KINETICS OF THE TRANSESTERIFICATION REACTION BETWEEN PHENYL CARBANILATE AND 1-OCTANOL

by

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ABSTRACT

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The kinetics of the transesterification reaction between phenyl carbanilate and 1-octanol were studied. The reaction was carried out in 1, 2-dimethoxy ethane as the solvent at a temperature of 100°. Two mechanisms for the transesterification were possible; a two-step mechanism involving dissociation to isocyanate or a bimolecular displacement involving a carbonyl addition intermediate. The rate constants for both the above mechanisms were calculated from the experimental data. Neither of the above mechanisms alone could account for the experimental data and a dual mechanism was postulated.

ACKNOWLEDGEMENTS

This work was part of an overall study on the mechanisms of the carbanilate-alcohol transesterification reaction. The study was initiated by Dr. Leon Rand and has been carried out under his supervision at the University of Detroit and at this University. Acknowledgement is gratefully given to Dr. Rand. The author also wishes to acknowledge the contribution of Dr. Bari Lateef and Mr. Jasvant Shah, who were part of the study and who developed many of the techniques used in this work.

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CHAPTER I

INTRODUCTION

The chemical properties and behavior of urethans have been studied for some time. Urethans undergo an ester interchange with active hydrogen compounds such as amines, alcohols, and carboxylic acids. There are different pathways by which this reaction may take place. The actual mechanism appears to depend on the reaction conditions employed such as solvent, catalyst, temperature, and nature of the carbamate.

It is possible that the reaction might proceed by way of a two-step mechanism in which there is an initial thermal dissociation to isocyanate. The isocyanate then would react with the active hydrogen compound to form a new carbamate. Another mechanism by which the reaction could proceed is a direct bimolecular displacement involving a carbonyl addition intermediate.

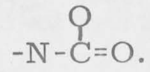
There have been opposing views as to which mechanism best describes the reaction. For N-monosubstituted carbamates the two-step mechanism involving dissociation to isocyanate was supported by Davis and Blanchard,[1] Gaylord,[2] Mukaiyama,[3] Tartakovskaya,[4] Lateef, Reeder, and Rand,[5] and Shah.[6] The carbonyl addition intermediate was supported by Saunders and Frisch[7] and Sal'nikova and coworkers.[8] Sal'nikova and coworkers studied the transesterification between aryl carbanilates and 1-hexanol in ortho-dichlorobenzene. The overall reaction was interpreted as a bimolecular nucleophilic displacement, even though phenyl isocyanate was identified as an intermediate.

It is the purpose of this research to study the kinetics of the transesterification reaction between phenyl carbanilate and n-octanol in glyme and to further clarify the precise mechanism of the ester interchange reaction.

CHAPTER II

HISTORICAL

Carbamates are carbonic acid esters with the characteristic configuration



$$-N-\overset{O}{\overset{|}{C}}=O.$$

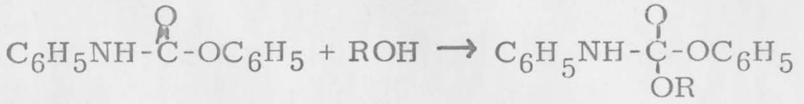
They are formed as a result of the reaction of isocyanates or carbamyl chlorides with hydroxy compounds.

The ester interchange between aryl carbamates and aliphatic alcohols yields alkyl carbamates and phenols. Polyurethans are prepared from blocked isocyanates by this method. A blocked isocyanate is a compound that contains no free isocyanate groups. Blocked isocyanates are formed by the reaction of a free isocyanate group with an active hydrogen compound.

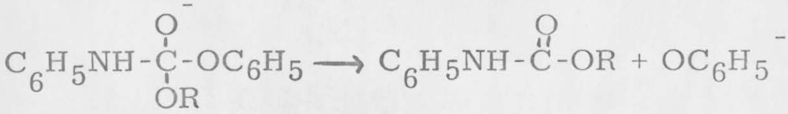
$$R-N=C=O + H-X \rightarrow R-NH-\underset{\overset{\|}{O}}{C}-X \qquad (1)$$

Phenols appear to be the best blocking agents, but other compounds, such as tertiary alcohols, thiols, secondary aromatic amines, and 1, 3-dicarbonyl compounds have been used.[9] Blocked isocyanates are unreactive at room temperatures, but will react at higher temperatures.

The reaction of blocked isocyanates with alcohols may proceed by a carbonyl addition intermediate,[7, 8]



$$C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_6H_5 + ROH \longrightarrow C_6H_5NH\text{-}\underset{OR}{\overset{O^-}{\overset{|}{C}}}\text{-}OC_6H_5 \qquad (2)$$



$$C_6H_5NH\text{-}\underset{OR}{\overset{O^-}{\overset{|}{C}}}\text{-}OC_6H_5 \longrightarrow C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR + OC_6H_5^- \qquad (3)$$

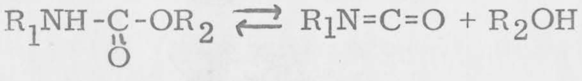
or by a two-step process,[1, 3, 5, 6] in which there is a thermal dissociation to free isocyanate. The actual pathway may depend on a number of variables such as the nature of the carbamate, catalyst, temperature, solvent, and concentration.

On the basis of finding second order kinetics for the reaction between phenyl carbamate and dibutylamine, Saunders and Frisch[7] have supported the carbonyl addition intermediate.

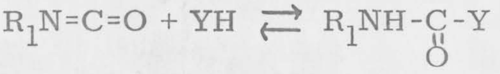
The ester interchange between aryl carbanilates and 1-hexanol was studied by Sal'nikova et. al.[8] in orthodichlorobenzene. The reaction was interpreted as a bimolecular nucleophilic displacement involving a carbonyl addition intermediate, although phenyl isocyanate was shown to be present during the reaction. Second order rate constants were calculated for this reaction.

Gaylord and Scroog[2] studied the reactions of N, N-disubstituted and N-monosubstituted carbamates with alcohols. For N, N-disubstituted carbamates, which can not dissociate reversibly to isocyanate, they proposed a mechanism involving the carbonyl addition intermediate.

Mukaiyama et. al.[3] studied the kinetics of ester interchange between substituted benzyl carbamates and active hydrogen compounds such as carboxylic acids, amines, and amino alcohols at temperatures of 130° C. to 170° C. They proposed the following two-step mechanism,

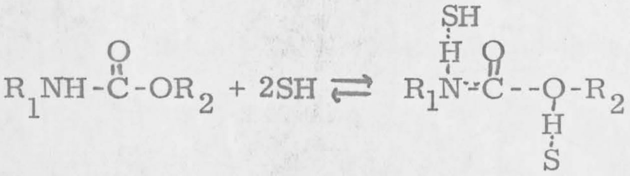


$$R_1NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR_2 \rightleftarrows R_1N{=}C{=}O + R_2OH \tag{4}$$

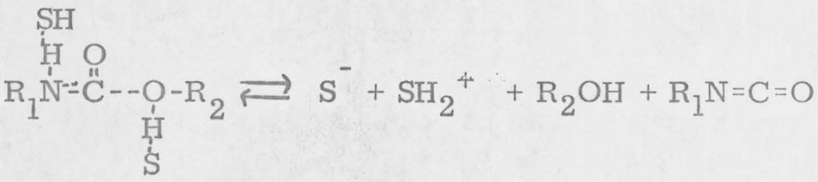


$$R_1N{=}C{=}O + YH \rightleftarrows R_1NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}Y \tag{5}$$

where YH is the active hydrogen compound. Psuedo first-order kinetics were found and the authors suggested reaction (4) as the rate determining step. It was later pointed out[5] that Mukaiyama's results were more consistent with reaction (5) as the rate determining step than with reaction (4) as the rate determining step. Mukaiyama suggested a termolecular mechanism for the dissociation of the carbamates,



$$R_1NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR_2 + 2SH \rightleftarrows R_1\overset{\overset{\overset{SH}{\vdots}}{H}}{\overset{|}{N}}\text{-}\text{-}\overset{\overset{O}{\|}}{C}\text{-}\text{-}\underset{\underset{\underset{S}{\vdots}}{H}}{\underset{|}{O}}\text{-}R_2 \tag{6}$$

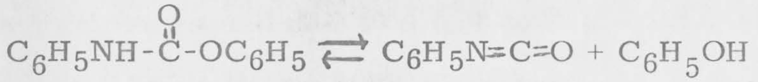


$$R_1\overset{\overset{\overset{SH}{\vdots}}{H}}{\overset{|}{N}}\text{-}\text{-}\overset{\overset{O}{\|}}{C}\text{-}\text{-}\underset{\underset{\underset{S}{\vdots}}{H}}{\underset{|}{O}}\text{-}R_2 \rightleftarrows S^{-} + SH_2^{+} + R_2OH + R_1N{=}C{=}O \tag{7}$$

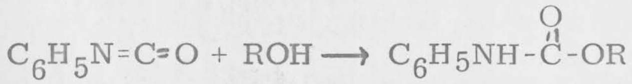
with SH as the solvent.

Lateef, Reeder, and Rand[5] studied the thermal dissociation of aryl carbanilates in ethylene glycol dimethyl ether without the addition of a catalyst. Phenyl carbanilate dissociated to the extent of 23% at 90°C. and 63% at 150°C. Equilibrium was reached within ten minutes at 90° and within 2 minutes at 150°. The concentration of phenyl isocyanate was determined by its absorption at 2262.5 cm^{-1}. In all cases the concentration of phenyl isocyanate rose rapidly and reached equilibrium, while the phenyl carbanilate concentration decreased to an equilibrium value. Electron withdrawing meta and para substituents on the phenolic ring increased the extent of dissociation.

On the basis of the above results, the authors[5] suggested equations (8) and (9) as the most probable mechanism for the transesterification of phenyl carbanilate with alcohols.



$$C_6H_5NH-\overset{\overset{O}{\|}}{C}-OC_6H_5 \rightleftarrows C_6H_5N{=}C{=}O + C_6H_5OH \qquad (8)$$



$$C_6H_5N{=}C{=}O + ROH \longrightarrow C_6H_5NH-\overset{\overset{O}{\|}}{C}-OR \qquad (9)$$

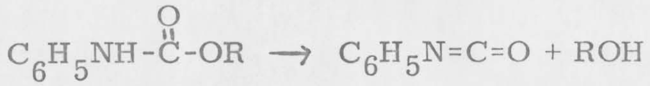
Reactions (8) and (9) have been studied separately in the literature. A review of these studies should assist in the investigation of the overall ester interchange reaction.

The Thermal Dissociation of Carbamates

Aliphatic carbamates dissociate to alcohols and isocyanate at temperatures around 200°C. Aryl carbamates dissociate readily at temperatures below 150°C.[5, 6] in the absence of alcohols and presumably do the same in the presence of alcohols. Equilibrium constants for reaction (8) have been found with benzene[6] and glyme[5] as the solvents.

Carbamates exhibit three pathways of thermal decomposition.[10]

1. Dissociation to isocyanate and alcohol

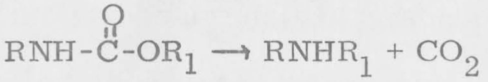


$$C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR \longrightarrow C_6H_5N{=}C{=}O + ROH \tag{10}$$

2. Formation of primary amine and olefin

$$RNH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2R_1 \longrightarrow RNH_2 + R_1\overset{H}{\overset{|}{C}}{=}CH_2 + CO_2 \tag{11}$$

3. Formation of secondary amine

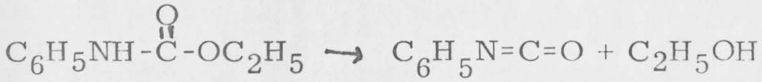


$$RNH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR_1 \longrightarrow RNHR_1 + CO_2 \tag{12}$$

Isocyanates are usually formed from N-monsubstituted carbamates or carbamoyl chlorides and reaction (12) usually occurs slowly at 150° and increases rapidly with an increase in temperature. The formation of primary amines and olefins usually occurs with tertiary alkyl carbamates. The formation of secondary amines occurs with allylic carbamates. Reactions (11) and (12) are high energy transformations requiring temperatures in excess of 230°.

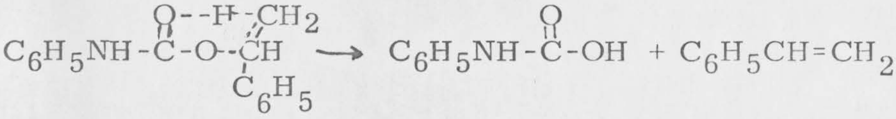
Tartakovskaya et. al.[4] studied the dissociation temperatures of aryl carbanilates in mineral oil by the use of infrared spectroscopy. The dissociation temperature was determined by the infrared spectrum of the N=C=O group. The dissociation temperatures ranged from 150° for p-tolyl carbanilate to 100° for p-nitrophenyl carbanilate. Ortho substituted phenols gave lower dissociation temperatures than para substituted phenols.

Dyer and Wright[11] studied the thermal degradation of alkyl N-phenyl carbanilates. Ethyl carbanilate was heated to 200° under reduced pressure and yielded phenyl isocyanate and alcohol. On the other hand, alpha-methylbenzyl carbanilate gave major amounts of aniline, alpha-methylbenzyl aniline, styrene, and carbon dioxide, when heated to 250° under atmospheric pressure. The authors proposed that ethyl carbanilate reacts by dissociation.

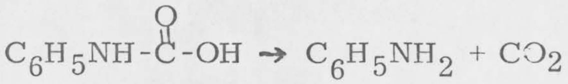


$$C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5 \rightarrow C_6H_5N{=}C{=}O + C_2H_5OH \qquad (13)$$

They also proposed that carbamate esters of secondary and tertiary alcohols decompose by an intramolecular cyclic mechanism.



$$C_6H_5NH\text{-}\overset{O\text{--}H\text{--}CH_2}{\overset{\|}{C}}\text{-}O\text{--}\underset{C_6H_5}{CH} \rightarrow C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + C_6H_5CH{=}CH_2 \qquad (14)$$

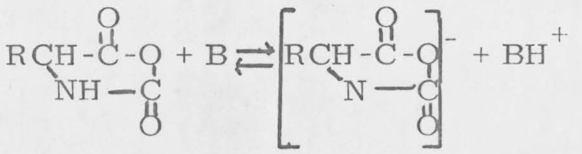


$$C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \rightarrow C_6H_5NH_2 + CO_2 \qquad (15)$$

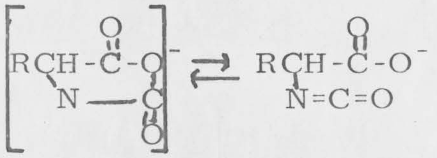
The dissociation of aryl carbanilates can be catalyzed by tertiary amines, but have been known to occur without an added catalyst. The dissociation of phenyl carbanilate in benzene at 150° did not go without an added catalyst.[6] The reverse of reaction (10) has been suggested by Farkas and Strohm[10] to go by way of an amine-phenol complex, rather than the previously postulated amine-isocyanate complex.[12] This mechanism could also apply to the forward reaction.

In the base-catalyzed degradation of N-alkyl carbamates Bortnick _et. al._[13] obtained 50-80% yields of secondary and tertiary isocyanates.

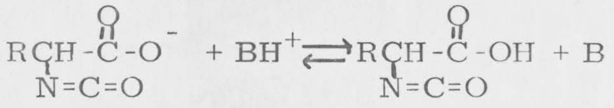
Kopple[14] studied the reaction of primary amino acid N-carboxy anhydride with amines and sodium methoxide yielding carbonic acid derivatives. He suggested that under basic conditions the reaction goes by way of an alpha-isocyanato acid intermediate and that these isocyanato acids could be intermediates in certain amino acid N-carboxy anhydride polymerization reactions.



$$\begin{array}{l}\mathrm{RCH-\overset{O}{\overset{\|}{C}}-O}\\ \quad\mathrm{NH-\underset{\overset{\|}{O}}{C}}\end{array} + \mathrm{B} \rightleftharpoons \left[\begin{array}{l}\mathrm{RCH-\overset{O}{\overset{\|}{C}}-O}\\ \quad\mathrm{N-\underset{\overset{\|}{O}}{C}}\end{array}\right]^- + \mathrm{BH}^+ \qquad (16)$$



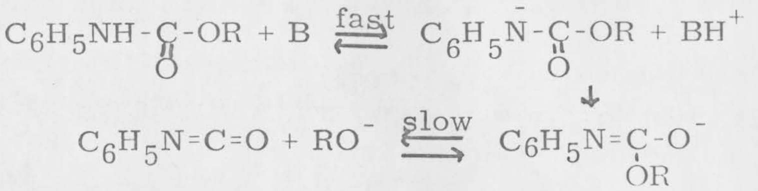
$$\left[\begin{array}{l}\mathrm{RCH-\overset{O}{\overset{\|}{C}}-O}\\ \quad\mathrm{N-\underset{\overset{\|}{O}}{C}}\end{array}\right]^- \rightleftharpoons \begin{array}{l}\mathrm{RCH-\overset{O}{\overset{\|}{C}}-O^-}\\ \quad\mathrm{N{=}C{=}O}\end{array} \qquad (17)$$



$$\begin{array}{l}\mathrm{RCH-\overset{O}{\overset{\|}{C}}-O^-}\\ \mathrm{N{=}C{=}O}\end{array} + \mathrm{BH}^+ \rightleftharpoons \begin{array}{l}\mathrm{RCH-\overset{O}{\overset{\|}{C}}-OH}\\ \mathrm{N{=}C{=}O}\end{array} + \mathrm{B} \qquad (18)$$

Kopple found that hydrogen is evolved from a solution of N-carboxy anhydride of alpha-aminoisobutyric acid in dioxane, which has been shaken with excess sodium hydride. The supernatant liquid then shows isocyanate absorption in its infrared spectrum.

Abbate, Farrissey, and Sayigh[15] have proposed three possible primary reactions which lead to the amine-catalyzed degradation of carbanilates.

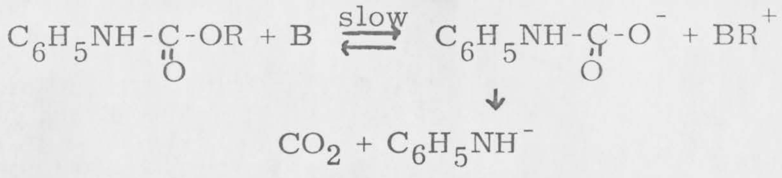


$$C_6H_5NH\text{-}\underset{O}{\underset{\|}{C}}\text{-}OR + B \xrightleftharpoons{fast} C_6H_5\overset{-}{N}\text{-}\underset{O}{\underset{\|}{C}}\text{-}OR + BH^+$$

$$\downarrow$$

$$C_6H_5N{=}C{=}O + RO^- \xrightleftharpoons{slow} C_6H_5N{=}\underset{OR}{\underset{|}{C}}\text{-}O^-$$

(19)

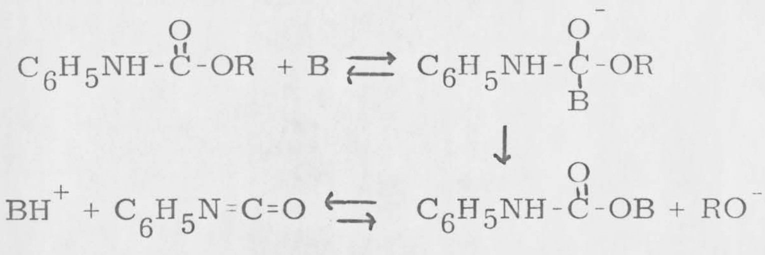


$$C_6H_5NH\text{-}\underset{O}{\underset{\|}{C}}\text{-}OR + B \xrightleftharpoons{slow} C_6H_5NH\text{-}\underset{O}{\underset{\|}{C}}\text{-}O^- + BR^+$$

$$\downarrow$$

$$CO_2 + C_6H_5NH^-$$

(20)

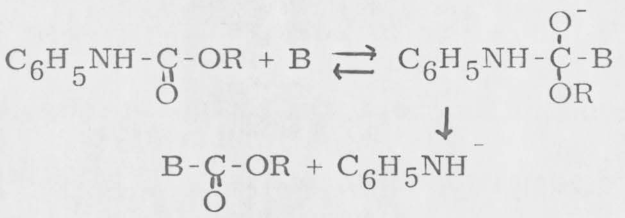


$$C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR + B \rightleftharpoons C_6H_5NH\text{-}\overset{O^-}{\overset{|}{\underset{B}{\underset{|}{C}}}}\text{-}OR$$

$$\downarrow$$

$$BH^+ + C_6H_5N{=}C{=}O \rightleftharpoons C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OB + RO^-$$

(21)



$$C_6H_5NH\text{-}\underset{O}{\underset{\|}{C}}\text{-}OR + B \rightleftharpoons C_6H_5NH\text{-}\overset{O^-}{\overset{|}{\underset{OR}{\underset{|}{C}}}}\text{-}B$$

$$\downarrow$$

$$B\text{-}\underset{O}{\underset{\|}{C}}\text{-}OR + C_6H_5NH^-$$

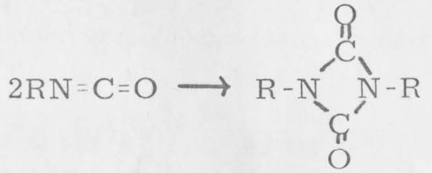
(22)

Reaction (19) occurs in preference to (21). Equation (22) shows a possible mechanism, if the base catalyst is an alkoxide and the leaving anion is a very weak base.[15] Reaction (20) is an irreversible reaction, once the carbonic acid loses carbon dioxide.[15] Reaction (19) is a reversible reaction and occurs much faster than without an added catalyst.[15]

Reactions of Isocyanates

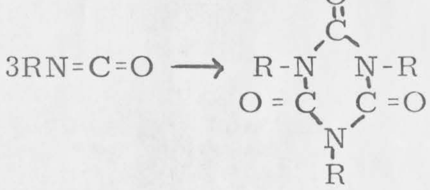
Isocyanates react with active hydrogen compounds such as amines, carboxylic acids, amides, urethans, and alcohols. Aryl isocyanates also form dimers and trimers.[7] Isocyanates can also react with specific catalysts, such as phosphine oxides, to form carbodiimides.[16]

1. Dimer formation



(23)

2. Trimer formation

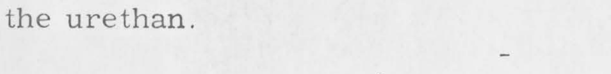


(24)

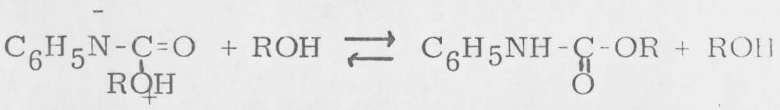
3. Carbodiimide formation

$$2RN{=}C{=}O \longrightarrow R\text{-}N{=}C{=}N\text{-}R + CO_2 \qquad (25)$$

When an alcohol reacts with an isocyanate, an ester is formed by the following process: the active hydrogen of the alcohol leaves that molecule and the RO and H attach to the isocyanate at their respective positions. The kinetics and mechanism of the alcohol-isocyanate reaction have been studied by many workers. The reaction appears to follow second order kinetics, but with an increase in the rate constant as the concentration of the alcohol is increased.[12] Baker and Gaunt proposed that the reaction proceeds through an alcohol-isocyanate intermediate complex. The complex then reacts with the alcohol forming the urethan.



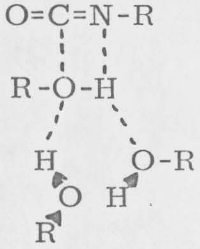
$$C_6H_5N{=}C{=}O + ROH \rightleftarrows C_6H_5\overset{-}{N}\text{-}\underset{R\underset{+}{O}H}{C}{=}O \qquad (26)$$



$$C_6H_5\overset{-}{N}\text{-}\underset{R\underset{+}{O}H}{C}{=}O + ROH \rightleftarrows C_6H_5NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR + ROH \qquad (27)$$

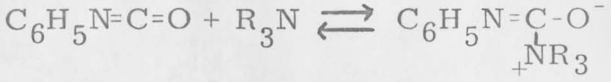
Sato[17] explained the above behavior as a mixture of second and third order kinetics. Others[18] suggested that hydrogen bonding was an important aspect in the mechanism of the alcohol-isocyanate reactions.

The reaction appears to proceed faster in nonpolar solvents, such as hydrocarbons, than in polar solvents such as ethers. Bruenner and Oberth[18] have explained this effect by suggesting that the rate is dependent on the concentration of the polymeric (self-associated) alcohol. Since in the alcohol polymer the O-H bond is more highly polarized, it is more reactive than either the monomeric alcohol or the alcohol hydrogen bonded to the solvent. Hence, the oxygen contains a larger negative charge. Bruenner and Oberth proposed a four-centered activated complex between the isocyanate and a unit of a cyclic alcohol polymer.

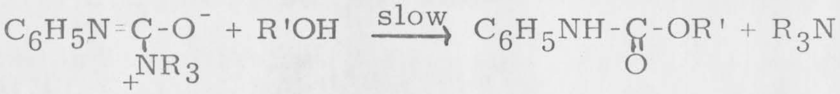


Entelis and coworkers,[19] however, did not observe a rate increase with an increase in alcohol concentration. Their reactions were psuedounimolecular, the alcohol concentration being 10^5 to 10^6 times that of the isocyanate. They interpreted their findings in terms of the changes in the energy of solvation of a postulated four-centered transition state.

Tertiary amines can act as catalysts for the isocyanate-alcohol reaction. Previously it was thought that the mechanism of the amine catalysis involved the formation of a zwitterionic amine-isocyanate complex which reacted with the alcohol.



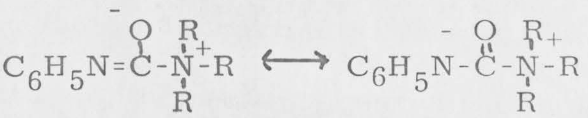
$$C_6H_5N{=}C{=}O + R_3N \rightleftarrows C_6H_5N{=}\underset{{}_{+}NR_3}{C}{-}O^- \qquad (28)$$



$$C_6H_5N{=}\underset{{}_{+}NR_3}{C}{-}O^- + R'OH \xrightarrow{slow} C_6H_5NH{-}\underset{\overset{\|}{O}}{C}{-}OR' + R_3N \qquad (29)$$

This mechanism was based on three propositions.

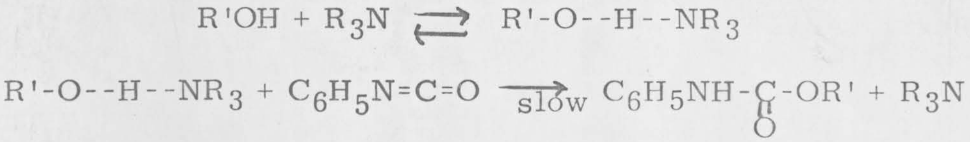
1. There was significant effect in catalytic activity brought about by the steric conditions of the amine. Unhindered, less basic amines showed higher catalytic activity than sterically hindered, stronger amines.[12]
2. Pestemer and Laurer[20] reported infrared evidence for the formation of a zwitterionic complex



$$C_6H_5N{=}\overset{{}^{-}O}{C}{-}\underset{R}{\overset{R}{\overset{+}{N}}}{-}R \longleftrightarrow C_6H_5N{-}\overset{{}^{-}O}{\overset{\|}{C}}{-}\underset{R}{\overset{R_{+}}{N}}{-}R$$

   between phenyl isocyanate and tertiary amines, giving absorption bands in the region of 1635-1652 cm^{-1}.
3. There was an isotope effect which increased with increasing base strength.[21]

Others[22] have rejected this theory for a complex between the alcohol and amine;



$$R'OH + R_3N \rightleftarrows R'{-}O{-}{-}H{-}{-}NR_3$$

$$R'{-}O{-}{-}H{-}{-}NR_3 + C_6H_5N{=}C{=}O \xrightarrow[slow]{} C_6H_5NH{-}\underset{\overset{\|}{O}}{C}{-}OR' + R_3N \qquad (30)$$

They have argued against the above points in the following manner:

1. The alcohol-amine complex does not exclude steric effects, since no free ions are formed and the amine-alcohol complex must react with the isocyanate.
2. Since the formation of Pestemer and Laurer's[20] complex occurred in a slow reaction, the amine catalyzed isocyanate alcohol reaction would show an induction period.
3. The O-H bond breaking occurs in the rate determining step of both mechanisms, therefore the isotope effect is of no significance in differentiating between the two.

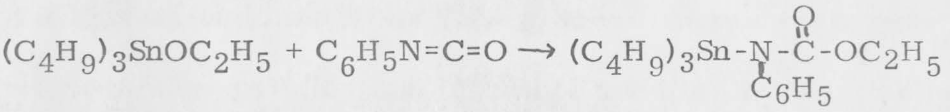
Also the amine-isocyanate complex should be independent of the alcohol, which is not the case, since the rate constant increases with an increase in alcohol concentration.[22]

An increase in rate, after partial conversion, has been found which is probably due to the increasing concentration of the carbamate formed. The carbamate product then must be able to exert a catalytic effect on the isocyanate-alcohol reaction. It appears that the catalysis of the alcohol-isocyanate reaction by carbamates depends upon the catalyst, the alcohol (the number of OH groups on the alcohol), and the effect of these two upon each other.[23]

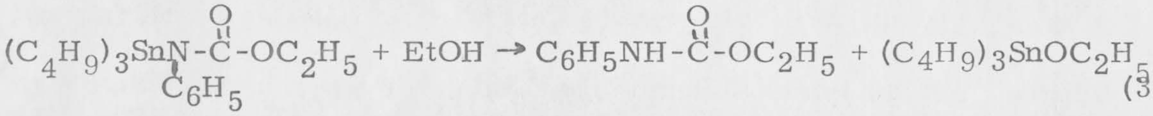
Metal compounds such as lead compounds, divalent and tetravalent tin compounds, and cobalt compounds can serve as catalysts for the isocyanate-alcohol reaction. Tetravalent tin compounds such as dibutyltin dilaurate appear to be the most effective. Alcohols and isocyanates are both known to form complexes with metal derivatives.

According to studies by Bloodworth and Davies,[24] tin (IV) alkoxides and isocyanates react together forming N-stannyl carbamates, which in turn react with alcohols yielding carbamates and tin alkoxides. A mechanism involving this type of a reaction has been proposed as in the following example of a dialkyltin compound.[24]

$$(C_4H_9)_3SnX + EtOH \rightleftarrows (C_4H_9)_3SnOC_2H_5 + HX \qquad (31)$$



$$(C_4H_9)_3SnOC_2H_5 + C_6H_5N{=}C{=}O \longrightarrow (C_4H_9)_3Sn\text{-}\underset{C_6H_5}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5 \qquad (32)$$



$$(C_4H_9)_3Sn\underset{C_6H_5}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5 + EtOH \rightarrow C_6H_5NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5 + (C_4H_9)_3SnOC_2H_5 \qquad (33)$$

CHAPTER III

EXPERIMENTAL

Materials

Phenyl isocyanate was obtained from Baker Chemical Co., pyridine was obtained from Fisher Scientific and both were used without further purification. Octanol used in the reaction mixture was purified by distillation retaining the center fraction. Triethylamine and glyme were both obtained from Eastman Organic Chemicals and purified by distillation. Phenol obtained from Baker Chemical Co. was distilled at 25 mm pressure and at a boiling point of 80°, the middle fraction being retained. This was carried out three times. See Table 1 for melting point.

Synthesis and Purification of the Carbamates

Phenyl carbanilate was prepared from phenol and phenyl isocyanate in benzene solution with pyridine as a catalyst. The solid particles were collected on a sintered glass funnel and recrystallized twice with heptane using a soxhlet apparatus. The solid was then purified by dissolving it in heptane using sufficient volume to produce a saturated solution. It was then heated to boiling and filtered hot to remove any insoluble material. The filtered solution was cooled and refiltered. The solid material was then dried overnight at room temperature and again overnight using an Abderhalden apparatus. Phosphorous pentoxide was used as the drying agent and toluene was refluxed around the material to be dried. The dried phenyl carbanilate was then stored in a vacuum desiccator, until use.

Octyl carbanilate was prepared in an analagous manner as phenyl carbanilate using 1-octanol and phenyl isocyanate in benzene solution with pyridine as a catalyst. The melting points of both compounds were taken with a Thomas Hoover melting point apparatus and are uncorrected.

TABLE I

MELTING POINTS

Compound	Melting point	Literature Value
Phenyl carbanilate	125-126° C.	125-126° C.[a]
Octyl carbanilate	73-73.4° C.	73° C.[b]
Phenol	40.5-42° C.	42° C.[c]

(a) Reference 5.
(b) Shriner, R.L., Fuson, R.C., and Curtin, D.Y. The Systematic Identification of Organic Compounds (New York: John Wiley and Sons, 1964), p. 317.
(c) Ibid, p. 374.

Solvent Purification and Solution Preparation

The solvent glyme, 1,2-dimethoxyethane, was purified by distillation from sodium ribbon using a self contained apparatus under a stream of dry prepurified nitrogen. The reflux ratio was 10:2. At the temperature of 83.5° the middle fraction was collected and redistilled using lithium aluminum hydride. The middle portion was collected in a specially designed volumetric flask equipped with a magnetic stirrer and containing the necessary amounts of phenyl carbanilate, octanol, and triethylamine (catalyst). Care was taken to minimize exposure to the moisture in the air. The volumetric flask was equipped with a teflon stopcock and an extension used for filling the reaction tubes.

The reactions were carried out using sealed Pyrex tubes of 2.2 ml. size. The tubes were dried by flame under dry nitrogen and then filled with approximately 1 ml. of solution. They were then placed in an acetone-dry ice bath and sealed individually under vacuum. The tubes were stored in the freezer, until ready for use.

The glass equipment was cleaned with cleaning solution (acid dichromate), let set overnight, rinsed, and set in water overnight. It was then dried with acetone and flamed out under a stream of dry nitrogen, before using.

Analysis of Products

To determine the concentration of the reactants and products a calibration curve was drawn up. The absorbance of octyl carbanilate in glyme was measured at 11 different concentrations and the net absorbance, after subtracting the base line, was plotted against the concentration. The calibration curve (Figures 1 and 2) was in accordance with Beer's Law with an extinction coefficient of 1004. For the calibration curve of phenyl carbanilate 10 measurements were taken which followed Beer' Law with an extinction coefficient of 932 (Figure 3). Data for phenyl isocyanate was used from the work of A.B. Lateef.[5] The absorption maxima and extinction coefficients are shown in Table 2.

TABLE 2

INFRARED MAXIMA AND EXTINCTION COEFFICIENTS

Compound	ν max cm^{-1}	ϵ_{max}[a]
Octyl Carbanilate	1736	1004 ± 12
Phenyl Carbanilate	1757	932 ± 8
Phenyl Isocyanate	2262.5	1310 ± 50[b]

(a) By least squares correlation including the origin ± standard deviation in slope.

(b) Reference 5.

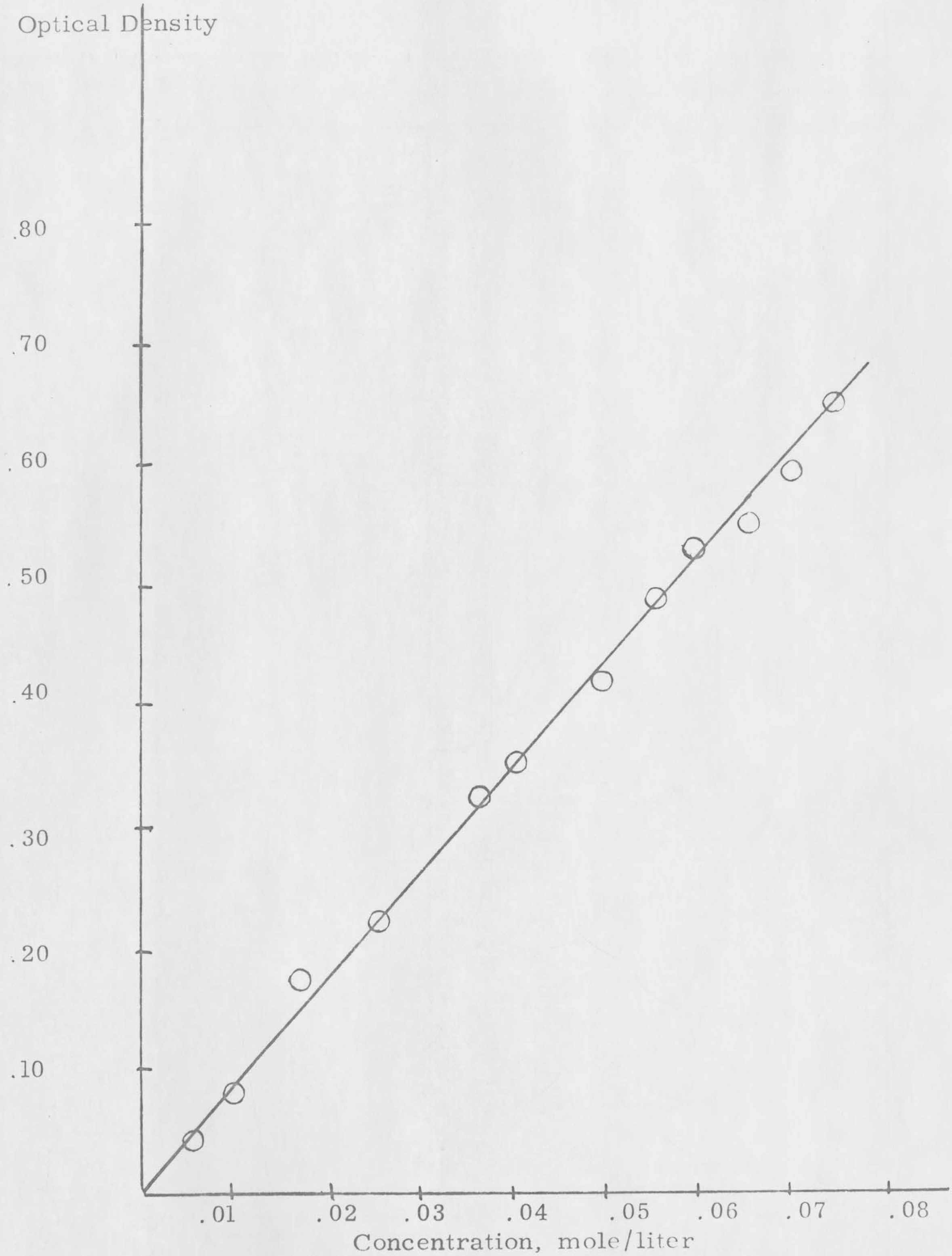


Fig. 1. Concentration of octyl carbanilate versus optical density at 1736 cm^{-1}.

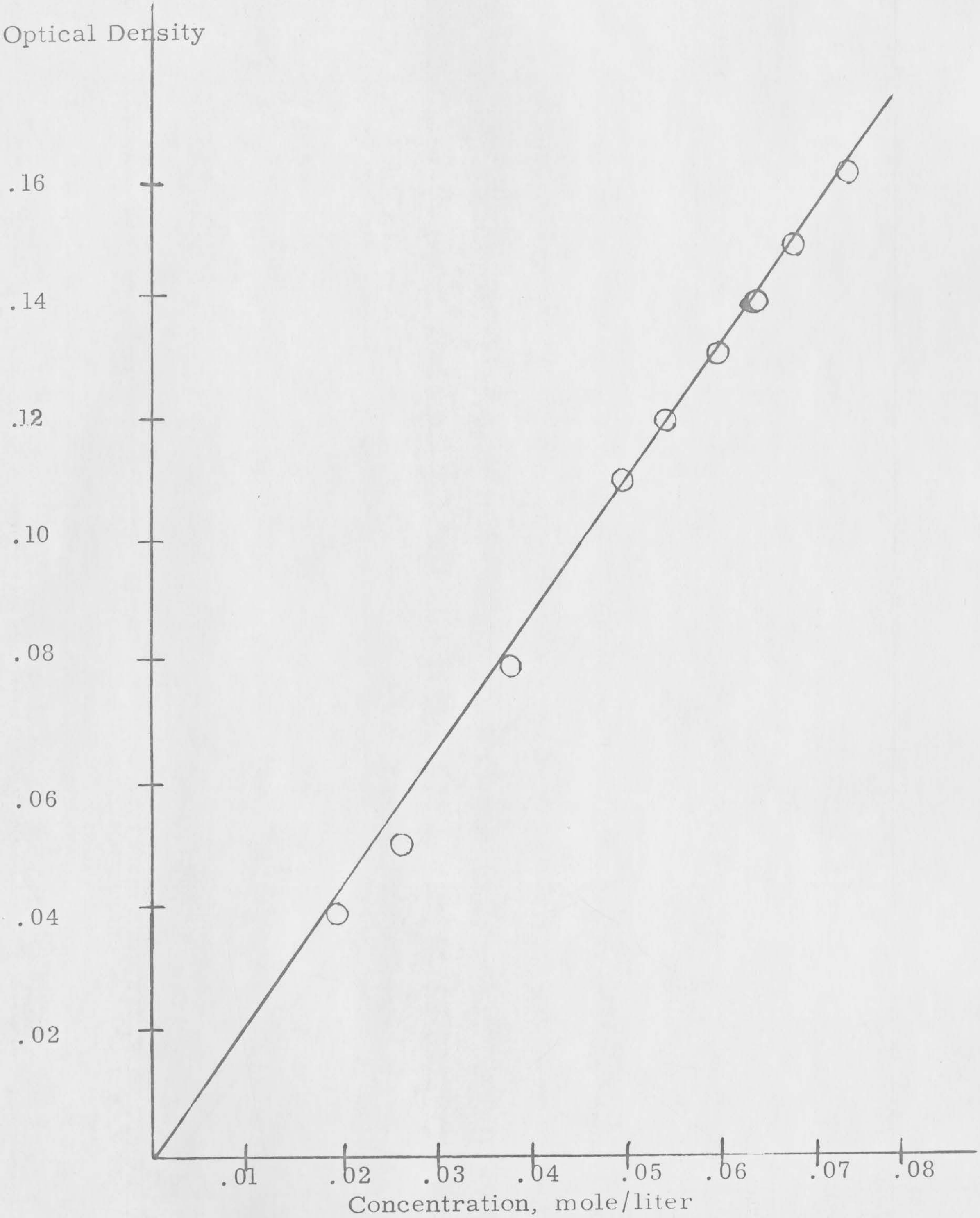


Fig. 2. Concentration of phenyl carbanilate versus optical density at 1736 cm^{-1}.

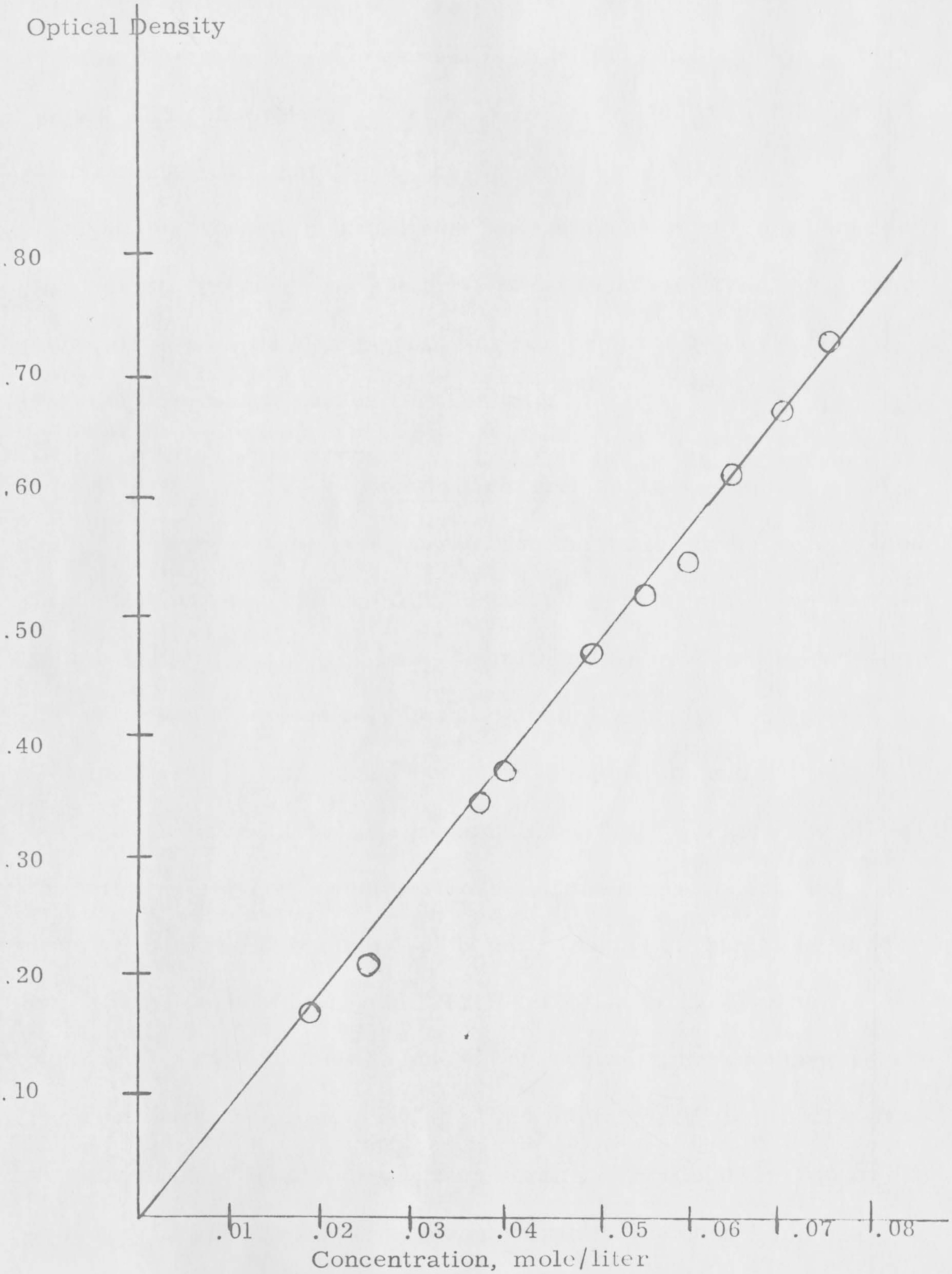


Fig. 3. Concentration of phenyl carbanilate versus optical density at 1757 cm^{-1}.

The infrared spectra of the solutions were measured in a 0.1 mm Irtran cell on a Beckman IR-12 double beam spectrophotometer. The absorption peaks measured were 1757 cm^{-1} (phenyl carbanilate), 1736 cm^{-1} (octyl carbanilate), and 2262.5 cm^{-1} (phenyl isocyanate). A scan was taken on each measurement from 1600 cm^{-1} to 4000 cm^{-1} to check for bands resulting from side reactions. The concentration of the components were determined by Beer's Law plots of absorbance versus concentration.

Kinetic Measurements

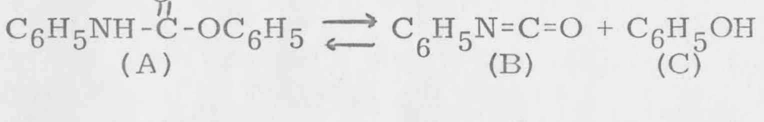
To carry out the desired reaction the sealed tubes were placed in a constant temperature oil bath, the temperature of which was maintained at 100 ± 0.1^0 C. The tubes were then taken out at different time intervals and placed quickly in an acetone-dry ice bath for quenching. The mixture was then brought to room temperature and the tubes opened. A 0.1 mm Irtran cell was filled with the solution and placed in the infrared spectrophotometer. The infrared absorbance was read as quickly as possible at 1757 cm^{-1} (phenyl carbanilate), 1736 cm^{-1} (octyl carbanilate), and 2262.5 cm^{-1} (phenyl isocyanate). No more than four minutes elapsed between the time the tubes were removed from the oil bath and the time the infrared absorbance was measured. The spectrum was then scanned from 1600 cm^{-1} to 4000 cm^{-1}. No extraneous peaks appeared on the scan. In each case the concentration of phenyl carbanilate decreased as the reaction time increase and the concentration of octyl carbanilate increased. Each day that a measurement was taken the absorbance of the solvent at each νmax was read. The daily solvent absorbance was then subtracted from the measured absorbance.

Three different reactions were attempted; the first with approximately equal concentration of octanol and phenyl carbanilate, the second with an excess of alcohol, the third with an excess of phenol added to approximately equal amounts of octanol and phenyl carbanilate. The concentration of phenyl carbanilate, octyl carbanilate, and phenyl isocyanate versus time are shown in Tables 3, 4, and 5 and Figures 4, 5, and 6.

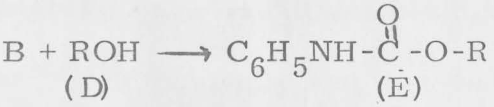
CHAPTER IV

RESULTS AND DISCUSSION

The precise mechanism for the ester interchange between phenyl carbamate and alcohols is not known for certain. Under specific conditions it appears likely that the reaction may go by way of the following two-step mechanism.



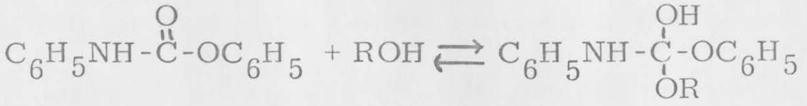
$$\underset{(A)}{C_6H_5NH-\overset{\overset{O}{\|}}{C}-OC_6H_5} \rightleftarrows \underset{(B)}{C_6H_5N=C=O} + \underset{(C)}{C_6H_5OH} \qquad (34)$$



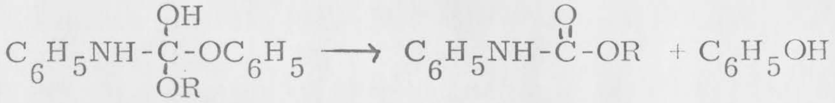
$$B + \underset{(D)}{ROH} \longrightarrow \underset{(E)}{C_6H_5NH-\overset{\overset{O}{\|}}{C}-O-R} \qquad (35)$$

Reaction (34) is very fast relative to the overall ester interchange. Reaction (35) is nominally second order and is the rate determining step.

There are other pathways by which this reaction may proceed. The transesterification of N, N-disubstituted carbamates is catalyzed by alkoxide ions and has been shown to proceed by a carbonyl addition intermediate. It has been suggested that the transesterification of N-monosubstituted carbamates also proceeds by a carbonyl addition intermediate.[7, 8] As applied to the ester interchange between phenyl carbanilate and alcohols, such a mechanism is shown below in equations (36) and (37).



$$C_6H_5NH-\overset{O}{\overset{\|}{C}}-OC_6H_5 + ROH \rightleftarrows C_6H_5NH-\underset{OR}{\overset{OH}{C}}-OC_6H_5 \qquad (36)$$



$$C_6H_5NH-\underset{OR}{\overset{OH}{C}}-OC_6H_5 \longrightarrow C_6H_5NH-\overset{O}{\overset{\|}{C}}-OR + C_6H_5OH \qquad (37)$$

Proton exchange could perhaps occur in this intermediate by way of the nitrogen atom.

It has been established[4, 5, 6] that aryl carbamates dissociate rapidly and reversibly at temperatures of 90° or above to give phenyl isocyanate and phenol, as shown in equation (34). The equilibrium constant for the dissociation of phenyl carbanilate at 100° was shown to be 1.05×10^{-2} mole/liter.[5] It is possible that reactions (34), (35) (36), and (37) occur simultaneously and that the two competing mechanisms are responsible for the transesterification.

The purpose of the present research was to study the kinetics of the overall ester interchange reaction of phenyl carbanilate and n-octanol in order to further clarify the mechanism.

A solution with an initial concentration of 0.075 mole/liter in phenyl carbanilate and 0.075 mole/liter in 1-octanol showed no change in compostion, after 24 hours at 100° in the absence of a catalyst. The reaction proceeded at a reasonable rate with about 10 mole % of triethylamine added as a catalyst. The reaction was followed by observing the absorbance of phenyl carbanilate, octyl carbanilate, and phenyl isocyanate in the infrared. The reaction starting with approximately equal amounts of phenyl carbanilate and 1-octanol proceeded as in Tables 3 and 4 and in Figures 4 and 5. The reaction was also carried out in the presence of a large excess of alcohol and is shown in Table 5 and Figures 6 and 7.

The concentration of phenyl carbanilate decreased as the transesterification proceeded, while the concentration of octyl carbanilate increased. Phenyl isocyanate appeared, reaching its highest concentration in about 3 hours, when about 16% of the carbanilate had reacted. It remained at that steady state concentration for about 9 more hours, after which time about 35% of the carbanilate had reacted. When equimolar quantities of phenyl carbanilate and alcohol were used, the reaction reached 50% completion in about 35 hours (Figure 5). Somewhat less time was required to reach 50% completion for the reaction shown in Figure 4, where the concentration of octanol was higher. In the presence of a large excess of 1-octanol the formation of phenyl isocyanate was suppressed and none could be detected by infrared spectroscopy. The reaction reached 50% completion in about 3 hours (Figure 6). Under these conditions the reaction appeared to follow first-order kinetics up to about 43% conversion.

If the rate of disappearance of phenyl carbanilate and the rate of appearance of octyl carbanilate can be explained by the mechanism in equations (34) and (35), then the rate constants can be evaluated in the following manner. For the sequential reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + C \tag{38}$$

$$B + D \xrightarrow[k_2]{} E \tag{39}$$

where A equals $C_6H_5NH\text{-}\underset{\substack{\| \\ O}}{C}\text{-}OC_6H_5$, B equals $C_6H_5N{=}C{=}O$, C equals C_6H_5OH, D equals $n\text{-}C_8H_{17}OH$, and E equals $C_6H_5NH\text{-}\overset{\substack{O \\ \|}}{C}\text{-}OC_8H_{17}\text{-}n$, the rate of appearance of phenyl isocyanate is given by

$$\frac{d(B)}{dt} = k_1[A]-k_{-1}[B][C]-k_2[B][D] \tag{40}$$

and the rate of appearance of octyl carbanilate is given by

$$\frac{d(E)}{dt} = k_2[B][D]. \tag{41}$$

If $a=[A]$ at zero time

$b=[D]$ at zero time

$x=[B]$ at time t

$y=[E]$ at time t

Then $a-x-y=[A]$ at time t

$x+y=[C]$ at time t

$b-y=[D]$ at time t

$$\frac{dx}{dt} = k_1(a-x-y)-k_{-1}(x)(x+y)-k_2(x)(b-y) \tag{42}$$

$$\frac{dy}{dt} = k_2(x)(b-y) \tag{43}$$

The system of simultaneous differential equations could not be solved, since equations (42) and (43) are nonlinear. However, equation (43) can be solved empirically for k_2 at any arbitrary time t by using the values of x and y in Figures 4 and 5, where x may be either the concentration of phenyl isocyanate or may be calculated from the concentration of phenyl carbanilate and octyl carbanilate. Thus,

$$k_2 = \frac{-\left[\ln(b-y) - \ln b\right]}{(x)(t)} \tag{44}$$

In the presence of a large excess of octanol a steady state condition can be assumed in which $k_2[D] \gg k_{-1}[C]$ and the reaction should follow first-order kinetics.

$$\frac{d(E)}{dt} = k_1[A] \tag{45}$$

$$\text{and } k_1 = \frac{-\left[\ln(a-y) - \ln a\right]}{t} \tag{46}$$

The equilibrium constant K for the dissociation of phenyl carbanilate has been measured in glyme in the absence of alcohol. If it is assumed that this constant is not changed appreciably in glyme by the change in solvent polarity associated with the addition of octanol, the k_{-1} in equation (38) may be evaluated by

$$K = \frac{k_1}{k_{-1}} \; . \tag{47}$$

On the other hand, if the rate of disappearance of phenyl carbanilate and the rate of appearance of octyl carbanilate were to be explained entirely by the carbonyl addition mechanism in equations (36) and (37), the phenyl isocyanate would still be present, but would not be an intermediate. Under these conditions the reaction should follow second-order kinetics.

For the sequential reactions

$$A + D \underset{k_{-1}}{\overset{k}{\rightleftarrows}} I \qquad (48)$$

$$I \xrightarrow[k_2]{} E + C, \qquad (49)$$

where $k_4 \gg k_{-3}$, A, C, D, and E have their previous significance and I is the carbonyl addition intermediate, the rate of appearance of octyl carbanilate is given by

$$\frac{d(E)}{dt} = k_3[A][D]. \qquad (50)$$

Assigning the same values to a, b, x, and y as previously, where x is treated as a constant as in equation (44), the above equation becomes

$$\frac{dy}{dt} = k_3(a-x-y)(b-y) \qquad (51)$$

$$\text{and } k_3 = \frac{1}{(b-a+x)t} \ln\left[\frac{(a-x)(b-y)}{b(a-x-y)}\right]. \qquad (52)$$

When a large excess of alcohol is used, the reaction would follow first-order kinetics regardless of which mechanism operates.

There are certain additional factors to consider, when interpreting the rate curves in Figures 4 through 7. One is that the transesterification reaction did not proceed in the absence of a catalyst, but did proceed in the presence of a triethylamine catalyst. It appears reasonable to assume that the amine enters equations (38) and (39) as a first-order term (see chapter II) and also enters equations (48) and (49) as a first-order term by way of complex formation between the amine and alcohol. Then k_{-1}, k_1, k_2, and

k_3 are presumably composite constants which contain the concentration of amine. As the reaction proceeds and phenol is produced, a fairly stable complex must be formed between the amine and phenol, consequently decreasing the concentration of amine and decreasing the value of k_1, k_{-1}, k_2, and k_3. In benzene the equilibrium constant for the complex formation between phenol and triethylamine was reported to be 35.5 liters/mole.[15] If this equilibrium constant were valid in glyme, the concentration of amine should decrease to 50% of its initial value, when half of the transesterification reaction had occurred. Presumably the equilibrium constant for the amine-phenol reaction would be smaller in glyme than in benzene, since glyme is the more basic solvent. From the dissociation constant of phenol and triethylamine in water the equilibrium constant for the amine-phenol reaction in water can be estimated at 13 liters/mole.[26] If this equilibrium constant were valid in glyme containing octanol, the concentration of amine should decrease to 68% of its initial value, when half of the transesterification reaction had occurred. Accordingly it appears reasonable to assume that the rate constants for the transesterification should decrease as the reaction progresses. Attempts were made to carry out the transesterification in the presence of a large excess of phenol, but the reaction proceeded at a rate too slow to obtain accurate data.

A further consideration in interpreting the rate curves is that there are other factors which can catalyze k_2, in particular alcohols and carbamates. In the former case catalysis by the alcohol would depend on the reactivity of the O-H bond. In the case of the carbamates presumably both the phenyl carbanilate and octyl carbanilate will do this.

We can assume that with an excess of alcohol a psuedounimolecular rate constant will be obtained which will be consistent with k_1 in the above. With excess alcohol the kinetic expression is derived as shown in equations (45) and (46). A plot of ln(a-y) versus time will give a straight line for a first-order reaction with a slope equal to $-k_1$. Ln(a-y) can be plotted both as A_t and as $0.075-E_t$ and the lines should be identical within experimental error. Figure 7 shows the above plot for 0.746 mole/liter of 1-octanol. The plot is a straight line up to about 105 minutes (42% conversion) and then departs from linearity, presumably owing to the effect of the phenol produced. There are still traces of phenyl carbanilate after 73 hours. Using the value of K from the work of A. B. Lateef[5] we can calculate k_{-1}, since $K = k_1/k_{-1}$. The rate should not depend on the concentration of alcohol then, except in so far as the alcohol may change the polarity of the solvent. The value of k_1 was calculated as 6.2×10^{-3} min.^{-1} and k_{-1} as 5.9×10^{-1} min.^{-1} These rate constants are only valid, if the reaction proceeds by the mechanism in equations (34) and (35).

Values for k_2 were calculated from the experimental data (Tables 6 and 7) and were not consistent with the proposed mechanism involving prior dissociation.

The rate of the transesterification reaction starts out at a value higher than can be explained by the amount of isocyanate produced before 200 minutes. The values for k_2 are too high in the early stages of the reaction. After the steady state, the concentration of isocyanate is decreasing so rapidly that it can not account for the high rate of transesterification (k_2). Due to the phenol-amine complex, k_2 should continually decrease. The transesterification rate k_2 starts out high, goes to a minimum, and then begins increasing, while k_3 for the bimolecular process is fairly constant through out the reaction.

As shown in Tables 8 and 9, the rate constant (k_3) is fairly constant for a bimolecular mechanism involving a carbonyl addition intermediate. This would indicate that the reaction proceeded exclusively by such a mechanism, independently of the reversible dissociation of phenyl carbanilate also taking place. However, if this were the case, the results would indicate that $k_{-1}[C_6H_5OH] >> k_2[ROH]$, which does not appear reasonable.

If the transesterification occurred only by the carbonyl addition mechanism, then no phenyl isocyanate would react with the alcohol. In the early stages of the reaction the concentration of phenyl isocyanate should have approximately the same value that it had when no alcohol was present. Actually the concentration of phenyl isocyanate found in the absence of alcohol[5] was four times the present value. Also if the reaction were exclusively bimolecular, then the increasing concentration of phenol should very rapidly decrease the concentration of isocyanate. In actuality the isocyanate concentration remains fairly constant from 200 to 600 minutes.

A reasonable explanation for the shape of the curves in Figures 4, 5, and 6 is that the two proposed mechanisms are operating simultaneously. If this is so, then the steady state concentration of phenyl isocyanate represents two opposing trends. As the reaction proceeds, the increasing phenol concentration tends to lower the rate of formation of phenyl isocyanate and the decreasing alcohol concentration tends to raise the rate of formation of phenyl isocyanate. In Figure 7 the addition of excess alcohol would give a pseudo-unimolecular rate representing a combination of k_2 and k_3 and the actual rate constants would not be available from it.

There is some scatter in the experimental data, as shown in Figures 4 and 5, but it is not pronounced enough to alter the conclusions. It therefore, appears certain that the transesterification of phenyl carbanilate with n-octanol at 100° proceeds by two mechanisms simultaneously. This means that $k_2\left[C_6H_5N{=}C{=}O\right]$ and $k_3\left[C_6H_5NH\text{-}COOC_6H_5\right]$ must be similar in magnitude. At temperatures higher than 100°, K is much larger.[5] Therefore, the concentration of isocyanate is greater at 150° than in the present case. Under these circumstances it is possible that the prior dissociation mechanism may take precedence, but this remains to be determined.

TABLE 3

REACTION BETWEEN 0.087 MOLE/LITER 1-OCTANOL AND 0.075 MOLE/LITER PHENYL CARBANILATE

Time	Absorbance			Concentration			
(min.)	1736	1757 (cm^{-1})	2262.5	Carbanilate Phenyl	Carbanilate Octyl	Isocyanate	Total
0	0	72.5	0	.075	0	0	.075
0	0	70.5	0	.074	0	0	.074
17	3.7	68.5	1.5	.072	.002	.001	.075
30	4.8	63	3	.067	.006	.002	.075
60	4	62	6.5	.066	.005	.004	.075
185	4	58	9	.062	.005	.007	.074
300	11.5	52	10.5	.055	.013	.007	.075
356	7.5	54	9.5	.056	.009	.007	.073
600	15.8	46.5	10	.049	.019	.007	.075
660	17.7	40.5	8.5	.043	.021	.006	.070
720	19.5	40	8.5	.042	.023	.006	.071
851	14.7	41.5	8	.043	.017	.005	.065
978	19.5	39.5	7.5	.042	.023	.005	.070
1170	21.2	34	5.5	.036	.025	.004	.065
1260	19.7	38.5	6	.041	.023	.004	.068
1680	25	31.5	4	.033	.030	.003	.066
3300	31.5	24	1.5	.025	.037	.001	.063

TABLE 4

REACTION BETWEEN 0.076 MOLE/LITER 1-OCTANOL AND 0.075 MOLE/LITER PHENYL CARBANILATE

Time (min.)	Absorbance 1736	1757 (cm^{-1})	2262.5	Concentration Carbanilate Phenyl	Octyl	Isocyanate	Total
0	2.2	68.5	0	.073	.002	0	.075
0	.5	72	0	.075	.0004	0	.074
0	0	72	0	.075	0	0	.075
0	0	71.5	0	.075	0	0	.075
0	.5	70.5	0	.074	.0004	0	.074
37	1.4	67	4.5	.071	.002	.002	.075
90	2.1	61	6.5	.064	.002	.005	.071
173	3.3	60	10	.063	.004	.008	.075
300	5	57	10	.061	.006	.008	.075
360	5.7	56	9	.059	.007	.007	.073
460	10	52.5	10.5	.055	.012	.008	.075
540	12.8	45.5	10.5	.049	.016	.008	.073
840	13.7	51	9.5	.054	.017	.007	.078
960	14.8	46	6.5	.048	.018	.005	.071
1045	18.4	40.5	6	.043	.022	.005	.070
1140	17.3	45	6.5	.048	.021	.005	.072
1440	18.1	44	5	.047	.022	.004	.073
1560	23.1	38.5	7	.041	.027	.006	.074
1620	20.7	38	5.5	.040	.024	.004	.068

TABLE 4, CONT.

Time	Absorbance			Concentration			
(min.)	1736	1757 (cm^{-1})	2262.5	Carbanilate Phenyl	Carbanilate Octyl	Isocyanate	Total
1749	23.1	39.5	6	.042	.027	.005	.074
1800	23.1	38.5	5.5	.041	.027	.004	.072
1920	21.7	37.5	4	.040	.026	.003	.069
2040	26.2	34	4.5	.036	.031	.003	.070
2543	28.2	30.5	4.5	.032	.034	.003	.069
2715	30.4	32	5.5	.034	.036	.004	.074
2919	28.4	31.5	3.5	.034	.034	.003	.071
4140	35.2	21	3.5	.022	.041	.003	.066

TABLE 5

REACTION BETWEEN 0.075 MOLE/LITER PHENYL CARBANILATE AND 0.746 MOLE/LITER 1-OCTANOL

Time (min.)	Absorbance			Concentration			
	1736	1757 (cm^{-1})	2262.5	Carbanilate Phenyl	Carbanilate Octyl	Isocyanate	Total
0	.5	69	0	.073	0	0	.073
0	.4	69	0	.073	0	0	.073
0	1.5	68	0	.072	0	0	.073
10	3.5	66	0	.070	.004	0	.074
15	6.8	63.5	0	.067	.008	0	.075
25	9.0	57.5	0	.061	.012	0	.073
30	9.5	58	0	.061	.012	0	.073
40	12.9	54	0	.057	.016	0	.073
45	13.5	53	0	.056	.017	0	.073
45	15.7	51	0	.054	.019	0	.075
53	16.3	50	0	.053	.020	0	.073
60	15.3	50.5	0	.053	.018	0	.072
65	17.8	50	0	.053	.021	0	.074
85	23.8	45	0	.048	.027	0	.075
90	22.6	44	0	.046	.027	0	.073
95	22.6	44	0	.046	.027	0	.073
105	24.9	41	0	.043	.030	0	.073
120	23.9	41	0	.043	.029	0	.072
125	25.7	38.5	0	.041	.031	0	.073

TABLE 5, CONT.

Time	Absorbance			Concentration			
(min.)	1736 (cm^{-1})	1757 (cm^{-1})	2262.5 (cm^{-1})	Carbanilate Phenyl	Carbanilate Octyl	Isocyanate	Total
135	26.7	38	0	.041	.032	0	.073
150	27.9	36.5	0	.039	.034	0	.073
165	28	36	0	.038	.034	0	.072
180	28.2	35	0	.037	.035	0	.072
195	29.3	33	0	.035	.035	0	.072
210	29.8	33.5	0	.035	.035	0	.070
240	33	32	0	.034	.037	0	.071
4432	59	2	0	.002	.071	0	.072
27225	58.5	1	0	.001	.069	0	.070

TABLE 6

TRANSESTERIFICATION OF 0.075 MOLE/LITER PHENYL CARBANILATE WITH 0.076 MOLE/LITER N-OCTANOL. SECOND-ORDER RATE CONSTANTS CALCULATED FROM FIG. (5), ASSUMING THE PRIOR DISSOCIATION MECHANISM OF EQUATIONS (34) AND (35).

Time	k_2 (liters mole^{-1} min.$^{-1}$)	
(min.)	Based on $C_6H_5NHCOOC_6H_5$	Based on $C_6H_5NHCOOC_8H_{17}$
30	.444	.221
90	.120	.059
173	.049	.036
300	.046	.034
360	.044	.039
460	.045	.047
540	.043	.047
840	.047	.047
960	.056	.052
1050	.064	.057
1140	.067	.058
1440	.075	.063
1560	.077	.064
1620	.076	.065
1750	.072	.063
1800	.077	.066
1920	.083	.069
2040	.081	.069
2530	.088	.079
2720	.085	.077

TABLE 7

TRANSESTERIFICATION OF 0.075 MOLE/LITER PHENYL CARBANILATE WITH 0.087 MOLE/LITER N-OCTANOL. SECOND-ORDER RATE CONSTANTS CALCULATED FROM FIG. (4), ASSUMING THE PRIOR DISSOCIATION MECHANISM OF EQUATIONS (34) AND (35).

Time (min.)	k_2 (liters mole^{-1} min.$^{-1}$) Based on $C_6H_5NHCOOC_6H_5$	Based on $C_6H_5NHCOOC_8H_{17}$
17	1.02	1.36
30	.39	.58
60	.097	.25
185	.046	.084
300	.055	.077
356	.065	.076
600	.060	.059
660	.066	.064
720	.073	.067
851	.087	.075
978	.083	.068
1170	.098	.072
1260	.096	.070
1680	.118	.080

TABLE 8

TRANSESTERIFICATION OF 0.075 MOLE/LITER PHENYL CARBANILATE WITH 0.076 MOLE/LITER N-OCTANOL. SECOND-ORDER RATE CONSTANTS CALCULATED FROM FIG. (5), ASSUMING THE CARBONYL ADDITION MECHANISM OF EQUATIONS (36) AND (37).

Time	k_3 (liters mole^{-1} min.$^{-1}$)	
(min.)	Based on $C_6H_5NHCOOC_6H_5$	Based on $C_6H_5NHCOOC_8H_{17}$
30	.0061	.012
90	.0043	.0088
173	.0044	.0062
300	.0043	.0058
360	.0036	.0056
460	.0038	.0061
540	.0063	.0057
840	.0057	.0057
960	.0054	.0058
1050	.0052	.0059
1140	.0050	.0059
1560	.0045	.0057
1620	.0046	.0056
1750	.0045	.0053
1800	.0045	.0055
1920	.0045	.0055
2040	.0046	.0055
2530	.0047	.0053
2720	.0047	.0052

TABLE 9

TRANSESTERIFICATION OF 0.075 MOLE/LITER PHENYL CARBANILATE WITH 0.087 MOLE/LITER N-OCTANOL. SECOND-ORDER RATE CONSTANTS CALCULATED FROM FIG. (4), ASSUMING THE CARBONYL ADDITION MECHANISM OF EQUATIONS (36) AND (37).

Time	k_3(liters mole^{-1} min.$^{-1}$)	
(min.)	Based on $C_6H_5NHCOOC_6H_5$	Based on $C_6H_5NHCOOC_8H_{17}$
17	.0187	.0139
30	.016	.011
60	.014	.0055
185	.0093	.0049
300	.0088	.0061
356	.0088	.0074
600	.0071	.0074
660	.0074	.0076
720	.0071	.0078
851	.0066	.0080
978	.0060	.0078
1170	.0051	.0075
1260	.0050	.0075
1680	.0043	.0074

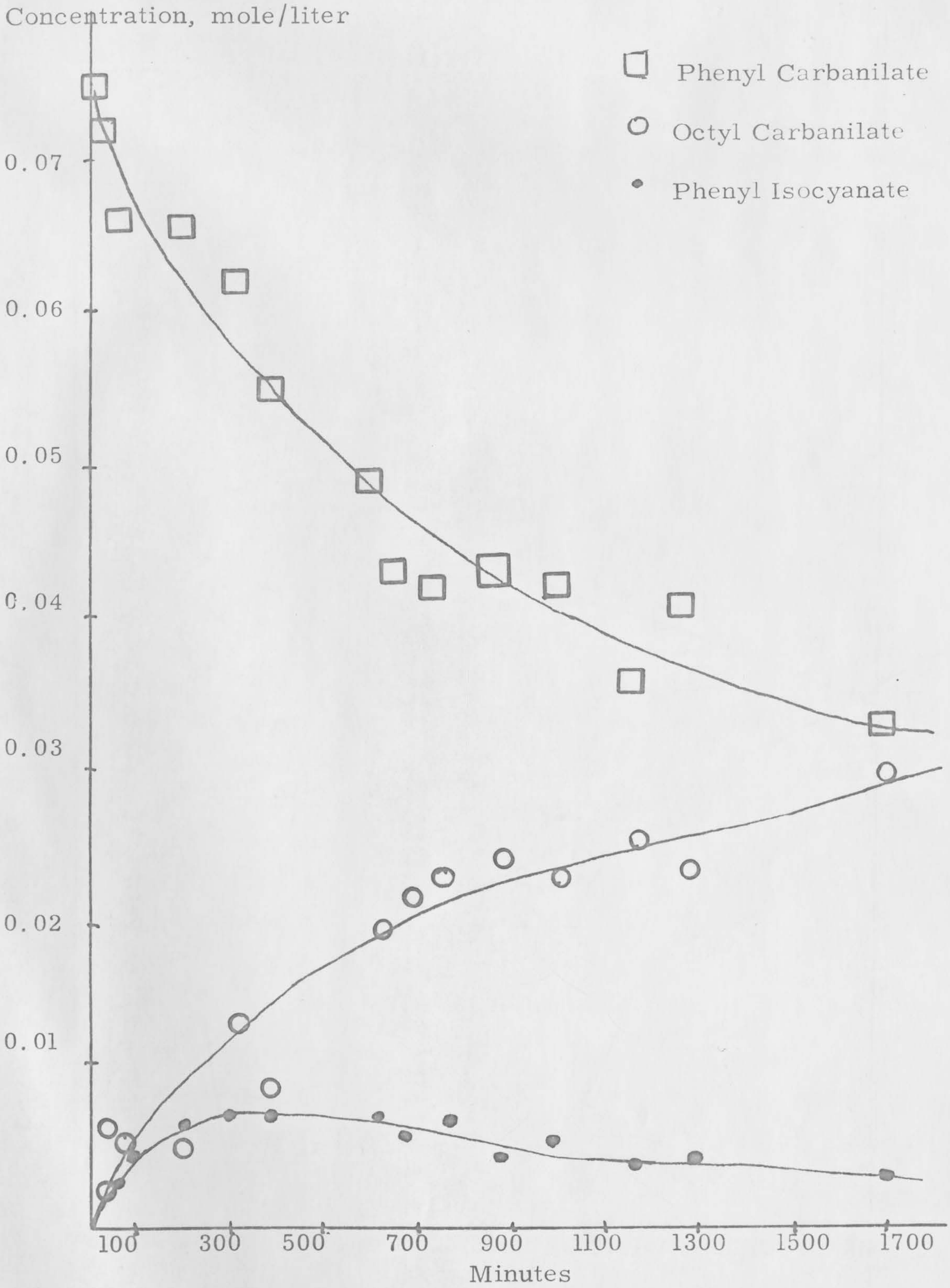


Fig. 4. Reaction between 0.087 mole/liter n-octanol and 0.075 mole/liter phenyl carbanilate.

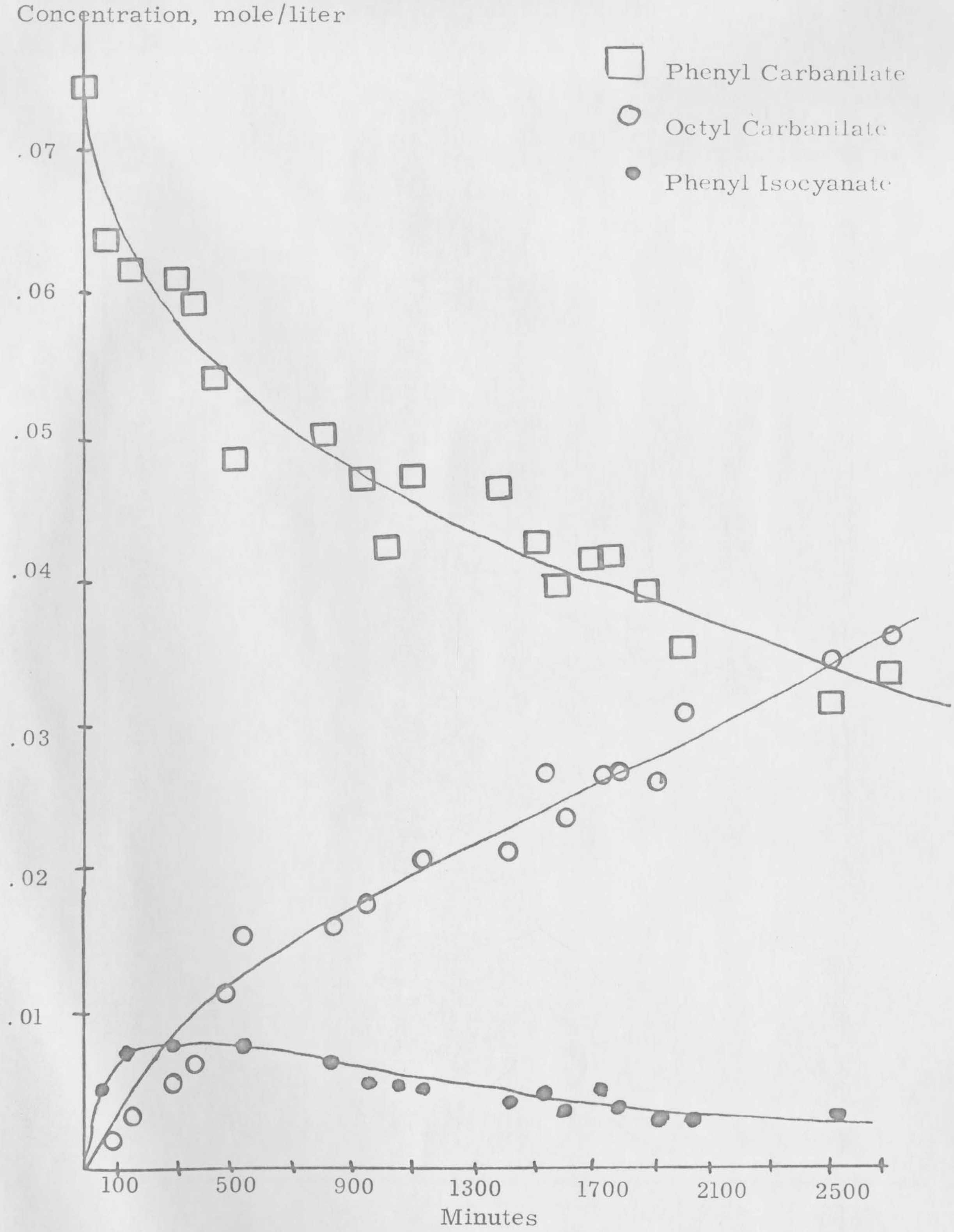


Fig. 5. Reaction Between 0.076 mole/liter n-octanol and 0.075 mole/liter phenyl carbanilate.

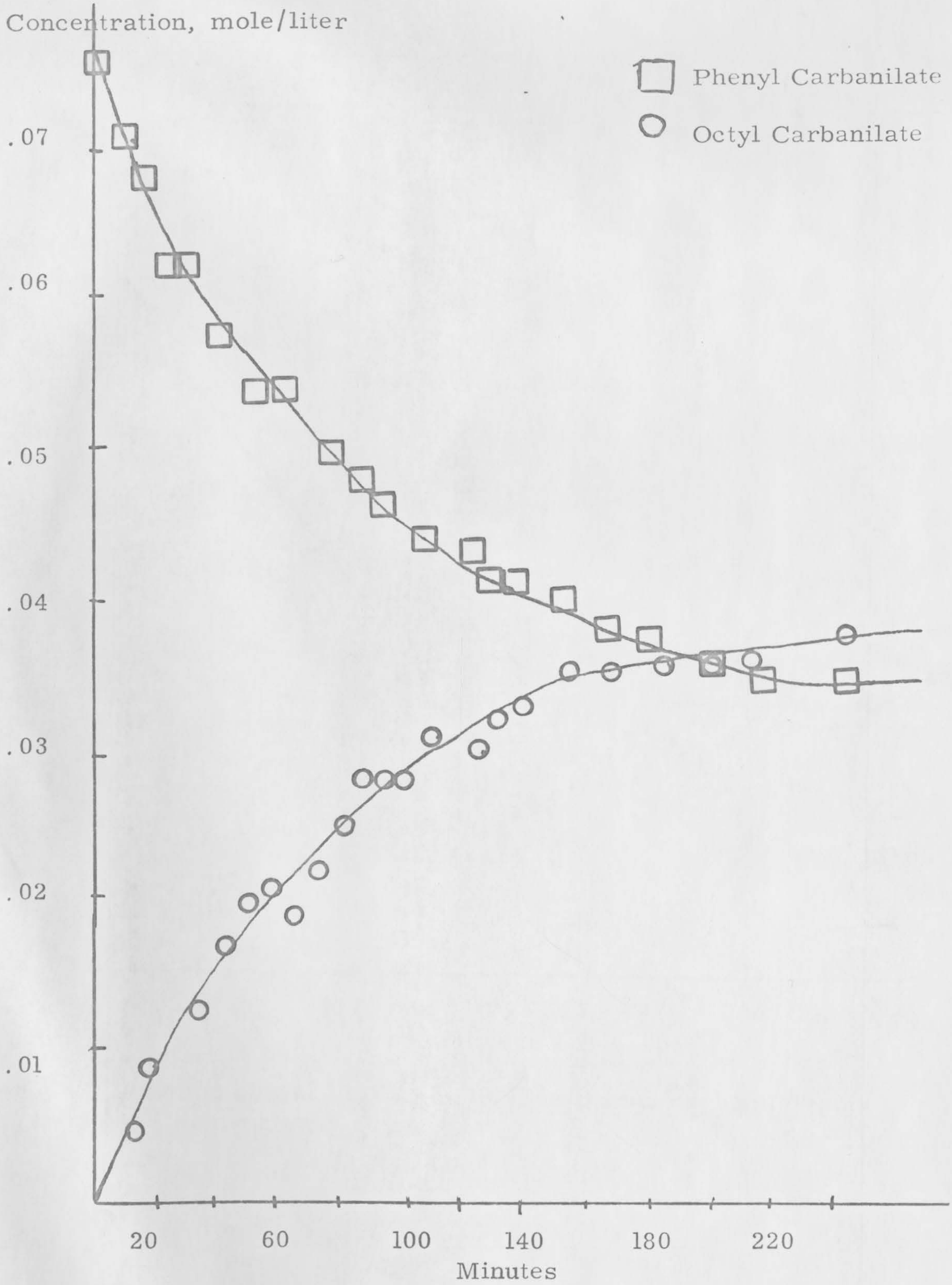


Fig. 6. Reaction between 0.075 mole/liter phenyl carbanilate and 0.746 mole/lite n-octanol.

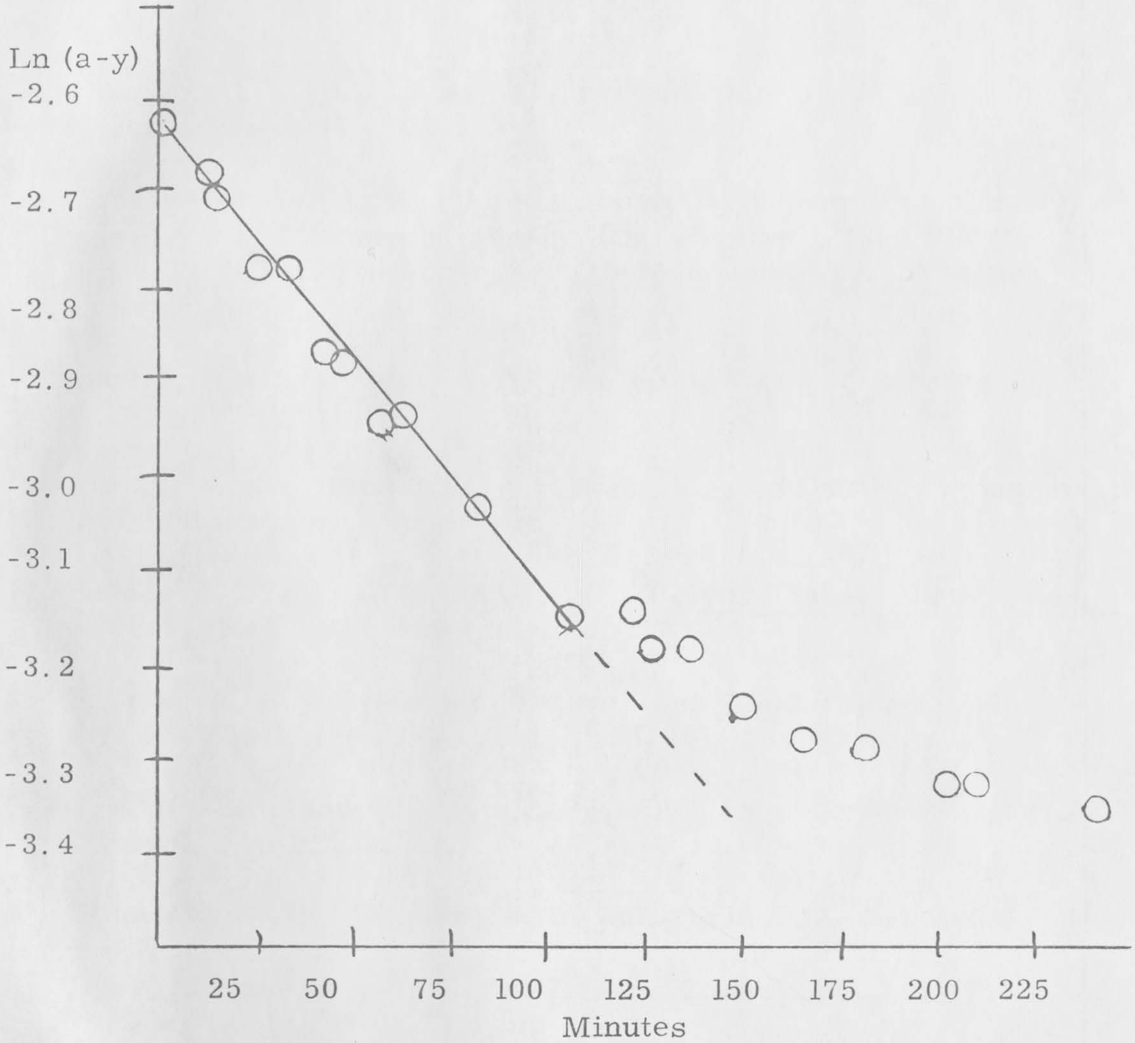


Fig. 7. Reaction between 0.075 mole/liter phenyl carbanilate and 0.746 mole/liter n-octanol.

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