KINETICS

OF THE REACTION BETWEEN

PHENYL ISOCYANATE AND ANILINE

BY

MARIE H. KASPARIAN

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ABSTRACT

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 $8.20 \times 10^{-3} \pm 0.10 \times 10^{-3}$ l^2/m^2-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^3/m^3-sec at $25^{o}C$.

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

TABLE OF CONTENTS

LIST OF TABLES

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.

$$(R)Ar-N=C=O + (R)Ar-NH_2 \quad ------\rightarrow \quad (R)Ar-NH-\overset{\overset{\text{O}}{\|}}{C}-NH-Ar(R)$$
$$\text{isocyanate} \quad \text{amine} \qquad\qquad\qquad \text{urea}$$
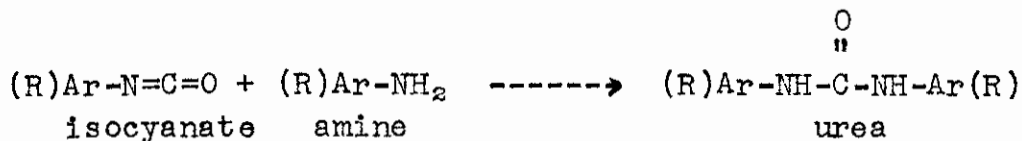
The rate of the reaction has been thought to depend on the first power of the concentration of each reactant.

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[2a] in 1934. It was then[2b] 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[2a]. 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.[2c] 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[4]. 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[3] 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[6 - 11] of the analogous urethane formation.

I-2 Kinetics and Mechanism

A. Alcohol-Isocyanate 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 Verbanc[8] in 1957.

The earliest work on the kinetics of the action of isocyanates on alcohols was that of Davis and Farnum[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, i-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[7]. 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 Stagg[3] method of analysis for isocyanates Baker

and Holdsworth[7a] 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, Mallat and Wilson[5], (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:

$$Ar\text{-}N\text{=}C\text{=}O + R_3N \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \quad Ar\text{-}N\text{=}C\text{-}\ddot{O}:^{\ominus}$$
$$\underset{R_3N}{\overset{|}{}} {}^{\oplus}$$

Complex

$$Complex + MeOH \overset{k_3}{\dashrightarrow} NH.ArCO_2Me + R_3N$$

$$Ar\text{-}N\text{=}C\text{=}O + MeOH \overset{k_0}{\dashrightarrow} NH.ArCO_2Me$$
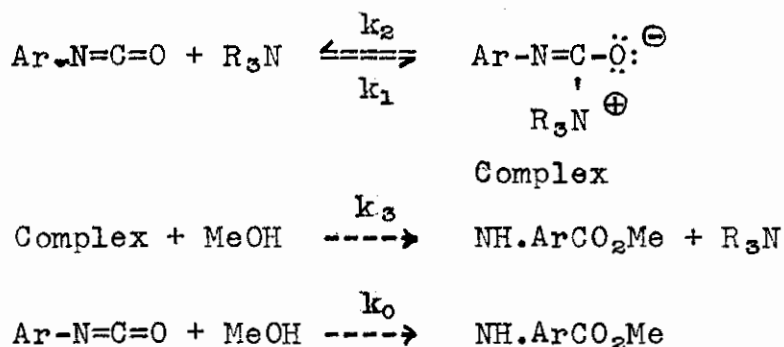
With this mechanism at hand repulsion energies between adjacent substituent groups in the complex were calculated for the different bases and isocyanates used. Higher repulsion energies were obtained for the dialkyl anilines. This confirmed the suggestion of explaining in terms of steric effects the 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[7b,c] 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 —

$$Ar-N=C=O + ROH \overset{k_2}{\underset{k_1}{\rightleftharpoons}} \quad \underset{\substack{ROH \\ \oplus \\ Complex}}{Ar-N=C-\overset{\ominus}{\ddot{O}:}}$$

$$Complex + ROH \overset{k_3}{\dashrightarrow} Ar.NHCO_2R + ROH$$
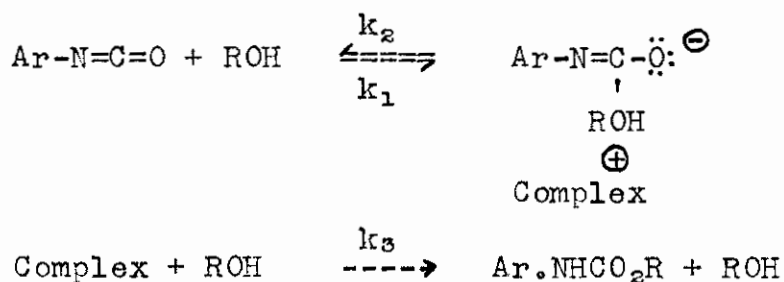
The experimental results obtained from the uncatalyzed reactions were verified by Dyer et al.[6] who used dilatometric methods for studying the rates of n-butyl and sec-butyl alcohols with phenyl isocyanate and confirmed their results by chemical analysis.

A rate expression was derived[7a] by assuming a steady

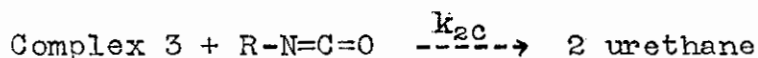state concentration of the complex. The resulting expression
after rearrangement was:

$$\frac{[ROH]}{k_0} = \frac{k_2}{k_1 k_3} + \frac{[ROH]}{k_1}$$

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

A study[7b,d,e] of the base-catalyzed reaction in di-n-
butyl ether and benzene as solvents, at two different temp-
eratures made possible the evaluation of k_1 and E_1, activa-
tion energy associated with k_1, 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 given 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_0 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 Mesrobian investiga-
ted the "spontaneous" reaction of alcohols with phenyl iso-
cyanate in a variety of solvents[9]. Their results indicate
that the rate is dependent chiefly on the dielectric constant
of the solvent — a point which had 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-workers[7b,c,d] for the uncatalyzed reaction was
modified.

(i) $2ROH \rightleftharpoons$ Complex 1
$\qquad k_{1a}$

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

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

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

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

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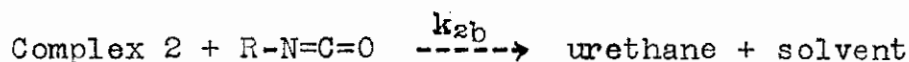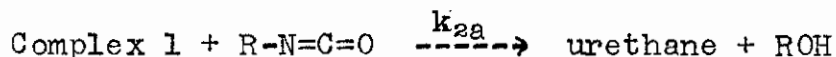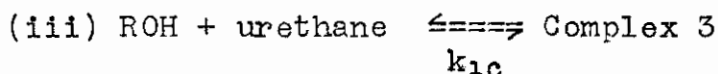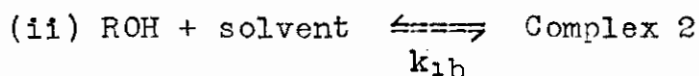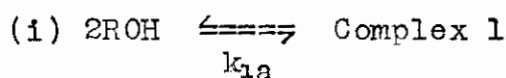
where k_1's are the equilibrium constants and k_2's are the
rate constants. Reactions (i) and (iii) were found to
predominate in non-hydrogen bonding solvents whereas (ii)
and (iii) were so in hydrogen-bonding ones.

B. Amine-Isocyanate Reactions.

It was only after such a detailed study of the iso-
cyanate-alcohol reaction kinetics that the simple picture
of isocyanate-amine reactions became suspect[8]. Recently, a
review article by Arnold, Nelson and Verbanc[8] mentioned
some kinetic experiments involving the reaction of different
aromatic isocyanates with aromatic amines in dioxane as
solvent. The study was done by Craven who had presented
the report at an American Chemical Society Symposium on
isocyanates[4]. The rates were found to be affected more by
changes in amine concentration than in isocyanate concentra-
tion; the reactions were observed to be catalyzed by the
product ureas 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 $R_0 = k i_0 a_0^n$, where i_0, a_0 are initial concentrations 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[8] with the alcohol-isocyanate reaction mechanism and relying on the observations from experiments, Craven has proposed two competing reactions for amine-isocyanate systems:

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

$$1. \quad Ar-N=C=O + Ar-NH_2 \xrightleftharpoons[k_1]{k_2} Ar-N=C-\ddot{O}:^{\ominus}$$
$$| \atop ArNH_2 \atop \oplus$$
$$Complex$$

$$2. \quad Complex + Ar-NH_2 \xrightarrow{k_3} (ArNH)_2C=O + Ar-NH_2$$
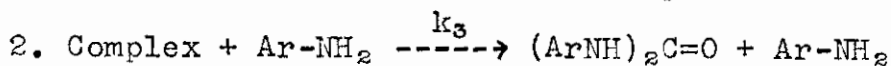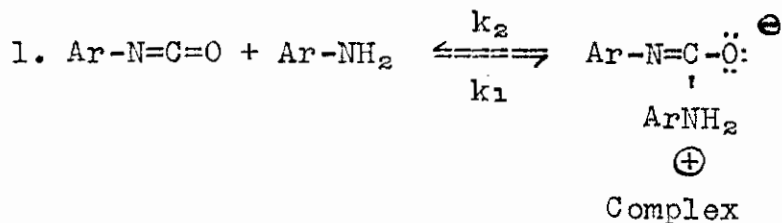
II. Catalyzed Step, which is important later in the course
of the reaction,

1. $Ar-N=C=O + Ar-NH_2 \underset{k_1}{\overset{k_2}{\rightleftharpoons}}$ Complex

2. Complex + $(ArNH)_2C=O \overset{k_3'}{-----\rightarrow} 2(ArNH)_2C=O$
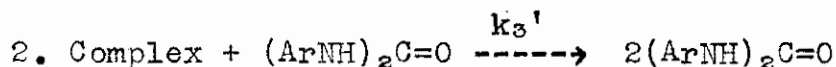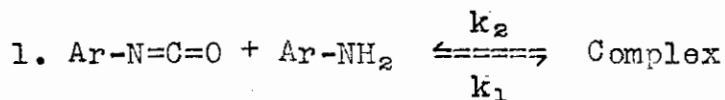
Using the uncatalyzed path, the initial rate expression
was found to be,

$$R_o = \frac{k_1 k_3 i_0 a_0^2}{k_2 + k_3 a_0}$$

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

I-3 Methods of Analysis

The technique of/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[13].

Very sharp end points were obtained through the use of very slightly basic solvents[12]. The first titrations of organic amines were done in glacial acetic acid solvent using a mineral acid in glacial acetic acid as the titrant[13,14]. 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[15] was $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$. Aniline and other bases were titrated in benzene and chloroform the titrant being hydrogen chloride dissolved in benzene[12]. p-Toluenesulfonic acid in benzene was tried as a titrant by Dietzel and Paul[12], but it proved to be too weak to give good results.

Fritz[16a] 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[14,19].

Titrations in non-aqueous media were found to be particularly useful in the quantitative determination of aliphatic[17] and aromatic[18] primary, secondary and tertiary amines in amine mixtures.

The method has been applied to a variety of substances

- 12 -

using both visual indicators and potentiometric procedures[12].

EXPERIMENTAL PROCEDURE

II-1 Introduction

The experimental procedure involves the preparation of different solutions of n- and di-n-butylamine, aniline, ethyl and phenyl isocyanates in benzene and in chlorobenzene, 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 diprotic and hydrogen

chloride is volatile[19].

The titrant solution was prepared according to the
directions specified by Fritz[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[16a]. In this particular case, water is undesira-
ble 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)[12]. The
solution was then standardized against potassium acid
phthalate dissolved in glacial acetic acid to a methyl
violet end point[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 (Merck, 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 per-
chloric 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 22 with a glass indicator electrode and silver-silver chloride reference electrode. The end point color does not agree with the end point reported by Fritz[16a].

A sample of the solution of amine in benzene was pipeted 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 Stagg 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), a

heating device and a stirrer was used for controlling the temperature of reaction mixtures. The thermometer used read accurately five hundreths 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°C. so that the uncertainty involved in the temperature readings is of the order of 0.20 to 0.3 °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°C. At intervals, samples were analyzed by titration. The isocyanate concentration was found to be unchanged, whithin 1% deviation, over a period of one week.

(ii) Similar trials involving the isocyanate together with product carbanilide (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 pipetes. 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° for about thirty minutes to attain temperature equilibrium. Known volumes of the stock solutions were pipeted 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 mls. were with-
drawn at appropriate intervals and were run directly into a
previously chilled (near 10-15°) 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 aniline was titrated to the first dis-
appearance 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 urea 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[12].
A small error was introduced in the reading of the volume of
the pipetted sample but this seemed to be insignificant.

(ii) Runs involving the determination of isocyanate
during the progress of the reaction.- The experimental
method used for the determination of the isocyanate concentra-
tion 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 infra-
red radiation at 2257 cm^{-1} (4.43 μ) of the isocyanate
group was utilized for plotting the course of the
reaction[20,21].

Calibration Curve for Phenyl Isocyanate in Benzene
Saturated with Carbanilide.

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
0.1095 mm. The infrared spectrum was scanned from 4 to
4.7 μ using a Perkin Elmer Infracord Spectrophotometer
Model 137, 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 iso-
cyanate band occurred. The carbon dioxide absorption peak
(4.2 μ) occurred in the scanned region, very close to the
wavelength studied. This was no problem because the iso-
cyanate 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 μ 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 x 10^{-2} and 0.64 x 10^{-2} m/l. The curve thus obtained
(Fig. 1) showed a negative deviation from Beer's law, the
apparent molar absorption coefficient being 930 at the
beginning and 897 at the end of the curve.

The runs with excess amine were carried out similarly
to those with excess isocyanate as described above. The
reaction vessel was kept in the thermostat. Small samples
were taken at intervals and placed in the 0.1095 mm. cell.
The spectrum was scanned between 4 and 4.7 μ 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/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.)
specially when the initial points were considered. On the
average, the first reading was taken after 100 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
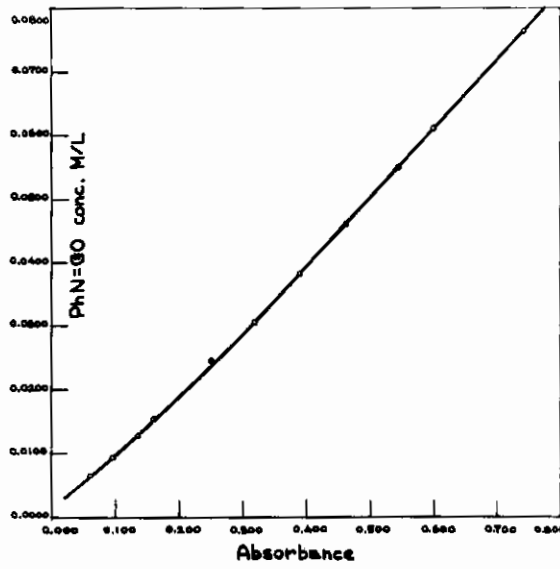
Fig. 1 Calibration curve; phenyl isocyanate concentra-
      tion (m/l) versus absorbance

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 so long as the initial concentrations are not exactly the same.

$$\frac{1}{B_0 - A_0} \ln \frac{A_0 B}{B_0 A} = k_2 t , \qquad (1)$$

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 $\ln \frac{A_0 B}{B_0 A}$ 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[8]. To find the second order rate

- 22 -

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_2 obtained were not constant for different initial reactant concentrations. They seemed to depend on the initial concentrations of both reactants. The values for k_2 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 iso-cyanate-aniline system in chlorobenzene were treated using the expression for a third order reaction,

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

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

$$A + B \dashrightarrow \text{products}$$
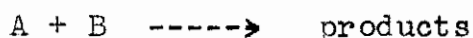
the use of equation (2) requires that the initial concentrations of A and B be the same or nearly the same. If the reaction is third order, a plot of $1/c^2$ against time will give a straight line with $2k_3$ as its slope. Such a treatment of the data is summarized in Table 1.

<div align="center">Table 1</div>

c_0(aniline), m/l	c_0(PhNCO), m/l	k_3, l^2/m^2-sec
0.0643	0.0602	6.3×10^{-2}
0.0330	0.0352	1.14×10^{-1}
0.0318	0.0298	1.24×10^{-1}
0.0211	0.0197	1.38×10^{-1}

In some cases, a downward drift of the points was observed after 75-80% 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

c_o(aniline), m/l	c_o(PhNCO), m/l	k_3, l^2/m^2-sec
0.0707	0.0662	7.70×10^{-2}
0.0360	0.0328	9.00×10^{-3}
0.0353	0.0331	7.65×10^{-2}
0.0240	0.0218	9.10×10^{-3}
0.0235	0.0221	0.194

There does not seem to be a consistency in the k_3 values obtained.

Some experiments were done using as the 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[22] 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 Carbanilide

To reduce the effect of autocatalysis by the product urea to its minimum all the runs to follow were carried/in benzene saturated with carbanilide. Values of the coefficient k_3/k_3' for the system phenyl isocyanate-aniline reported by Craven[4] in 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 solubility of the urea in the s olvent. This effect is treated quantitatively later in part IV.

A. Experiments with Excess Isocyanate

In the present study, the reactions were carried in an appreciable excess of phenyl isocyanate. In this way, the isocyanate concentration was kept approximately constant throughout the reaction; the rate of the reaction then assumed a dependence on the aniline concentration alone.

The rate expression for the general reaction is

$$\text{Rate} = K \; [A]^a \; [I]^i \qquad (3)$$

where k is the rate constant for the overall reaction, $[A]$ and $[I]$ are the initial concentrations of aniline and phenyl isocyanate respectively, the exponents 'a' and 'i' being the order of the reaction in these reactants.

For the special case where isocyanate remains constant throughout the reaction, the above rate expression reduces to

$$\text{Rate} = k' \, [A]^a \qquad (4)$$

where k', the apparent rate constant of the reaction, is the product of k and $[I]^i$.

$$k' = k \, [I]^i \qquad (5)$$

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 $\dfrac{1}{[\text{aniline}]^{a-1}}$ 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),

$$\log k' = \log k + i \log [I] \qquad (6)$$

Using equation (6) 'i' can be calculated from the slope of a plot of log k' versus log $[I]$; log k then would be the intercept of the plot.

Considering the second order plots in aniline con-centration, k' values were obtained for the runs involving excess isocyanate. The apparent rate constants were
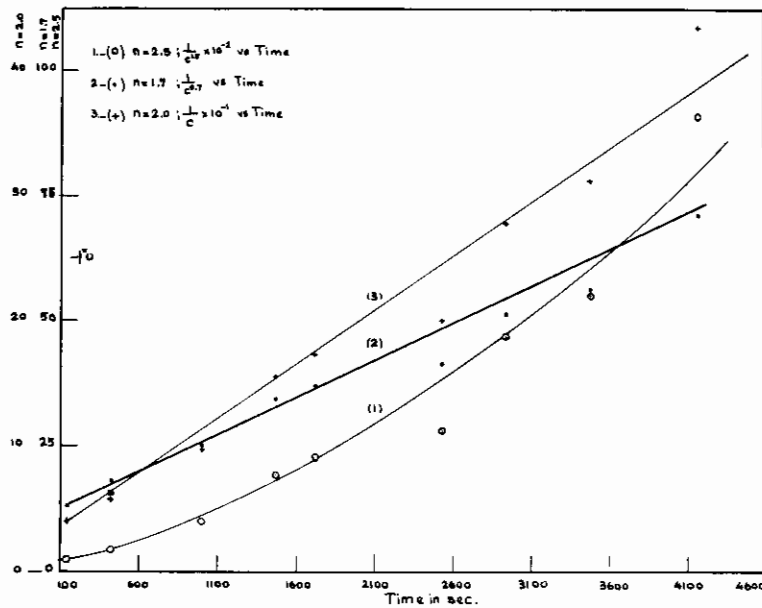
Fig. 2 $1/[A]^{a-1}$ $(1/m)$ versus time in sec for

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 iso-
cyanate concentrations (Table 3).

Table 3

c_0(PhNCO),m/l	c_0(PhNCO)/c_0(aniline)	k'[*], 1/m-sec
0.1342	3.77	1.29×19^{-2}
0.1496	4.10	1.76×10^{-2}-1.85×10^{-2}
0.2222	6.28	4.23×10^{-2}-4.43×10^{-2}
0.2795	7.85	6.74×10^{-2}-6.84×10^{-2}
0.3746	10.34	6.47×10^{-2}-7.92×10^{-2}

* Range of k' values determined from the slopes of the dif-
ferent possible straight lines that could be drawn through the
points.

Log k' 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 (6) this is 'i', the
order in isocyanate. The value of k was calculated from the
intercept to be 1.13 l^3/m^3-sec. Values other than 2.0 were
given to 'a'; the curves obtained by plotting log k' 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 concentra-
tion was kept in appreciable excess all through the reaction.
This is the reverse of the situation described in section A
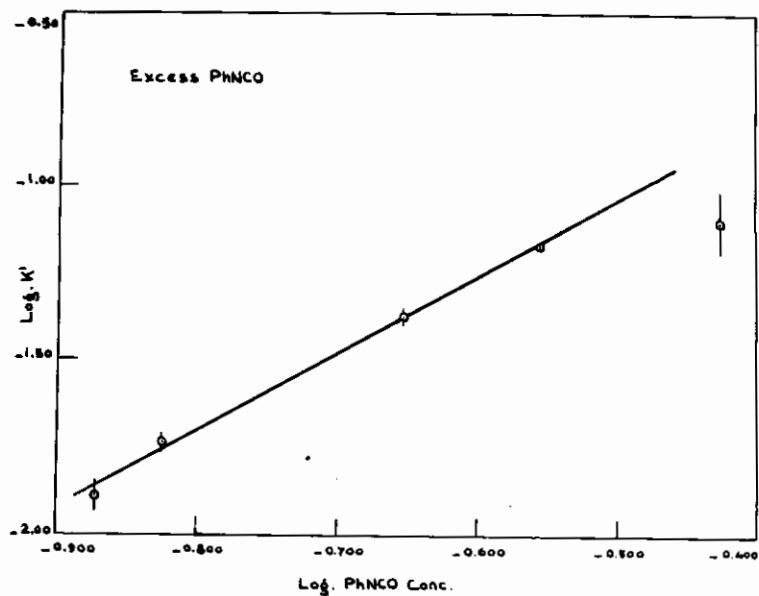
Fig. 3   Plot of log k' versus log [I] , where [I]is
the initial isocyanate concentration for
the different runs with excess isocyanate.

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 19). For the present reaction,

$$k'' = k \; [A]^a \qquad (7)$$

and therefore,

$$\log k'' = \log k + a \log [A] \qquad (8)$$

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

By considering the plots of $\log [iso]$ 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. $\dfrac{[A]}{[I]}$, 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
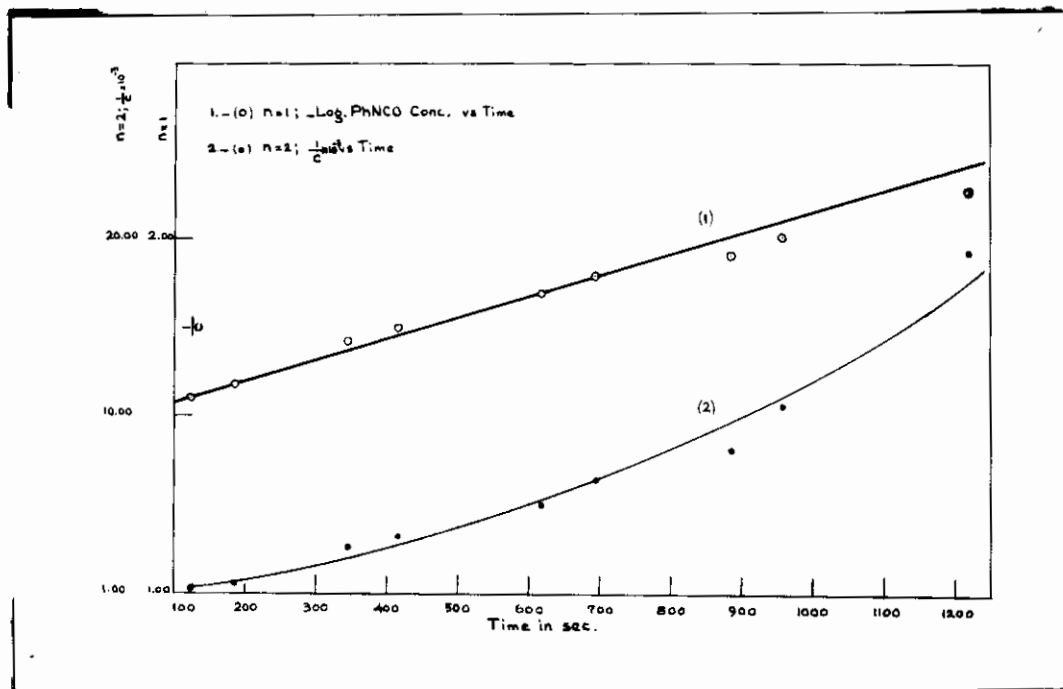
Fig. 4   For experiments with excess aniline:

      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 4

c_o(aniline), m/l	c_o(aniline)/c_o(PhNCO)	k" * 1/m-sec
0.3821	11.27	1.27×10^{-3}
0.2698	7.96	6.22×10^{-4}
		6.89×10^{-4}
0.2248	7.97	4.56×10^{-4}
0.1771	4.10	2.39×10^{-4}
		2.47×10^{-4}
0.1686	3.82	1.76×10^{-4}
		2.00×10^{-4}
0.1300	2.92	2.59×10^{-4}
		2.98×10^{-4}
		1.85×10^{-4}
0.1124	3.99	1.77×10^{-4}
		2.02×10^{-4}
		2.23×10^{-4}

* Range of k" value.

k" appears to decrease with decrease in the initial aniline concentration. A plot of log k" versus log $[A]$ gave (Fig. 5) a curve. The curvature was more pronounced at lower values of the ratio $\dfrac{[A]}{[I]}$ 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
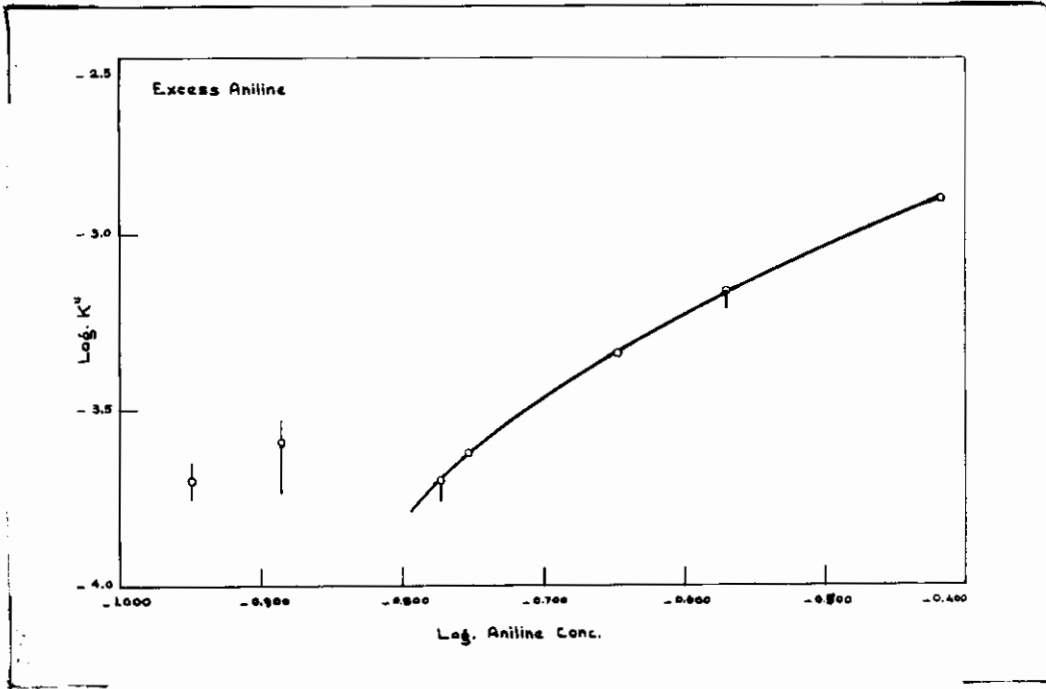
Fig. 5   Plot of log k'' versus log [A] where[A]is
         the initial aniline concentration for the
         different runs with excess aniline.

this straight line is 'a', the order in aniline, 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 $8.20 \times 10^{-3} \pm 0.10 \times 10^{-3}$ which can be considered as the average value for the third order rate constant of the reaction at $25^{\circ}C$.

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 ± 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[4] and others[8] have proposed a general mechanism for the reaction of isocyanates and amines. Craven's scheme consists of the following steps:

1. $\text{Ar-N=C=O} + \text{Ar-NH}_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{Complex}$

       i   a   c

2. $\text{Complex} + \text{Ar-NH}_2 \overset{k_2}{\longrightarrow} (\text{ArNH})_2\text{C=O} + \text{Ar-NH}_2$

        c   a   u   a

3. $\text{Complex} + (\text{ArNH})_2\text{C=O} \overset{k_3}{\longrightarrow} 2(\text{ArNH})_2\text{C=O}$

        c   u   2u

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

$$R_0 = \frac{k_1 k_2 i_0 a_0^2}{k_{-1} + k_2 a_0}$$

- 32 -

where the subscripts zero refer to initial conditions. For $k_2 a_0 \gg k_{-1}$, the reaction should follow second order kinetics according to the above mechanism. On the other hand, for $k_{-1} \gg k_2 a_0$, 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 urea is only slightly soluble in this solvent. This fact can be shown quantitatively by considering some numerical values of the ratio $\left(\dfrac{k_2}{k_3} \right)$. This ratio was found by Craven[4] 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 carbanilide in benzene was measured to be about 0.11 gm/l at $18^{\circ}C$. Therefore, the product concentration in the experiments using benzene as solvent, described in sections III-3 and III-4 will not exceed 5×10^{-4} m/l. From reactions (2) and (3) above,

$$\frac{R_3}{R_2} = \frac{k_3 c u}{k_2 c a} = 0.043$$

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 carbanilide. 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. $Ar-N=C=O + Ar-NH_2 \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}}$ Complex 1
    i a c_1

2. Complex 1 $+ Ar-NH_2 \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}}$ Complex 2
    c_1 a c_2

3. Complex 2 $\overset{k_3}{\longrightarrow}$ $(ArNH)_2C=O + Ar-NH_2$
    c_2 u a

3'. $\left[\text{Complex 1} + (ArNH)_2C=O \overset{k_3'}{\longrightarrow} 2(ArNH)_2C=O \right]$
    c_2 u 2u

4. Complex 2 $+ Ar-N=C=O \underset{\text{slow}}{\overset{k_4}{\longrightarrow}} 2(ArNH)_2C=O$
    c_2 i 2u
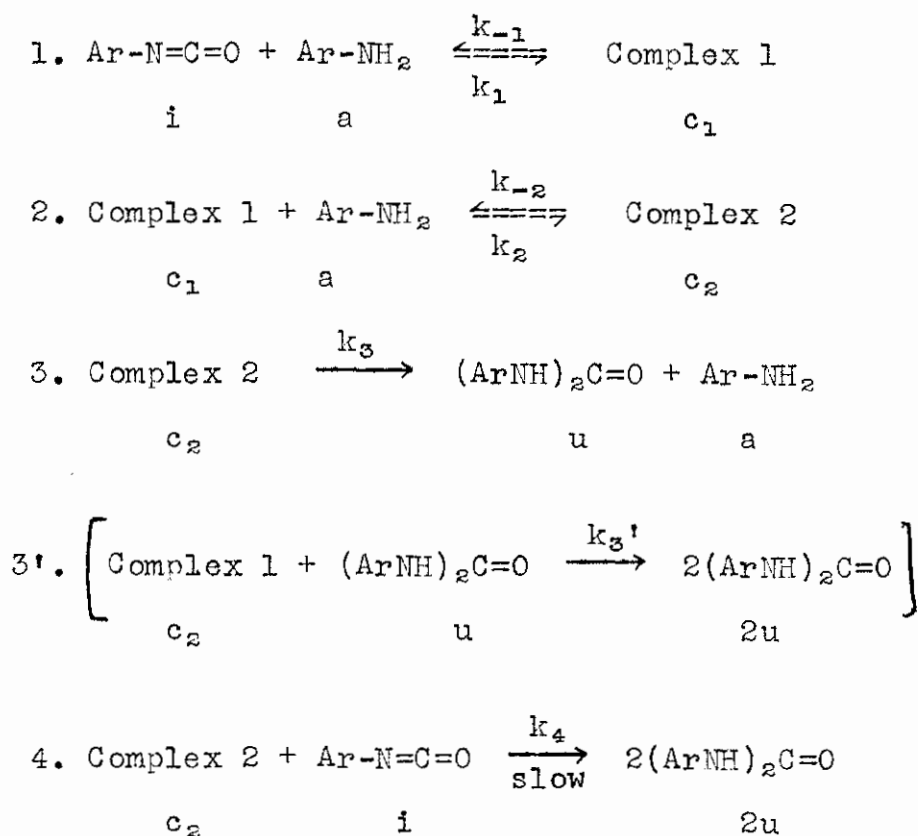
The flow sheet presented below shows the inter-relations of the intermediates involved.
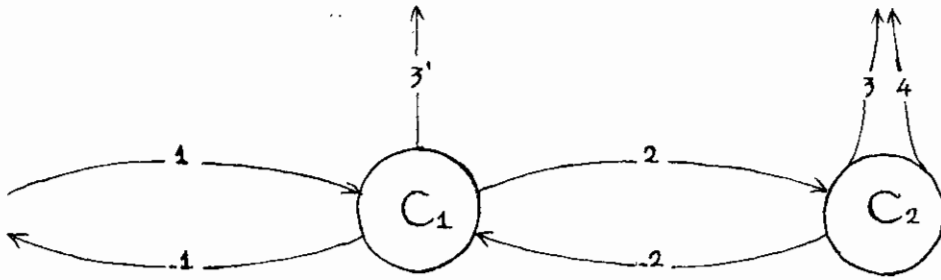
By making the following assumptions a rate expression was derived for the new mechanism:

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

b) Reactions (3) and (4) are slow. Consequently complexes c_1 and c_2 have appreciable life-times 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'),

$$c_1 = \frac{k_1 a i}{k-1} \, ,$$

$$c_2 = \frac{k_2 c_1 a}{k-2} \qquad \frac{k_1 k_2 a^2 i}{k-1 k-2}$$

then, the corresponding rate expression would be:

$$\frac{du}{dt} = 2k_4 \ \times \ \frac{k_1}{k-1} \ \times \ \frac{k_2}{k-2} \ (a^2 i^2)$$

$$= 2k_4 K_1 K_2 (a^2 i^2) \qquad\qquad (A)$$

Where K_1 and K_2 are the corresponding equilibrium cons-

tants 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,

$$c_1 = \frac{k_1 ia}{k_{-1}}$$

$$c_2 = \frac{k_2 c_1 a}{k_{-2}} = \frac{k_1 k_2 ia^2}{k_{-1} \ k_{-2}}$$

$$= K_1 K_2 ia^2$$

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

$$\frac{du}{dt} = k_3 K_1 K_2 ia^2 \qquad\qquad (B)$$

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[7] and others[4,8] have suggested the following structure for this complex:

$$Ar - \overset{\oplus}{\underset{\cdot\cdot}{N}}H_2$$
$$\downarrow$$
$$Ar - N = C = \overset{\cdot\cdot}{\underset{}{O}}: ^{\ominus}$$
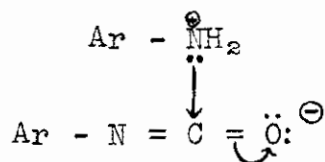
Complex 2 is a trimolecular one probably of the type given by Craven[4] as:

$$
\begin{array}{c}
Ar - \underset{\cdot\cdot}{N} \nearrow^{H} \\
\qquad\quad \searrow H \longleftarrow \quad :M \\
\downarrow \qquad\qquad\qquad\qquad | \\
Ar - N = C = \overset{\cdot\cdot}{O}: \longrightarrow H
\end{array}
$$
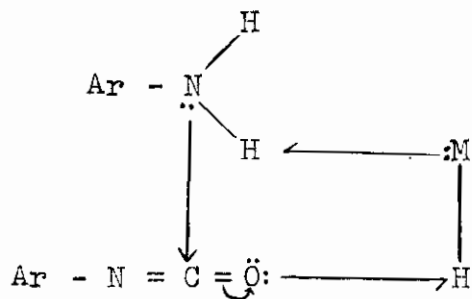
where HM represents a proton acceptor-donor.

In this study complex 2 would be:

$$
\begin{array}{c}
Ar - \underset{\cdot\cdot}{N} \nearrow^{H} \\
\qquad\quad \searrow H \longleftarrow \\
\downarrow \qquad\qquad\qquad \overset{Ar}{\underset{|}{:N}} \diagdown H \\
Ar - N = C = O \longrightarrow H
\end{array}
$$
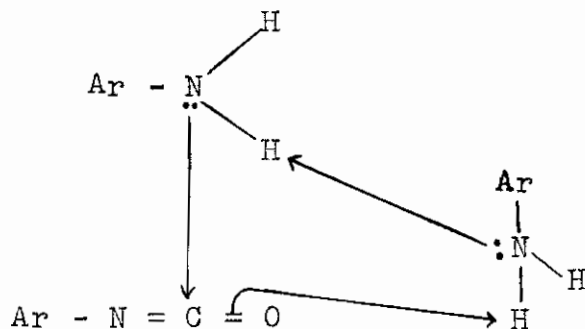
which, in excess aniline, breaks up to give a molecule of

aniline and another molecule of the enol-form of the product urea.

$$
\begin{array}{c}
\text{Ar} \\
| \\
\text{H} - \overset{..}{\text{N}} - \text{H}
\end{array}
\qquad \text{and} \qquad
\begin{array}{c}
\text{Ar} - \overset{\displaystyle H}{\text{N:}} \\
| \\
\text{Ar} - \text{N} = \text{C} - \text{O} - \text{H}
\end{array}
$$
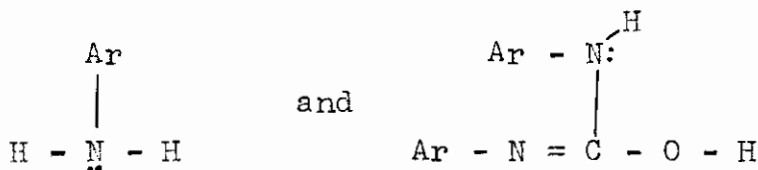
The enolic form of the product molecule then tautomerizes to give N,N'-diphenyl urea as shown:

$$
\begin{array}{c}
\text{Ar} - \overset{\displaystyle H}{\text{N:}} \\
| \\
\text{Ar} - \text{N} = \text{C} - \text{OH}
\end{array}
\quad \rightleftharpoons \quad
\begin{array}{c}
\text{Ar} - \overset{\displaystyle H}{\text{N}} \\
| \\
\text{Ar} - \underset{\displaystyle H}{\text{N}} - \text{C} = \text{O}
\end{array}
$$

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

$$
\begin{array}{c}
\text{Ar} - \text{N} \underset{\displaystyle H}{\overset{\displaystyle H}{}} \\
\\
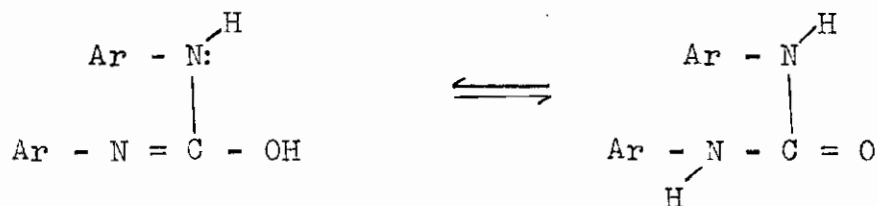\text{Ar} - \text{N} = \text{C} = \text{O}
\end{array}
\qquad
\begin{array}{c}
\text{O} = \text{C} = \text{N} - \text{Ar} \\
\\
\underset{\displaystyle H}{\overset{\displaystyle H}{\text{N}}} - \text{Ar}
\end{array}
$$

Intermediate complex

$\downarrow$

$$
\begin{array}{c}
\text{Ar} - \overset{\displaystyle H}{\text{N}} \\
| \\
\text{Ar} - \text{N} = \text{C} - \text{OH}
\end{array}
\qquad \text{and} \qquad
\begin{array}{c}
\text{H} - \text{O} \\
\quad\; \diagdown \text{C} = \text{N} - \text{Ar} \\
\text{H} \diagup \\
\quad\; \diagdown \text{N} - \text{Ar}
\end{array}
$$
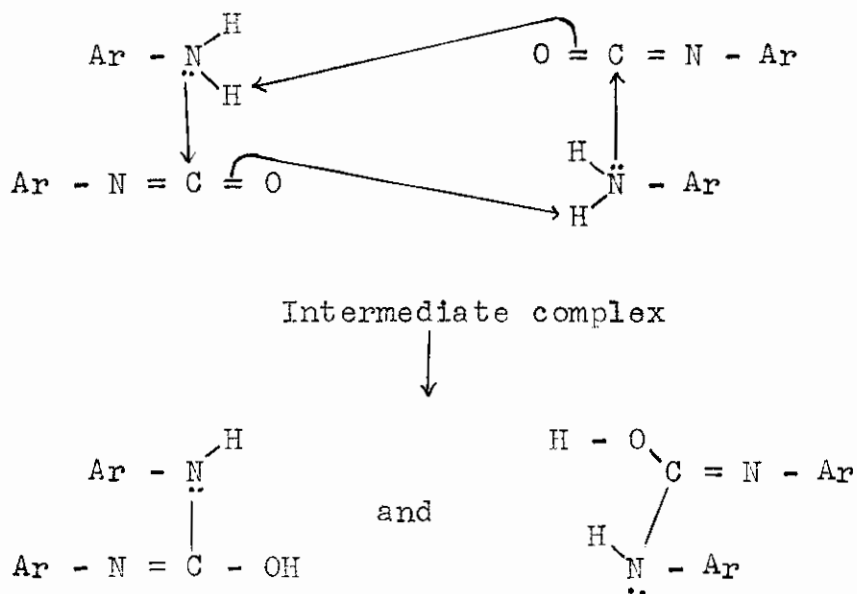
These complexes are undoubtedly relatively unstable and do not have long lifetimes. They are probably present

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 postu-

lated to account for the kinetics of the alcohol-isocyanate

reaction as well[7,4]. 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. How-

ever, 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 informa-

tion. The mechanism proposed by Craven[4] and others[8] 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 ($>C=C=O$) and diazomethane ($>C=N=N$) families and the reactions of the methylenes produced have been extensively studied[1,2]. Methylene radicals were found to add into carbon-hydrogen bonds[2,3] 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 ($-N=C=O$). The substituted imine 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 Lorenz[6].
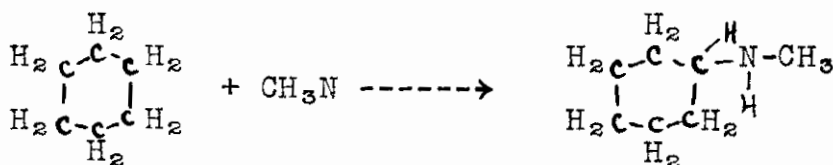
The ultraviolet absorption maximum for methyl iso-cyanate was found to be below 207 mμ. Readings beyond this wavelength could not be taken because the instrument (Beckman Model DU Spectrophotometer) used was not sensitive in that region of the spectrum.
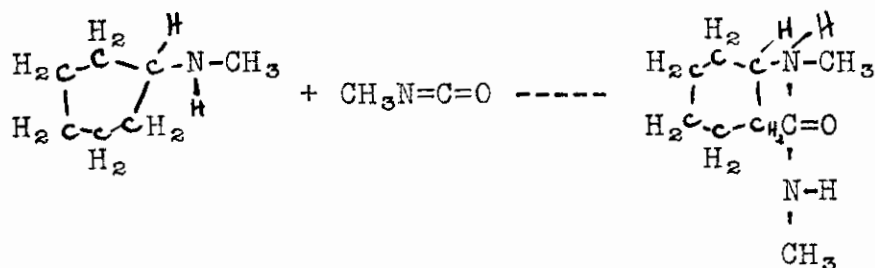
The infrared spectrum of methyl isocyanate was taken in cyclohexane and carbon tetrachloride as solvents, using a Perkin Elmer Model 112 Spectrophotometer. The following are the principal bands observed:

Wavelength cm^{-1}	Cyclohexane	Carbon tetrachloride
2920	wk.	wk.
2276	st.	st.
1411	wk.	wk.
1167	wk.	wk.
859	-	med. st.
854	-	wk.

The strong band at 2276 cm^{-1} characteristic of iso-cyanates had been reported[7] to occur at 2232 cm^{-1}. The value found here agrees with that found for other iso-cyanates[8].

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.

$$H_2C \overset{H_2}{\underset{\underset{H_2}{C-C}}{C}} \overset{H}{\underset{H}{C}}-N-CH_3 \quad + \quad CH_3N=C=O \quad ----$$

$$H_2C \overset{H_2}{\underset{\underset{H_2}{C-C}}{C}} \overset{H}{\underset{\underset{H}{c}}{C}} \overset{H}{\underset{C=O}{N}}-CH_3$$
$$N-H$$
$$CH_3$$

N, N'-dimethyl, N'-cyclo-

hexyl urea

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 mμ). Lead
(217 mμ) and zinc (214 mμ) 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 mμ) enclosed arcs (Phillips
Electrical 450 v. A.C.) were used for up to three hours
to irradiate a 3.63 x 10^{-2} molar solution of methyl iso-
cyanate 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 mμ) were used. The solution was examined in the
ultraviolet region after fourty five minutes of direct
irradiation from this source. Readings were taken in the
region 220 - 350 mμ. There was an appreciable change in
the spectrum after photolysis. The results were as follows:

λ, (mμ)	$A_{original}$	A_{final}
220	0.920	0.780
235	0.432	0.375
236	0.406	0.343
237	0.394	0.325
238	0.363	0.297
239	0.343	0.278
240	0.328	0.258
242	0.301	0.230
244	0.268	0.206
246	0.230	0.187
248	0.203	0.173
250	0.188	0.159
260	0.085	0.108
270	0.064	0.075
280	0.061	0.055
290	0.054	0.043
300	0.040	0.034
310	0.025	0.025
320	0.012	0.019
330	0.003	0.014
340	0.003	0.017
350	0.000	?

The final solution absorbs more than the original
one in certain regions as shown by the absorbance values
at 260 and 270 mμ. If real, this suggests the formation
of a new compound, probably the corresponding urea in

which the carbonyl group has a UV absorption maximum in
the neighborhood of 300 mμ[9]. 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
out.

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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