used.

By considering the plots of \(\log [\text{[An]}]\) versus time, \(k''\) values were obtained for the reaction with excess aniline. These first order plots were approximate straight lines (Fig. 4) although, in some runs which involved a low ratio of the initial reactant concentrations, i.e. \(\frac{[A]}{[\text{[An]}]}\), curvature was apparent. This is expected, since under these conditions the aniline concentration is no longer constant throughout the reaction. In such cases, the slope of the tangent to the curve was taken as \(k''\) for a particular initial isocyanate concentration. Curvature was also observed in some cases where the initial reactant concentration ratios were high although these are not included in the tabulated results.

The values for \(k''\) obtained in this manner are shown
Fig. 4 For experiments with excess aniline:

Curve 1. \(-\log [PhNCO]\) versus time (sec); test for first order.

Curve 2. \(1/ [PhNCO] \) (1/m) versus time (sec); test for second order.
in Table 4.

<table>
<thead>
<tr>
<th>$c_o$(aniline), m/l</th>
<th>$c_o$(aniline)/$c_o$(PhNO$_2$)</th>
<th>$k^n \text{1/m-sec}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3821</td>
<td>11.27</td>
<td>$1.27 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.2698</td>
<td>7.96</td>
<td>$6.22 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.89 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.2243</td>
<td>7.97</td>
<td>$4.56 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.1771</td>
<td>4.10</td>
<td>$2.39 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.47 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.1686</td>
<td>3.82</td>
<td>$1.75 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.00 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.1300</td>
<td>2.92</td>
<td>$2.59 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.98 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.85 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.1184</td>
<td>3.99</td>
<td>$1.77 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.02 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.33 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

* Range of $k^n$ value.

$k^n$ appears to decrease with decrease in the initial aniline concentration. A plot of log $k^n$ versus log $[A]$ gave (Fig. 5) a curve. The curvature was more pronounced at lower values of the ratio $[k]$ but by considering the uncertainty present in each point on the graph it was possible to draw a straight line. In equation (8) the slope of
Fig. 5 Plot of log $k^\#$ versus log $[A]$ where $[A]$ is the initial aniline concentration for the different runs with excess aniline.
this straight line is 'a', the order in x, and the intercept is log k where k is the rate constant for the overall reaction; 'a' was found to be 2.0 ± 0.1.

The value of k thus obtained is 8.20 x 10^{-3} ± 0.10 x 10^{-3} which can be considered as the average value for the third order rate constant of the reaction at 25°C.
IV DISCUSSION

The experimental results have shown that the reaction of phenyl isocyanate with aniline is third order overall when the initial reactant concentrations are almost equal and also when the aniline is present in excess concentration during the reaction. The order in aniline and phenyl isocyanate are approximately 2.0 \pm 0.1 and 1, respectively. However, when an appreciable excess of the isocyanate is used, the reaction changes to fourth order, being second order in each reactant.

Craven and others have proposed a general mechanism for the reaction of isocyanates and amines. Craven's scheme consists of the following steps:

1. \( \text{Ar}=\text{N}=\text{C}+\text{Ar}=\text{NH}_2 \xrightarrow{k_1} \text{Complex} \)
   \[ \text{Complex} \xrightarrow{k_2} \text{Complex} + \text{Ar}=\text{NH}_2 \]  
   \[ \text{Complex} + \text{Ar}=\text{NH}_2 \xrightarrow{k_3} \text{Complex} + \text{Ar}=\text{NH}_2 \]

2. \( \text{Complex} + \text{Ar}=\text{NH}_2 \xrightarrow{k_4} \text{Complex} + \text{Ar}=\text{NH}_2 \)
   \[ \text{Complex} + \text{Ar}=\text{NH}_2 \xrightarrow{k_5} 2\text{Complex} + \text{Ar}=\text{NH}_2 \]

The expression for the initial rate of reaction obtained from this mechanism, ignoring the catalyzed step (3), is

\[ R_o = \frac{k_1k_3}{k_1+k_2} \]

- 32 -
where the subscripts zero refer to initial conditions. For $k_{2o} \gg k_{-1}$, the reaction should follow second order kinetics according to the above mechanism. On the other hand, for $k_{-1} \gg k_{2o}$, the reaction should be third order overall. Under no circumstances can this mechanism explain the observed fourth order kinetics of the reaction.

Step (3) is not important as far as the reactions in benzene are concerned because the product area is only slightly soluble in this solvent. This fact can be shown quantitatively by considering some numerical values of the ratio $\left(\frac{k_2}{k_2}ight)$. This ratio was found by Graven to be 0.23 for the reaction of phenyl isocyanate with aniline in dioxane as solvent when the initial concentrations of aniline and phenyl isocyanate are 0.05 m/l. The solubility of carbam- 
lide in benzene was measured to be about 0.11 g/ml at 18°C. Therefore, the product concentration in the experiments using benzene as solvent, described in sections III-3 and III-4 will not exceed $5 \times 10^{-4}$ m/l. From reactions (2) and (3) above,

$$\frac{P_3}{P_2} = \frac{k_{2o}u}{k_{2o}} = 0.043$$

Assuming that the ratio of the rate constants does 
not change appreciably when the solvent is changed from 
dioxane to benzene, this value represents a probable maximum 
for the ratio of the rates of reactions (3) and (2) for all 
the reactions carried out in benzene solutions saturated
with carbamidine. This is true because the aniline concentration is one of the smallest initial amine concentrations used in the experiments described in sections III-3 and III-4.

An attempt was made to extend the postulated mechanism in order to account for the facts observed in this work. A modified mechanism which is consistent with the results of part III has the following scheme:

1. \[ \text{Ar-N}=\text{C}=\text{O} + \text{Ar-NH}_2 \xrightarrow{k_1} \text{Complex 1} \]
   \[ i \quad a \quad \xrightarrow{k_1} \quad c_1 \]

2. \[ \text{Complex 1} + \text{Ar-NH}_2 \xrightarrow{k_2} \text{Complex 2} \]
   \[ c_1 \quad a \quad \xrightarrow{k_2} \quad c_2 \]

3. \[ \text{Complex 2} \xrightarrow{k_3} (\text{ArNH})_2\text{C}=\text{O} + \text{Ar-NH}_2 \]
   \[ c_2 \quad u \quad a \]

3'. \[ \left[ \text{Complex 1} + (\text{ArNH})_2\text{C}=\text{O} \xrightarrow{k_3'} 2(\text{ArNH})_2\text{C}=\text{O} \right] \]
   \[ c_2 \quad u \quad 2u \]

4. \[ \text{Complex 2} + \text{Ar-N}=\text{C}=\text{O} \xrightarrow{k_{\text{slow}}} 2(\text{ArNH})_2\text{C}=\text{O} \]
   \[ c_2 \quad i \quad 2u \]

The flow sheet presented below shows the interrelations of the intermediates involved.
By making the following assumptions a rate expression was derived for the new mechanism:

a) Reactions (1) and (2) attain equilibrium quickly.

b) Reactions (3) and (4) are slow. Consequently complexes \( c_1 \) and \( c_2 \) have appreciable lifetimes in solution.

c) Reaction (3') is even slower.

For the reasons outlined above, reaction (3') is considered unimportant in all the experiments described in this study.

Under conditions where excess isocyanate is used, reaction (3) for the disappearance of complex 2 becomes less important relative to reaction (4). Disregarding steps (3) and (3'),

\[
c_1 = \frac{k_{a1}}{k-1},
\]

\[
c_2 = \frac{k_{a2}k_{a2}}{k-2} = \frac{k_1k_{a2}}{k-3k-2}
\]

then, the corresponding rate expression would be:

\[
\frac{du}{dt} = 2k_4 \times \frac{k_1}{k-1} \times \frac{k_{a2}}{k-2} (a^2t^2)
\]

\[
= 2k_4k_1k_{a2}(a^2t^2)
\]

(A)

Where \( K_1 \) and \( K_2 \) are the corresponding equilibrium cons-
stants for the reactions (1) and (2). It is apparent from
the above rate expression that the postulated new mechanism
gives fourth order kinetics under the specified conditions
and furthermore that the dependence is on the second power
for each reactant.

For reactions involving excess aniline step (4) becomes
less important relative to step (3). In this case,

\[ \frac{c_1}{k_{1a}} = \frac{k_{1a}c_1}{k_{-1}} = \frac{k_{1a}k_{2a}c_1}{k_{-1}k_{-2}} = k_{1a}k_{2a}c_1^2 \]

Since the rate of formation of products is proportional to
the concentration of \( c_2 \), then

\[ \frac{du}{dt} = k_{1a}k_{2a}c_1^2 \tag{3} \]

In experiments done with excess aniline the reaction
was found to be third order overall, approximately second
order in aniline and first order in isocyanate. Furthermore,
with excess isocyanate, the reaction changed to fourth order,
second order in each reactant. Equations (A) and (B) show
that the assumed mechanism is consistent with the observed
kinetics.

Several other mechanisms were tried. None of them
explained the experimentally determined order of the
reactions when excess isocyanate was present.

The mechanism proposed above is also chemically reasonable. The first step involves the formation of complex 1. Baker and co-workers and others have suggested the following structure for this complex:

\[
\text{Ar} \quad \begin{array}{c}
\downarrow \\
\text{N} \quad \text{C} \quad \text{H}_2\Theta
\end{array}
\]

Complex 2 is a trimolecular one probably of the type given by Craven as:

\[
\text{Ar} \quad \begin{array}{c}
\downarrow \\
\text{N} \quad \text{H}
\end{array}
\]

where HM represents a proton acceptor-donor.

In this study complex 2 would be:

\[
\text{Ar} \quad \begin{array}{c}
\downarrow \\
\text{N} \quad \text{H}
\end{array}
\]

which, in excess anilino, breaks up to give a molecule of
Anilines and another molecule of the enol-form of the product urea.

\[
\begin{align*}
\text{Ar} & \quad \text{and} \quad \text{Ar} - \text{N}^+\text{H} \\
\text{H} - \text{N} - \text{H} & \quad \text{Ar} - \text{N} = \text{C} - \text{O} - \text{H}
\end{align*}
\]

The enolic form of the product molecule then tautomerizes to give \( \text{N,N'} \)-diphenyl urea as shown:

\[
\begin{align*}
\text{Ar} - \text{N}^+\text{H} & \quad \text{Ar} - \text{N}^-\text{H} \\
\text{Ar} - \text{N} = \text{C} - \text{OH} & \quad \text{Ar} - \text{N} = \text{C} = \text{O}
\end{align*}
\]

Reaction (4) proceeds probably through the formation of an intermediate complex which has the right stoichiometry to yield two molecules of product.

\[
\begin{align*}
\text{Ar} - \text{N}^+\text{H} & \quad \text{O} = \text{C} = \text{N} = \text{Ar} \\
\text{Ar} - \text{N} = \text{C} = \text{O} & \quad \text{Ar} - \text{N} = \text{C} = \text{O}
\end{align*}
\]

Intermediate complex

\[
\begin{align*}
\text{Ar} - \text{N}^+\text{H} & \quad \text{N} = \text{O} = \text{C} = \text{N} = \text{Ar} \\
\text{Ar} - \text{N} = \text{C} - \text{OH} & \quad \text{Ar} - \text{N} = \text{C} - \text{OH}
\end{align*}
\]

These complexes are undoubtedly relatively unstable and do not have long lifetimes. They are probably present
in only minute concentrations in the reaction mixture. Nevertheless, the concentrations are large enough so that the equilibria described in reactions (1) and (2) are established over essentially the entire course of the reaction. Complexes similar to $c_1$ and $c_2$ have been postulated to account for the kinetics of the alcohol-isocyanate reaction as well. Further work might well be directed to a concrete demonstration of the existence of these complexes and a study of their nature.

In conclusion, the reaction of phenyl isocyanate with aniline in benzene as solvent follows third order kinetics (I) when equal initial reactant concentrations are used and (II) when aniline is in excess in the reaction mixture. However, with excess isocyanate, the reaction becomes fourth order overall.

A satisfactory mechanism for this reaction must be able to account for the above mentioned empirical information. The mechanism proposed by Graven and others is insufficient to explain all the observations of the present study. The mechanism suggested here does not rule out the previous mechanism but extends it to explain the results obtained from the more extensive kinetic experiments described in part III.
APPENDIX

Photolysis of Methyl Isocyanate

V-1 Introduction

The photolysis of compounds of the ketene (C=O=O) and diazoethane (C≡N≡N) families and the reactions of the methylene produced have been extensively studied \(^1\), \(^2\). Methylene radicals were found to add into carbon-hydrogen bonds \(^2\), \(^5\) to give longer chains and into carbon-carbon double-bonds \(^4\), \(^5\) to give substituted cyclopropanes, among other products.

This project was an attempt to study the analogous reactions of organic isocyanates (-N=O=-O). The substituted imines radicals expected from the photolysis of an alkyl isocyanate were expected to add into carbon-hydrogen bonds to give amines and into carbon-carbon double-bonds to give cyclic imines, among other products.

V-2 Experimental Procedure and Results

Methyl isocyanate was prepared by the alkylation of potassium cyanate in the presence of anhydrous sodium carbonate using dimethyl sulfate as the alkylating agent, following the method of Slotta and Lorentz \(^6\).

The ultraviolet absorption maximum for methyl isocyanate was found to be below 207 nm. Readings beyond this wavelength could not be taken because the instrument (Beckman Model DU Spectrophotometer) used was not sensitive in that region of the spectrum.

- 40 -
The infrared spectrum of methyl isocyanate was taken in cyclohexane and carbon tetrachloride as solvents, using a Perkin Elmer Model 112 Spectrophotometer. The following are the principal bands observed:

<table>
<thead>
<tr>
<th>Wavelength (cm⁻¹)</th>
<th>Cyclohexane</th>
<th>Carbon tetrachloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>2920</td>
<td>wk.</td>
<td>wk.</td>
</tr>
<tr>
<td>2276</td>
<td>st.</td>
<td>st.</td>
</tr>
<tr>
<td>1411</td>
<td>wk.</td>
<td>wk.</td>
</tr>
<tr>
<td>1167</td>
<td>wk.</td>
<td>wk.</td>
</tr>
<tr>
<td>859</td>
<td>-</td>
<td>med. st.</td>
</tr>
<tr>
<td>854</td>
<td>-</td>
<td>wk.</td>
</tr>
</tbody>
</table>

The strong band at 2276 cm⁻¹ characteristic of isocyanates had been reported to occur at 2232 cm⁻¹. The value found here agrees with that found for other isocyanates.

Preliminary liquid-phase experiments were performed with methyl isocyanate in excess cyclohexane. The expected amine was N-methyl cyclohexyl amine which in turn could react with the methyl isocyanate present to give the corresponding urea.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]
The photolysis was followed by the intensity of the characteristic strong infrared absorption band due to the isocyanate group at 2276 cm⁻¹. Other bands were absent in this region of the spectrum.

Several different light sources were used for the photolysis. The electrodes used have intense emission lines in the region where the ultraviolet absorption maximum of methyl isocyanate occurs (200 - 220 nm). Lead (217 nm) and zinc (214 nm) 115 v. D.C. open arcs were tried but the high temperatures obtained melted the electrodes; so, it was not possible for the arc to last more than 2 min.

Zinc and cadmium (228 nm) enclosed arcs (Phillips Electrical 450 v. A.C.) were used for up to three hours to irradiate a 3.83 x 10⁻² molar solution of methyl isocyanate in cyclohexane. Under no circumstances was the isocyanate concentration reduced by more than 1% during this period.

In an attempt to obtain a brighter light source, a
high-voltage (12kV) A.C. condensed spark discharge was constructed and lead electrodes (intense emission at 220 mp) were used. The solution was examined in the ultraviolet region after forty five minutes of direct irradiation from this source. Readings were taken in the region 220 - 350 mp. There was an appreciable change in the spectrum after photolysis. The results were as follows:

<table>
<thead>
<tr>
<th>λ (mp)</th>
<th>A&lt;sub&gt;original&lt;/sub&gt;</th>
<th>A&lt;sub&gt;final&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>0.929</td>
<td>0.780</td>
</tr>
<tr>
<td>235</td>
<td>0.432</td>
<td>0.375</td>
</tr>
<tr>
<td>236</td>
<td>0.406</td>
<td>0.343</td>
</tr>
<tr>
<td>237</td>
<td>0.334</td>
<td>0.285</td>
</tr>
<tr>
<td>238</td>
<td>0.363</td>
<td>0.297</td>
</tr>
<tr>
<td>239</td>
<td>0.343</td>
<td>0.278</td>
</tr>
<tr>
<td>240</td>
<td>0.328</td>
<td>0.258</td>
</tr>
<tr>
<td>242</td>
<td>0.301</td>
<td>0.230</td>
</tr>
<tr>
<td>244</td>
<td>0.288</td>
<td>0.226</td>
</tr>
<tr>
<td>246</td>
<td>0.283</td>
<td>0.187</td>
</tr>
<tr>
<td>248</td>
<td>0.202</td>
<td>0.173</td>
</tr>
<tr>
<td>250</td>
<td>0.188</td>
<td>0.159</td>
</tr>
<tr>
<td>250</td>
<td>0.065</td>
<td>0.108</td>
</tr>
<tr>
<td>270</td>
<td>0.064</td>
<td>0.075</td>
</tr>
<tr>
<td>280</td>
<td>0.061</td>
<td>0.035</td>
</tr>
<tr>
<td>290</td>
<td>0.064</td>
<td>0.043</td>
</tr>
<tr>
<td>300</td>
<td>0.049</td>
<td>0.034</td>
</tr>
<tr>
<td>310</td>
<td>0.025</td>
<td>0.026</td>
</tr>
<tr>
<td>320</td>
<td>0.013</td>
<td>0.019</td>
</tr>
<tr>
<td>330</td>
<td>0.008</td>
<td>0.014</td>
</tr>
<tr>
<td>340</td>
<td>0.003</td>
<td>0.017</td>
</tr>
<tr>
<td>350</td>
<td>0.000</td>
<td>?</td>
</tr>
</tbody>
</table>

The final solution absorbs more than the original one in certain regions as shown by the absorbance values at 260 and 270 mp. If real, this suggests the formation of a new compound, probably the corresponding was in
which the carbonyl group has a UV absorption maximum in
the neighborhood of 300 mū. However, no new bands were
observed in the infrared spectrum.

Unfortunately the transformer construction proved
to be faulty and no further experiments could be carried
cut.

The lack of positive evidence of photolysis might
be due to the fact that the light sources used do not
have sufficient energy in the proper region of the spectrum.
Attainment of stable excited states by the molecules after
the absorption of radiation at the absorption maximum
could also be a reason for lack of photolysis. This cannot
be decided on the basis of the work done in this study.
Useful information may be obtained from experiments with
brighter sources used for photolysis. The quantum yield
of the reaction can be determined by calibrating the light
source.

V-3 References to Appendix
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   1957, 781.
3. Deering, W. von E., Buttery, F.G., Laughlin, R.G., and
   72, 4496-7 (1956).
VI. BIBLIOGRAPHY

   c) ibid., 1949, 19.
   b) ibid., 22, 578 (1950).