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TITLE The Catalyzed Thermal Dissociation of Aryl Carbanilates in Benzene

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THE CATALYZED THERMAL DISSOCIATION OF ARYL CARBANILATES IN BENZENE

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ABSTRACT

THE CATALYZED THERMAL DISSOCIATION OF ARYL CARBANILATES IN BENZENE

Jasvant K. Shah
Master of Science in Chemistry
Youngstown State University, December, 1971

Recent studies in the mechanism of thermal dissociation of N-substituted carbamates have shown a duality in the reaction mechanism, depending upon the number of N-substituents. The present research was undertaken to investigate the equilibrium by which aryl carbanilates dissociate at elevated temperatures and to show how such factors as structure and chemical environment relate to this equilibrium.

Members of a series of meta- and para-substituted phenyl carbanilates were shown to undergo a rapid reversible dissociation in benzene with the added catalyst, dibutyltin dilaurate. The equilibrium constants for this dissociation were measured at four different temperatures ranging from 90°C to 150°C. The thermodynamic parameters were calculated. The value of enthalpy (ΔH) ranges between 13.5 and 16.4 kcal/mole, and the entropy (ΔS) values were 25.1 to 32.1 e.u. Results obtained from the present research were compared with those from the dissociation of aryl carbanilates in glyme. Introduction of an electronreleasing group into the ester lowered the values of the equilibrium constants. On the other hand, the electron-attracting groups in the ester increased the values of equilibrium constants. A probable mechanism is proposed for this dissociation.

ACKNOWLEDGEMENTS

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To my brother-in-law, Babulal T. Sheth, and my family for their constant encouragement and patient endurance throughout the labor. I am grateful in measure beyond words. Finally, the author wishes to thank his friends who knowingly or unknowingly made his task easier and enjoyable.. And, also I wish to thank Mr. Bharat Dave and Rajesh Bakhai, who helped to make the figures.

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CHAPTER I

INTRODUCTION

In the field of chemical technology there are a great number of industrially important products which are loosely called polyurethanes or urethanes. Some are homopolymer which are used as fibers, plastics and adhesives, elastomers and hard or flexible foams.

The carbamate group is a characteristic component of polyurethanes; therefore, the reaction of simple carbamates are of direct interest to the polymer chemist. The chemistry of the carbamate group has received less attention than the reaction by which it is formed. Few detailed studies have been made of the products resulting from the purely thermal dissociation of carbamate. It is well known that the carbamate is decomposed by heating to elevated temperatures. The thermal dissociation may take place via alternate routes leading to different end products.[1-5]

The N-monosubstituted carbamates decompose on heating to give an isocyanate and an alcohol (or phenol). To some extent,[6, 7] at higher temperatures carbamates appear to be in equilibrium with the isocyanate and alcohol (or phenol). A few such carbamates yield additional products.[8, 9]

The ester interchange reaction has been used for preparing carbamates of higher alcohols.[10] It has been known for some time that carbamates undergo an ester interchange reaction with alcohols, amines and other active hydrogen compounds.[1, 10-14] There are several different routes by which this reaction may proceed and the choice of a particular route appears to depend on the nature of the carbamate, the catalyst, the temperature, and the solvent.

There are two possible pathways for this reaction. One is based on a two-step process in which there is an initial unimolecular thermal dissociation to form isocyanate followed by a reaction with alcohol (or phenol) to yield the product carbamate. The second is a direct bimolecular displacement reaction.

Both dissociation to free isocyanate and a direct displacement are facile in the cases of aryl N-aryl carbamates[1] and can take place either in the presence or absence of the added catalyst depending on the temperature and solvent.

As part of an effort to clarify the mechanism of the overall ester interchange reaction, Lateef, Reeder and Rand[15] studied the thermal dissociation of aryl carbanilates in glyme. The equilibrium constant for this dissociation was determined spectrophotometrically. The significance of the thermodynamic parameters and Hammett correlation was discussed.

The present investigation was undertaken to gain a better understanding of the dissociation. For this purpose a study was made for dibutyltin dilaurate catalyzed thermal dissociation of N-monosubstituted aryl carbamates in benzene at different temperatures.

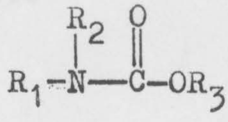
$$C_6H_5NHCOOAr \rightleftharpoons C_6H_5NCO + ArOH \qquad (1)$$

Infrared spectroscopy was used in the present work as an analytical method.

CHAPTER II

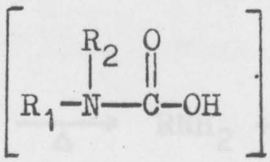
HISTORICAL

The polyurethanes contain a characteristic grouping



$$R_1{-}\overset{R_2}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OR_3$$

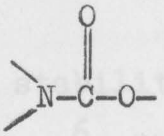
which is a mixed amide-ester of carbonic acid. These compounds are considered in the scheme of systematic organic nomenclature to be esters of the unstable carbamic acids.



$$\left[R_1{-}\overset{R_2}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OH\right]$$

Therefore, formal names of the polymers have been given as polycarbamates, although the term polyurethane is used in general discussion.

Carbamates are the reaction products of isocyanates or carbamyl halides with materials possessing hydroxyl groups, and have the characteristic configuration

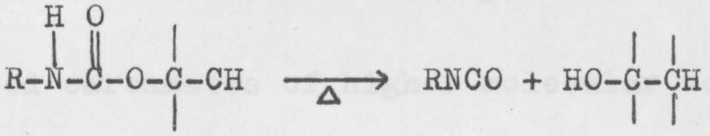


$$>N{-}\overset{O}{\overset{\|}{C}}{-}O{-}$$

To elucidate the reaction sequence and chemical behavior observed in the more complex polymeric systems, the study of a monomeric compound provides excellent clues.

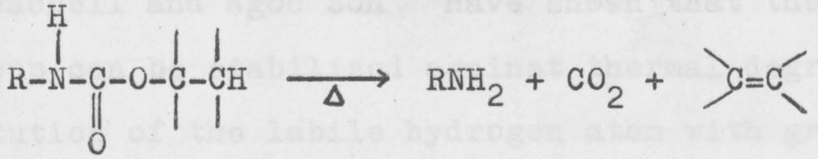
The basic chemistry of the urethanes has been known for over a hundred years. Urethanes, in general, are stable compounds. They can be stored indefinitely. They are decomposed by heating at moderate temperatures, however, and give products arising from three distinct paths:

1. Elimination of an alcohol (or phenol) with formation of an isocyanate



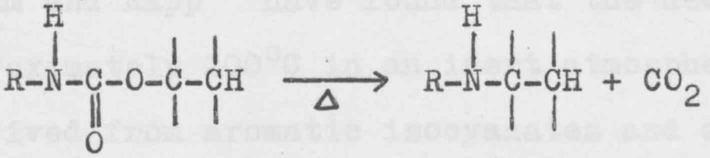
$$\mathrm{R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}C{-}CH} \xrightarrow[\Delta]{} \mathrm{RNCO + HO{-}C{-}CH} \qquad (2)$$

2. Elimination of carbamic acid (as an amine and carbon dioxide) with the formation of an olefin



$$\mathrm{R{-}\overset{H}{N}{-}\underset{\underset{O}{\|}}{C}{-}O{-}C{-}CH} \xrightarrow[\Delta]{} \mathrm{RNH_2 + CO_2 + {>}C{=}C{<}} \qquad (3)$$

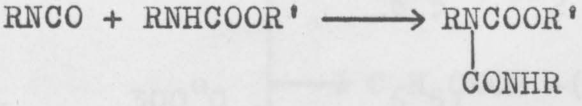
3. Decarboxylation to form a secondary amine and carbon dioxide



$$\mathrm{R{-}\overset{H}{N}{-}\underset{\underset{O}{\|}}{C}{-}O{-}C{-}CH} \xrightarrow[\Delta]{} \mathrm{R{-}\overset{H}{N}{-}C{-}CH + CO_2} \qquad (4)$$

Evidence for the stability of urethanes was shown in a publication of Metayer.[6] It was demonstrated that low molecular weight N-substituted carbamates are stable up to their boiling point and that they can be distilled without decomposition. However, carbamates of higher molecular weights and boiling points such as benzyl carbamate dissociate to alcohol and allophanate at elevated temperatures.

$$\mathrm{RNHCOOR'} \longrightarrow \mathrm{R'OH} + \mathrm{RNCO} \qquad (5)$$



$$\mathrm{RNCO} + \mathrm{RNHCOOR'} \longrightarrow \underset{\displaystyle \mathrm{CONHR}}{\mathrm{RNCOOR'}} \qquad (6)$$

allophanate

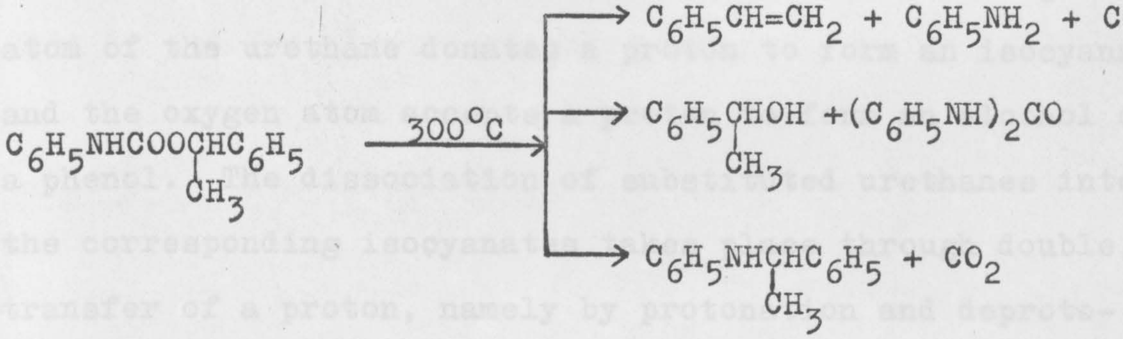
Monosubstituted carbamates of higher molecular weight decompose at elevated temperature to the isocyanate and alcohol. The N,N-disubstituted carbamates are uniformly very stable and distill without decomposition.

Beachell and Ngoc Son[16] have shown that the carbamate group can be stabilized against thermal degradation by substitution of the labile hydrogen atom with groups such as methyl and benzyl. The temperature of dissociation of the carbamate depends upon the chemical nature of the group adjacent to the carbamate linkage.

Ingham and Rapp[17] have found that the decomposition, at approximately 200°C in an inert atmosphere, of urethanes derived from aromatic isocyanates and aliphatic alcohols, proceed primarily through reaction (1). Urethanes based on phenols dissociate more readily than those based on alcohols at about 150°C.

Bortnick, *et al.*[2] obtained 50-80% yields of secondary and tertiary alkyl isocyanates from the base-catalyzed dissociation of N-alkyl carbamates.

Dyer, Newborn and Wright[1] reported all three modes of decomposition when the dissociation was carried out in the absence of solvents.



$$C_6H_5NHCOOCH(CH_3)C_6H_5 \xrightarrow{300^\circ C} \begin{cases} C_6H_5CH{=}CH_2 + C_6H_5NH_2 + CO_2 \\ C_6H_5CH(CH_3)OH + (C_6H_5NH)_2CO \\ C_6H_5NHCH(CH_3)C_6H_5 + CO_2 \end{cases} \quad (7)$$

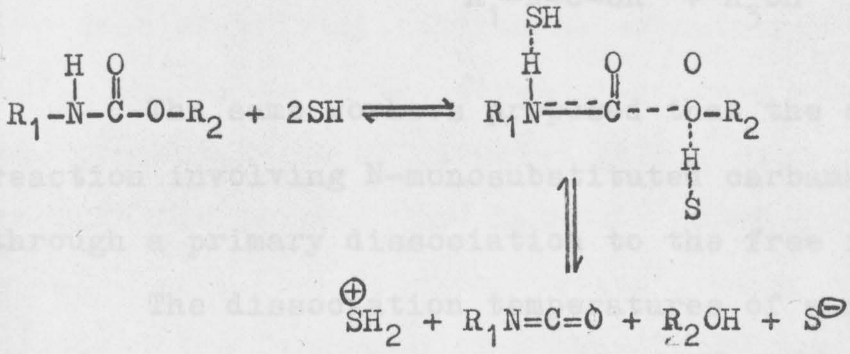
Griffin and Willwerth[18] observed the thermal dissociation of blocked toluene diisocyanates based on an 80/20 mixture of toluene-2,4 and toluene-2,6-diisocyanate. The blocked isocyanates based on phenols and upon β-dicarbonyl compounds dissociated to give a free isocyanate group while the adduct based on tert-butyl alcohol did not produce a free isocyanate but gave only isobutylene, carbon dioxide and the corresponding amine on heating. The lowest dissociation temperatures were observed in general with negatively substituted phenols.

Mukaiyama, <u>et al</u>.[11] have carried out the reaction of urethanes at 130-170°C with a 10:1 molar excess of active hydrogen compounds such as amines, carboxylic acids and amino alcohols. The dissociation of urethane was accelerated by both acid and base.[11] Pseudo-first order kinetics were reported. The rate determining step was assumed to be the dissociation of urethane into the corresponding isocyanate.

$$RNHCOOR' \rightleftharpoons R'OH + RNCO \qquad (8)$$

In the dissociation of urethanes, the nitrogen atom of the urethane donates a proton to form an isocyanate and the oxygen atom accepts a proton to form an alcohol or a phenol. The dissociation of substituted urethanes into the corresponding isocyanates takes place through double transfer of a proton, namely by protonation and deprotonation, usually with acid or base catalyst.

Mukaiyama, in his paper, suggests termolecular mechanism for the dissociation of carbamate:



$$R_1-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R_2 + 2SH \rightleftharpoons R_1\overset{\overset{SH}{\vdots}}{\overset{H}{\underset{}{|}}}\!\!N\text{=}\text{-}\text{-}\overset{\overset{O}{\|}}{C}\text{-}\text{-}\text{-}\underset{\underset{S}{\vdots}}{\underset{H}{\vdots}}{\overset{O}{O}}-R_2 \qquad (9)$$

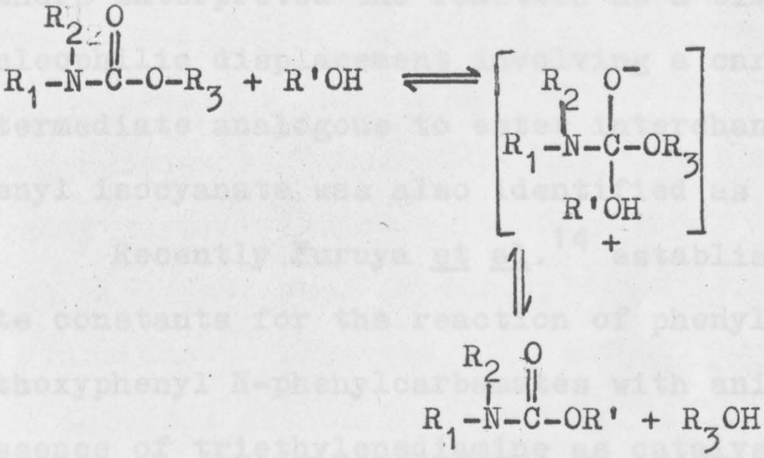
$$\Downarrow\!\Uparrow$$

$$\overset{\oplus}{SH_2} + R_1N{=}C{=}O + R_2OH + S^{\ominus}$$

where SH represents solvent.

Mukaiyama and Iwanami[11] have shown that in a series of meta- and para-substituted carbamates, the rate of dissociation increases with increasing electron-attracting power of the substituent on the ring attached to nitrogen, excluding steric effects. In an amine solvent, the value for Hammett's constant ρ was 0.538.

The reaction of carbamate with alcohol was studied by Gaylord and Sroog[12] as a procedure for the synthesis of new carbamates. For N,N-disubstituted carbamates these workers proposed a reaction mechanism involving a carbonyl addition intermediate analogous to that of a transesterification reaction.



$$R_1\text{-}N(R_2)\text{-}C(=O)\text{-}O\text{-}R_3 + R'OH \rightleftharpoons \left[R_1\text{-}N(R_2)\text{-}C(O^-)(\overset{+}{R'OH})\text{-}OR_3 \right] \rightleftharpoons R_1\text{-}N(R_2)\text{-}C(=O)\text{-}OR' + R_3OH \qquad (10)$$

The same workers proposed that the comparable reaction involving N-monosubstituted carbamates proceeded through a primary dissociation to the free isocyanate.

The dissociation temperatures of a number of solid aryl carbanilates suspended in mineral oil have been studied by Tartakovskaya et al.[19] by the use of infrared spectroscopy. The dissociation temperature, the lowest at which phenyl isocyanate could be identified in an infrared spectrum, ranged from 150° for p-tolyl carbanilate to 100° for p-nitrophenyl carbanilate.

Kopple[20] carried out the thermal dissociation of p-nitrophenyl carbanilate in dioxane, using trimethylamine as a catalyst. At room temperature, the equilibrium constant was about 2 x 10^{-3} mole/liter.

The displacement reaction of aryl carbanilates with n-hexanol was reported by Sal'nikova et al.[13] using o-dichlorobenzene as solvent. Second-order rate constants at 160°-180° were reported for this reaction. These authors interpreted the reaction as a bimolecular nucleophilic displacement involving a carbonyl addition intermediate analogous to ester interchange, although phenyl isocyanate was also identified as an intermediate.

Recently Furuya et al.[14] established first-order rate constants for the reaction of phenyl, p-tolyl and p-methoxyphenyl N-phenylcarbamates with aniline in the presence of triethylenediamine as catalyst in dioxane at 80°. The plots of the first order rate constant versus the concentration of catalyst gave a straight line passing through the origin. The Hammett plot gave a positive ρ value of 1.63. From conductivity data, these workers proposed the formation of a quaternary ammonium salt in the rate-determining step. p-Chlorophenyl and p-nitrophenyl N-phenyl carbamate satisfied a second order rate constant and the latter in the absence of catalyst gave the sym-disubstituted urea.

More recently Lateef, Reeder and Rand[15] studied the thermal dissociation of aryl carbanilates in ethylene glycol, dimethyl ether, without added catalyst. The dissociation was rapid and reversible. The equilibrium constants for this dissociation were measured at temperatures between 90.4° and 150°C (50° and 90.4°C in the case of p-nitrophenyl carbanilate). It was shown by these authors that phenyl carbanilate dissociation to the extent of 23% at 90.4° and 63% at 150°C. Equilibrium was reached within ten minutes at 90.4°C and within two minutes at 150°C. The Hammett plot gave a positive ρ value of 1.49-1.66, depending on the temperature.

However, the use of certain catalysts to lower the dissociation temperature has also been reported, notably tertiary amine salts of organic acids and certain metal catalysts such as dibutyltin dicarboxylates. Orlov and Tarakanov[21] reported that the polyurethane prepared from tolylene diisocyanate and polypropylene glycol was rapidly degraded in moist air by the addition of diethyltin dicaprylate. The catalyst split the carbamate groups to isocyanate and alcohol.

CHAPTER III

EXPERIMENTAL

Materials

White label phenyl isocyanate was obtained from Eastman Organic Chemicals and purified by distillation under a dry nitrogen atmosphere. meta-Cresol, m-methoxyphenol, p-methoxyphenol, m-nitrophenol, and p-iodophenol were obtained from Eastman Organic Chemicals and m-chlorophenol was obtained from J. T. Baker and Co. and were used without further purification. Hexane was obtained from Matheson, Coleman and Bell. The catalyst, dibutyltin dilaurate, was obtained from M & T Chemicals, Inc. Benzene was dried over sodium before use.

All of the glass reaction vessels were cleaned with concentrated H_2SO_4, followed by water and acetone rinse. The vessels were dried for at least one hour at 110° and cooled under dry nitrogen just prior to use.

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra of the solutions were measured in a 0.1 mm Irtran cell on a Beckman IR-12 double-beam spectrophotometer. Attention was focused on absorption due to phenyl isocyanate (2270 cm^{-1}) and the carbanilate (1757-1765 cm^{-1}). Concentrations of these species were determined from standard plots of absorbances versus concentration (Figures 3 - 7). The carbon-hydrogen analyses were performed by M-H-W Laboratories, Garden City, Michigan and by Crobaugh Laboratories, Cleveland, Ohio.

Synthesis and Purification of Aryl Carbanilates

Aryl carbanilates were prepared from phenyl isocyanate and the corresponding phenols in benzene solution, by the method of Shriner,[22] using a catalytic amount of pyridine. The precipitated grayish white solid was collected by suction filtration. The solid was purified by three recrystallizations from hexane using a soxhlet apparatus. Subsequently the solid was purified by recrystallization, by dissolving it in a sufficient volume of hexane to give a saturated or nearly saturated solution at the boiling point. The hot solution was filtered to remove insoluble material, which was present in trace amounts. The filtered solution then was allowed to cool while being stirred. It was then cooled in ice to obtain large crystals. The recrystallized substance was allowed to dry at room temperature. Any entrapped solvent was removed by crushing the crystal to a fine power and drying the powder in an Abderhalden apparatus under reduced pressure. Toluene was refluxed in the boiler, phosphorus pentoxide was placed at the cold vacuum connection end of the apparatus. The dry substance thus obtained was maintained in a desiccator to protect it from atmospheric contamination.

TABLE 1

PREPARATION, MELTING POINTS AND ELEMENTAL ANALYSES FOR ARYL CARBANILATES

Phenol	Aryl Carbanilates	Mp °C	Lit.Mp°C	Calcd., %		Found	
				C	H	C	H
Phenol	Phenyl	125-126.5	123[14]	73.22	5.20	72.80	5.29
m-Methyl	m-Methylphenyl	125-126	125[23]	73.99	5.77	73.74	5.60
m-Chloro	m-Chlorophenyl	123.5-124.5	124-125[24]	63.04	4.07	63.24	3.95
m-Iodo	m-Iodophenyl	135-136	---	46.04	2.97	45.92	2.95
p-Iodo	p-Iodophenyl	151-152.5	---	46.04	2.97	46.47	2.53
m-Methoxy	m-Methoxyphenyl	120-122	120-122.5[15]	69.12	5.39	68.88	5.80
p-Methoxy	p-Methoxyphenyl	135-137	135[14]	69.12	5.39	68.94	6.03
m-Nitro	m-Nitrophenyl	129-131	---	60.47	3.90	60.43	4.02

The melting points and carbon hydrogen analyses are shown in Table I.

Solvent Purification and Solution Preparation

Sym-diphenylurea, identified by its melting point (238°C), was formed when the solution of phenyl isocyanate was allowed to stand, with or without metal catalyst. The urea formed appears to be the results of moisture and of reaction of water with the isocyanate. It was necessary to prepare a fresh benzene solution of phenyl isocyanate as well as solutions of aryl carbanilate for each run.

Solvent purification and solution preparation were carried out in a self-contained apparatus under dry purified nitrogen.

Benzene was distilled three times from sodium wire. The dry benzene was distilled again from a fresh sodium wire using an 86 mm vacuum-jacketed column operated at a reflux ratio of 10:1. The first portion of the distillate was rejected and the middle fractions were collected into a specially designed volumetric flask equipped with a magnetic stirrer and containing the requisite amount of the carbanilate. The volumetric flask was provided with a Teflon stopcock and exit arm for filling the reaction vessels.

The dissociation was carried out in sealed Pyrex tubes of 2.2 ml capacity. Each tube was charged with one milliliter of the solution. The tube was dried by heating with a flame in a current of dry nitrogen just prior to use and provision was made that the system could be continuously purged with a slow stream of dry nitrogen gas. The tube was then immediately sealed with a gas-oxygen flame under vacuum and cooled in a dry ice-acetone bath.

Measurement

To carry out the dissociation, each tube was immersed in a thermostatted oil bath. The temperature in the thermostat was maintained to an accuracy of $\pm 0.1^{\circ}$. The tubes were withdrawn at various times and quickly quenched in a dry ice-acetone bath. The tubes were then allowed to warm to room temperature and opened, and an 0.1 mm Irtran cell for the infrared spectrometer was filled with the solution. The change in composition of the reaction mixture was checked for aryl carbanilate and phenyl isocyanate by the absorption maxima shown in Table II. Typically the isocyanate absorbance was measured within 4 - 6 minutes after removing the reaction tube from the oil bath.

A Calibration Curve

For an actual photometric determination, a calibration curve was employed. Such a curve was obtained by measuring the absorbance of solutions containing the carbanilate at different known concentrations and plotting the net absorbance (after subtracting the solvent absorbance) versus concentration. The calibration curve gave a straight line passing through the origin, i.e., it followed Beer's law (Figures 3 - 7).

The absorbance of the solution of dissociated carbanilate was measured for phenyl isocyanate at 2261 cm^{-1}; for the aryl carbanilate from its carbonyl absorbance. After subtracting solvent absorbance, the concentration of the desired species was read from the previously prepared calibration curve. A separate calibration chart was prepared for each aryl carbanilate and phenyl isocyanate. The absorption maxima are shown in Table 2.

TABLE 2

INFRARED MAXIMA FOR PHENYL ISOCYANATE
AND SUBSTITUTED PHENYL CARBANILATES

Compound	$V_{max.}$ cm^{-1}
Phenyl isocyanate	2261
Phenyl carbanilate	1761
m-Methoxyphenyl carbanilate	1761
p-Methoxyphenyl carbanilate	1759
p-Iodophenyl carbanilate	1764.5

Calculations

The equilibrium constants were calculated as the square of isocyanate concentration (I) divided by undissociated aryl carbanilate concentration (u).

The values of (I) and (u) at equilibrium were determined by plotting concentration versus time. The equilibrium concentration was taken as the concentration which did not change for a period of time as shown.

$$k_{eq} = \frac{(I)^2}{(u)} \qquad (11)$$

in Figures 8 - 23. Some scatter was seen in the case of p-iodophenyl carbanilate as seen in Figures 20 - 23.

The enthalpy (ΔH^o) was calculated by plotting log k_{eq} versus 1/T, where k_{eq} is the equilibrium constant at the absolute temperature T. Straight lines were obtained with slopes equal to $\Delta H/2.303R$ where R is the gas constant. These are shown in Figures 24 - 27.

The standard free energies for the reaction, ΔF^o, were calculated using the equation

$$\Delta F^o = -2.303RT \log k_{eq} \qquad (12)$$

The entropies of the reaction, ΔS^o, were calculated

$$\Delta F^o = \Delta H^o - T\Delta S^o \qquad (13)$$

A summary of thermodynamic parameters is shown in Table 3.

TABLE 3

THE CATLYZED THERMAL DISSOCIATION OF ARYL CARBANILATES IN BENZENE

Substituent	K, mol.l^{-1} x10^{2}				ΔH kcal/mole	ΔS e.u.
	150°C	130°	110°	90°		
H[a]	3.603	1.38	0.476	0.189	15.1	29.1
p-OCH$_3$[b]	0.978	0.47	0.21	0.051	14.9	26.1
m-OCH$_3$[b]	3.52	1.68	0.497	0.16	16.4	32.1
p-I[b]	3.36	1.38	0.692	0.225	13.5	25.1

(a) Initial concentration 0.07 mol.l^{-1}, 0.003 mol.l^{-1} catalyst concentration.

(b) Initial concentration 0.06 mol.l^{-1}.

CHAPTER IV

RESULTS AND DISCUSSION

The Catalyzed Thermal Dissociation of Aryl Carbanilates in Benzene

Recent studies in the mechanisms of the thermal dissociation of N-substituted carbamates have shown a duality in the reaction mechanism, depending upon the number of N-substituents. Evidence for this duality is found, for example, in the rate of hydrolysis of N-mono and N,N-disubstituted carbamates. N-monosubstituted carbamates are hydrolyzed by alkali about 10^6 times faster than the N,N-disubstituted carbamates.[25]

The purpose of the present research was to investigate the equilibrium by which aryl carbanilates dissociate at elevated temperatures, and to show how such factors as structure and chemical environment relate to this equilibrium. Specifically, the present research was designed to compare the equilibrium constants and thermodynamic parameters of this dissociation in benzene with those of the dissociation of aryl carbanilates in glyme which were studied by Lateef, Reeder and Rand.[15] In this way the effect of solvent on the initial and final states of the reaction may be assessed.

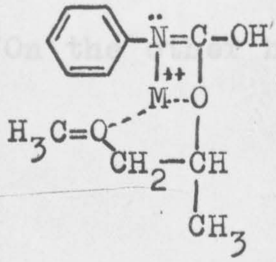
A study of the thermal dissociation of phenyl carbanilates in benzene, without the added catalyst, showed that at an initial concentration of 0.075 M and a temperature of 150°, the composition of the solution remained unchanged over the course of 2 hours. The absence of reaction was judged by the nonappearance in the infrared spectrum of the phenyl isocyanate band at 2270 cm^{-1} and the constant intensity of the carbamate band.

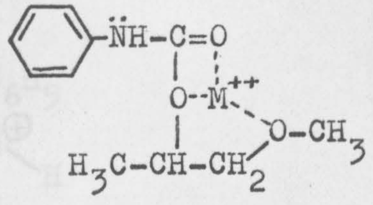
To accelerate the dissociation, dibutyltin dilaurate (DBTDL) was tested as a catalyst. This compound is an effective catalyst in polyurethane synthesis.[26-31] With this catalyst, the aryl carbanilates dissociated rapidly into isocyanate and the corresponding phenol over a temperature range of 90°C to 150°C.

Typical plots of the concentration of aryl carbanilate and phenyl isocyanate versus time at different temperatures are shown in Figures 8 - 23. Table III summarizes the equilibrium constants along with the thermodynamic parameters for the carbanilates obtained by a least-square plot of log k against 1/T (Figures 24-27).

In the case of the unsubstituted phenyl carbanilate, the initial concentration was 0.07 mol/liter. The sum of isocyanate concentration and phenyl carbanilate concentration at equilibrium should, therefore, be 0.07 mol/liter. Actually, this sum ranged between 0.065 and 0.071 mol/liter, well within experimental error. In the case of the substituted phenyl carbanilates, the initial concentration was 0.06 mol/liter. The sum of the carbanilate and isocyanate concentration at equilibrium ranged between 0.038 and 0.053 for *m*-methoxyphenyl carbanilate, 0.054 and 0.055 for *p*-methoxyphenyl carbanilate, and 0.052 and 0.060 for *p*-iodophenyl carbanilate. In the cases where this sum was low, some of the starting material must have disappeared to give compounds other than phenyl isocyanate and phenols. However, no extraneous infrared absorption bands were seen in the 1600 to 1800 cm^{-1} or 2000 to 2200 cm^{-1} region, or in any other region of the spectrum. This appears to rule out the formation of dimers,[32] trimers,[32] allophanates,[33] or carbodiimides[34] in competition with the dissociation reaction. These compounds have absorption bands at 1790 cm^{-1}, 1710 cm^{-1}, 1280 cm^{-1}, and 2170 cm^{-1}, respectively. It appears likely that the above lack of additivity may have resulted from the formation of sym-diphenylurea. This compound was formed very quickly in earlier experiments with benzene containing traces of water. It was insoluble in benzene and settled out quickly, and therefore did not absorb in the infrared. In the present case, the water may have been absorbed after the tubes were opened and before the infrared absorption could be measured. The presence of catalyst in this system would accelerate the formation of the urea greatly. A further source of error in these experiments would be the recombination of the phenol with phenyl isocyanate. The techniques used in this work were developed for use with a glyme solvent without catalyst,[15] under conditions in which the recombination of the phenol and isocyanate is slow at room temperature. In benzene solvent, and with a catalyst, such reactions are much faster than in glyme.[35]

The dissociation of aryl carbanilates in benzene did not proceed without catalyst, but occurred rapidly in the presence of dibutyltin dilaurate, a catalyst which is known to promote the formation of polyurethanes.[26-31] All catalyzed reactions involve the formation of some kind of an intermediate species formed by reaction between the catalyst and the substrate that is undergoing reaction. Smith[36] has reported evidence based on infrared spectra for the presence of a ternary complex as the reactive intermediate in the alcohol-isocyanate reaction catalyzed by metal salts. In our study, mixtures of 4.3 - 5 mole % dibutyltin dilaurate in 0.06 - 0.07 M carbanilates were examined. However, infrared spectroscopy yielded no conclusive evidence for complex formation between aryl carbanilate and catalyst or between phenyl isocyanate and catalyst. It seems, at this catalyst level, that the concentration of any complex intermediate is below that required for detection by infrared. Evidence for complex formation between aryl isocyanate and alkyltin alkoxide was provided by Bloodworth and Davies,[37] through the isolation of an adduct which was characterized as the N-stannyl carbamate. Evidence for complex formation between isocyanate catalyst and alcohol-catalyst was reported by Reegen and Frisch.[38] These authors used a freezing point depression method for determining the molecular weights of complexes. Possible structures of chelate rings in complexes involving 1-methoxy-2-propanol, proposed by these authors are

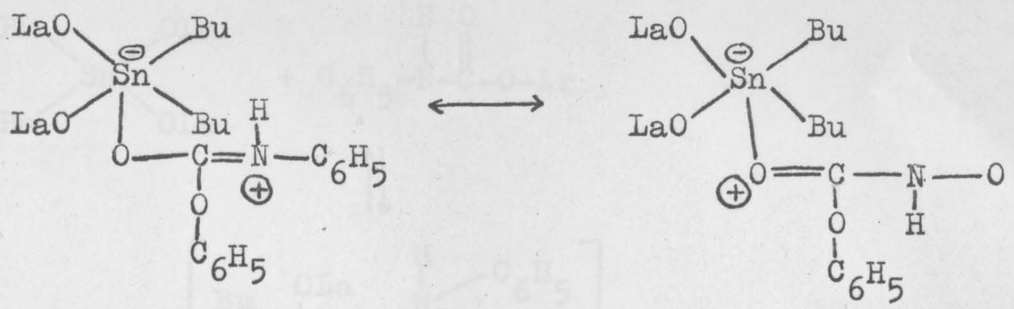




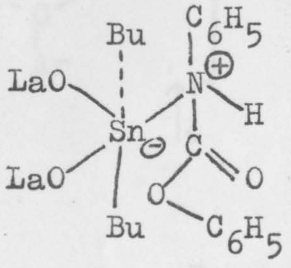
Carbamate formation would then take place by rearrangement of the hydroxyl proton to the nitrogen of the isocyanate group.

Since a catalyst can change the rate but not the equilibrium, it follows that a catalyst must accelerate the forward and reverse reaction in the same proportion, since $k_{eq} = k_f/k_r$, where k_f = rate constant of forward reaction, k_r = rate constant of reverse reaction. Thus, a catalyst that accelerates the formation of the carbamate from alcohol and isocyanate must also accelerate the dissociation of the carbamate into isocyanate and phenol through the same intermediate complex, by the principle of microscopic reversibility.

On the basis of the work reported by Smith,[36] Reegen and Frisch,[38] the structure for complex can be given as



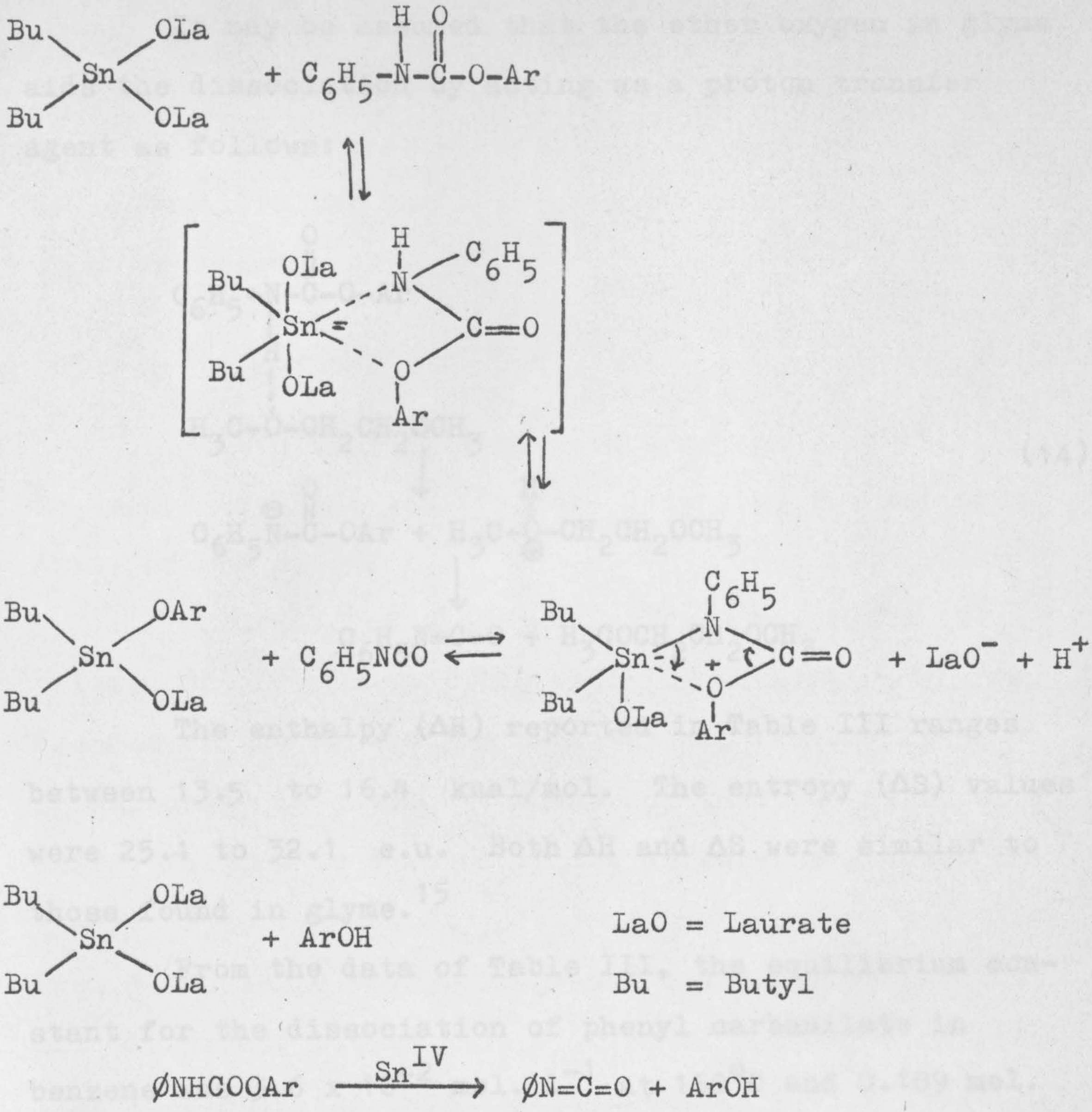
On the other hand,



comes from the work of Bloodworth and Davies,[37] where LaO = laurate, Bu = butyl.

As mentioned before, Bloodworth and Davies[37] isolated the adduct and identified it as N-stannoyl carbamate. Thus it is reasonable to assum an Sn-N bond rather than the Sn-O bond shown in the structure proposed by Smith,[36] Reegen,[38] etc.

Considering this fact, the most obvious mechanism for this catalyzed dissociation is given in Figure 1.



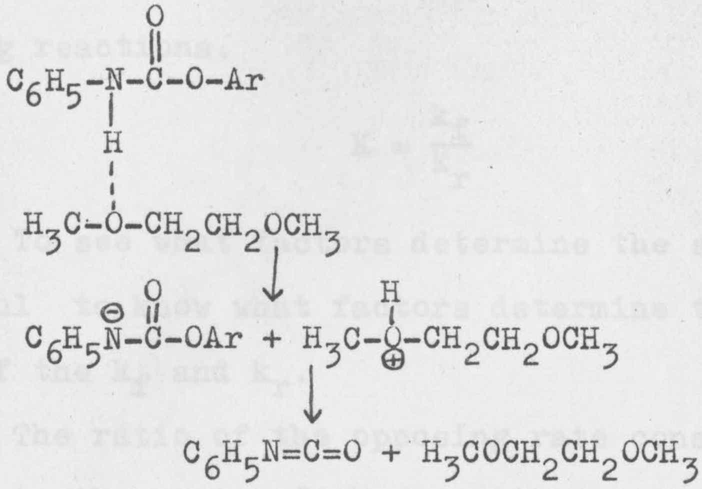
LaO = Laurate

Bu = Butyl

$$\text{ØNHCOOAr} \xrightarrow{\text{Sn}^{IV}} \text{ØN=C=O} + \text{ArOH}$$

Fig. 1. Possible scheme for the dissociation of aryl carbanilates, catalyzed by dibutyltin dilaurate.

It may be assumed that the ether oxygen in glyme aids the dissociation by acting as a proton transfer agent as follows:



$$C_6H_5\text{-}\underset{\underset{\vdots}{H}}{\overset{}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-O-Ar} \quad \cdots \quad H_3C\text{-}\ddot{O}\text{-}CH_2CH_2OCH_3 \longrightarrow C_6H_5\overset{\ominus}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-OAr} + H_3C\text{-}\overset{H}{\underset{\oplus}{O}}\text{-}CH_2CH_2OCH_3 \longrightarrow C_6H_5N{=}C{=}O + H_3COCH_2CH_2OCH_3 \qquad (14)$$

The enthalpy (ΔH) reported in Table III ranges between 13.5 to 16.4 kcal/mol. The entropy (ΔS) values were 25.1 to 32.1 e.u. Both ΔH and ΔS were similar to those found in glyme.[15]

From the data of Table III, the equilibrium constant for the dissociation of phenyl carbanilate in benzene was 3.6×10^{-2} mol. l^{-1} at 150°C and 0.189 mol. l^{-1} at 90°C while that of p-methoxyphenyl carbanilate was 0.978×10^{-2} and 0.051 mol. l^{-1}, respectively. Thus the equilibrium constant for unsubstituted carbanilate is about 3.6 times larger than for p-methoxyphenyl carbanilate. The equilibrium constant at 150° for the dissociation of phenyl carbanilate, from the data obtained in this work, is 3.6×10^{-2} mol. l^{-1}, as compared to 9.39×10^{-2} mol. l^{-1}, the value reported earlier for this compound in glyme.[15] The equilibrium constant for a given system increases as the temperature increases.

In a reversible reaction, the equilibrium constant, K, is equal to the ratio of the rate constants of the opposing reactions.

$$K = \frac{k_f}{k_r} \qquad (15)$$

To see what factors determine the size of K, it is useful to know what factors determine the relative sizes of the k_f and k_r.

The ratio of the opposing rate constants is related to the ratio of the opposing activation energy. Because of the particular mathematical (logarithmic) relationship involved, it turns out that the ratio of energy factors is related to the difference between the energy of activation (E_{act}'s.) of the opposing reactions. From a schematic energy diagram (Figure 2), we see that the difference between the E_{act}'s. of the opposing reaction is simply the enthalpy change (ΔH) of the reaction.

There is no evidence in the literature regarding the effect of solvents on the rate for the forward reaction, <u>i.e.</u> dissociation, but there is such evidence regarding the rate for the reverse reaction, <u>i.e.</u> association. The reaction of phenyl isocyanate with alcohol is slower in ether solvents than in hydrocarbon solvents, and the reaction is still slower in diglyme.[35] The energy barrier for the reverse reaction in the case of

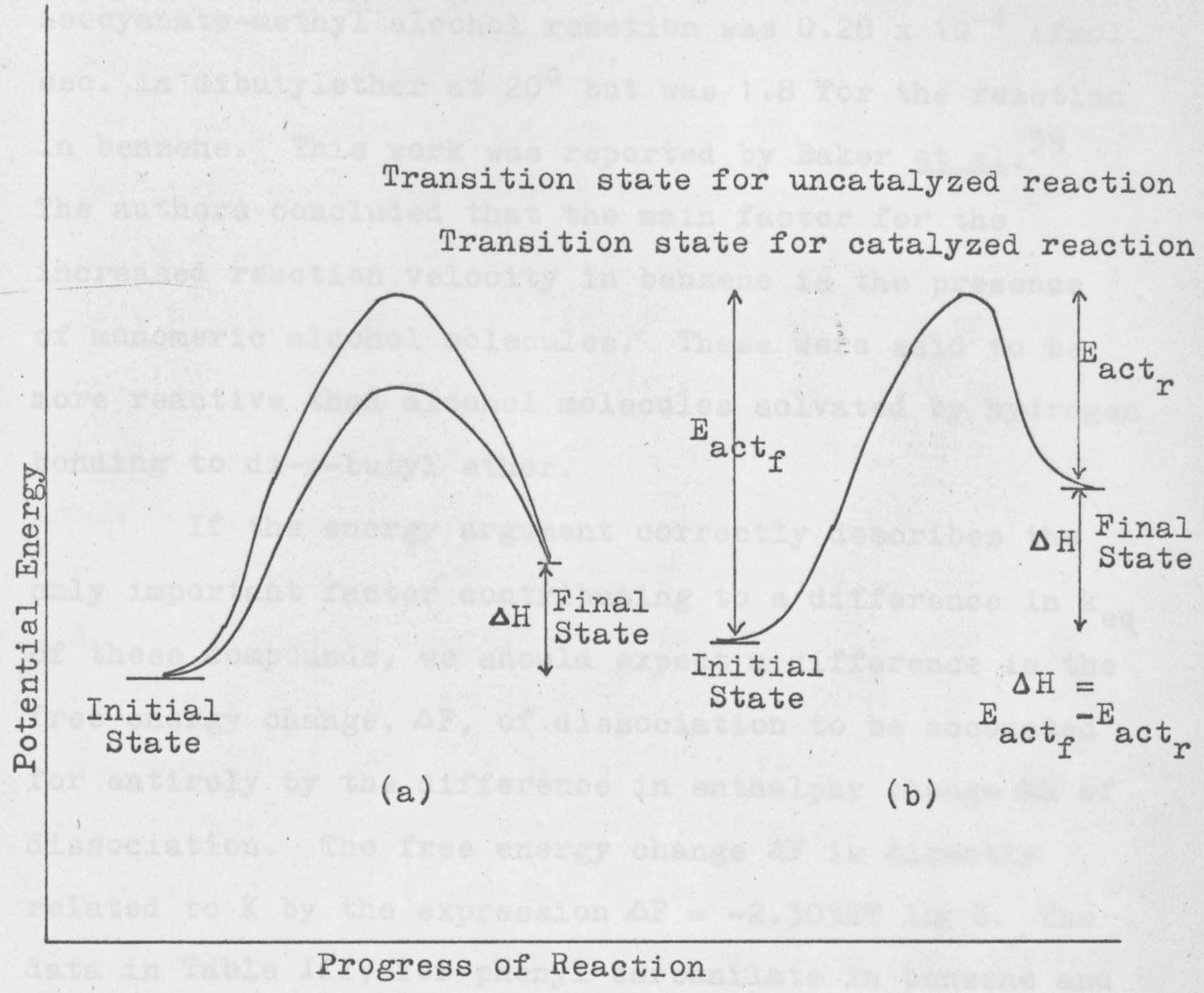


Fig. 2. Plot for a reversible reaction. (a) Glyme as solvent. (b) Benzene as solvent.

benzene is lower than that of glyme. This is shown schematically in Figure 2.

The rate constant for the uncatalyzed phenyl isocyanate-methyl alcohol reaction was 0.28×10^{-4} l/mol. sec. in dibutylether at 20^{o} but was 1.8 for the reaction in benzene. This work was reported by Baker et al.[39] The authors concluded that the main factor for the increased reaction velocity in benzene is the presence of monomeric alcohol molecules. These were said to be more reactive than alcohol molecules solvated by hydrogen bonding to di-n-butyl ether.

If the energy argument correctly describes the only important factor contributing to a difference in k_{eq} of these compounds, we should expect a difference in the free energy change, ΔF, of dissociation to be accounted for entirely by the difference in enthalphy change ΔH of dissociation. The free energy change ΔF is directly related to K by the expression $\Delta F = -2.303RT \log K$. The data in Table III, for phenyl carbanilate in benzene and in glyme, as an example, contradicts this, since together 1 kcal difference in ΔH and 1 e.u. difference in ΔS makes up a 0.77 difference in ΔF of dissociation. The entropy change ΔS, is the quantity that, with ΔH, determines the value of K, comparing the stability of the carbanilate with the stability of the phenyl isocyanate and the phenol. The product is more polar than the reactant, while benzene is neither a good nucleophile nor polar, so the reverse reaction goes well in benzene. Glyme is a polar solvent, and it may stabilize the product phenyl isocyanate and the phenol and solvate these molecules more readily and push the equilibrium more toward dissociation than association, and hence K is larger.

In summary, the dissociation of the aryl carbanilate in the non-polar solvent benzene and in the polar solvent glyme, shows only small change in ΔH and very little change in the dissociation constant. A greater variation in the dissociation constant may have been prevented by compensating change in the entropy with change in enthalpy.

The equilibrium constants obtained in this work did not follow the Hammett relationship. In earlier work,[15] the equilibrium constants obtained in glyme solvent did give a reasonable fit to the Hammett relationship. This may have resulted from lack of compensation between entropies and heat of solvation in benzene (see discussion, Ref. 15) or possibly from the sources of error discussed earlier.

The above study of the equilibrium involved in the dissociation of aryl carbanilates is of interest because it is one step in the ester interchange reaction which these compounds undergo. It would be interesting also to study the rate of the dissociation, as well as the overall rate of the ester interchange reaction.

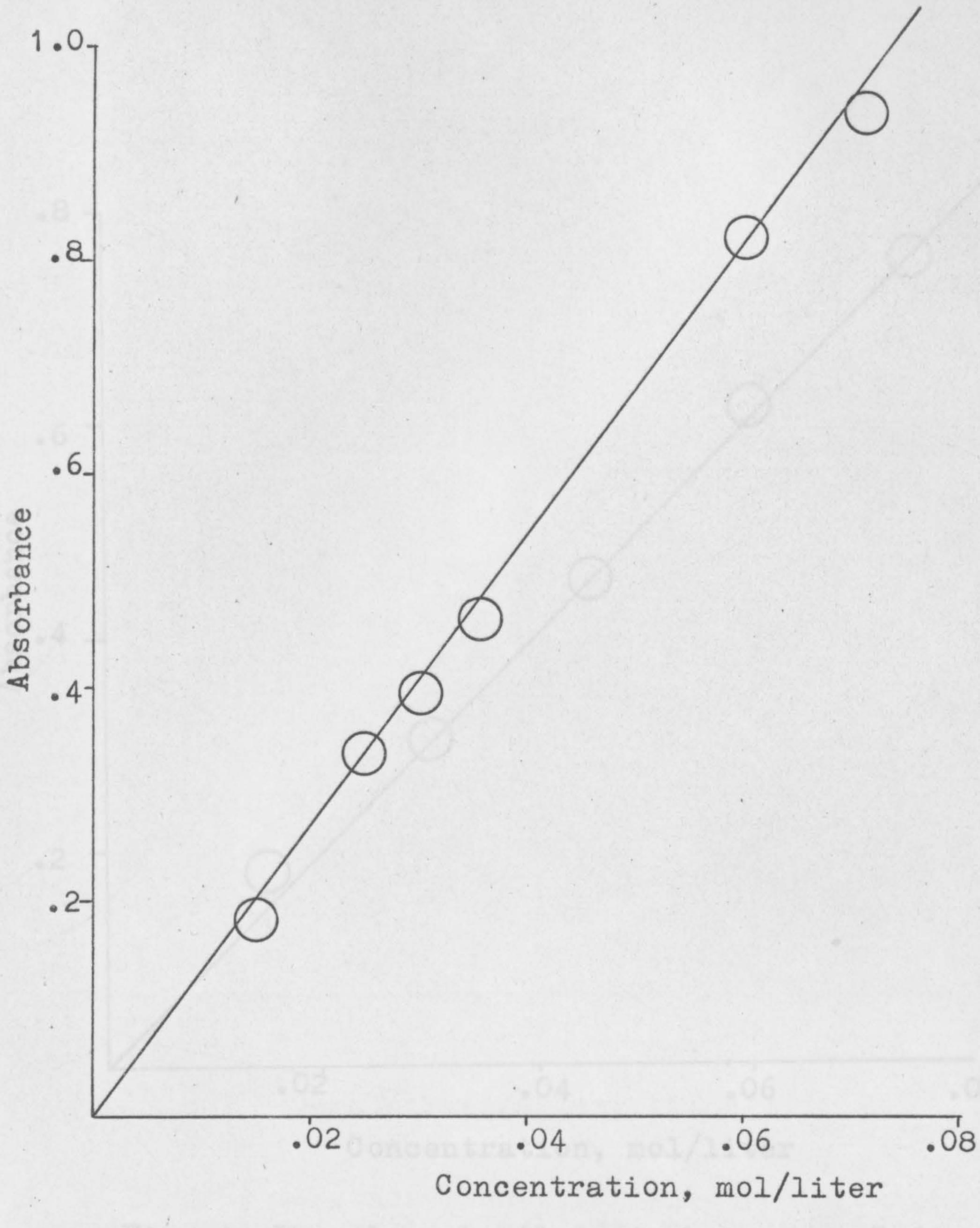


Fig. 3. Phenyl isocyanate in benzene. Infrared absorbance at 2261 cm^{-1} *vs.* concentration.

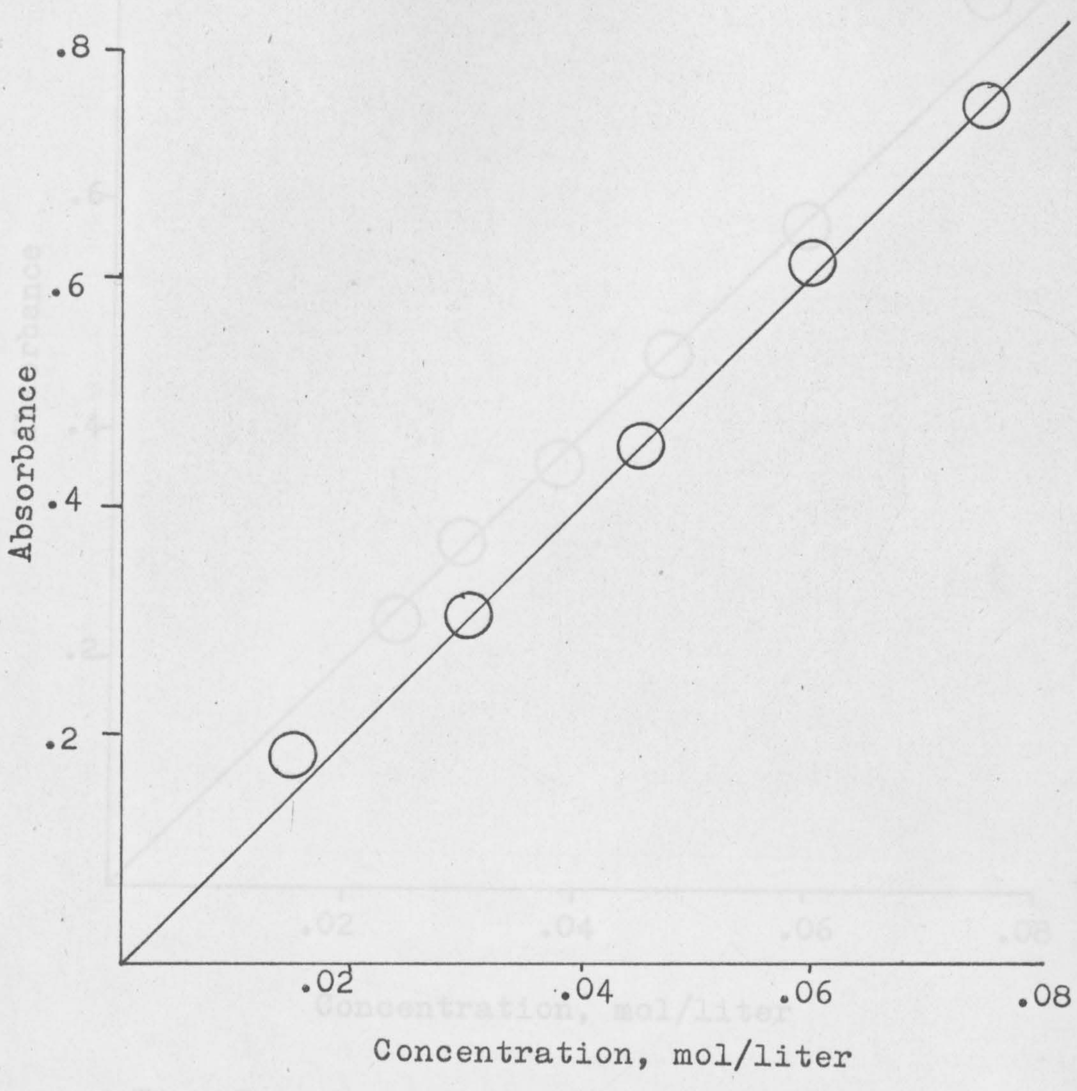


Fig. 4. Phenyl carbanilate in benzene. Infrared absorbance at 1761 cm^{-1} *vs.* concentration.

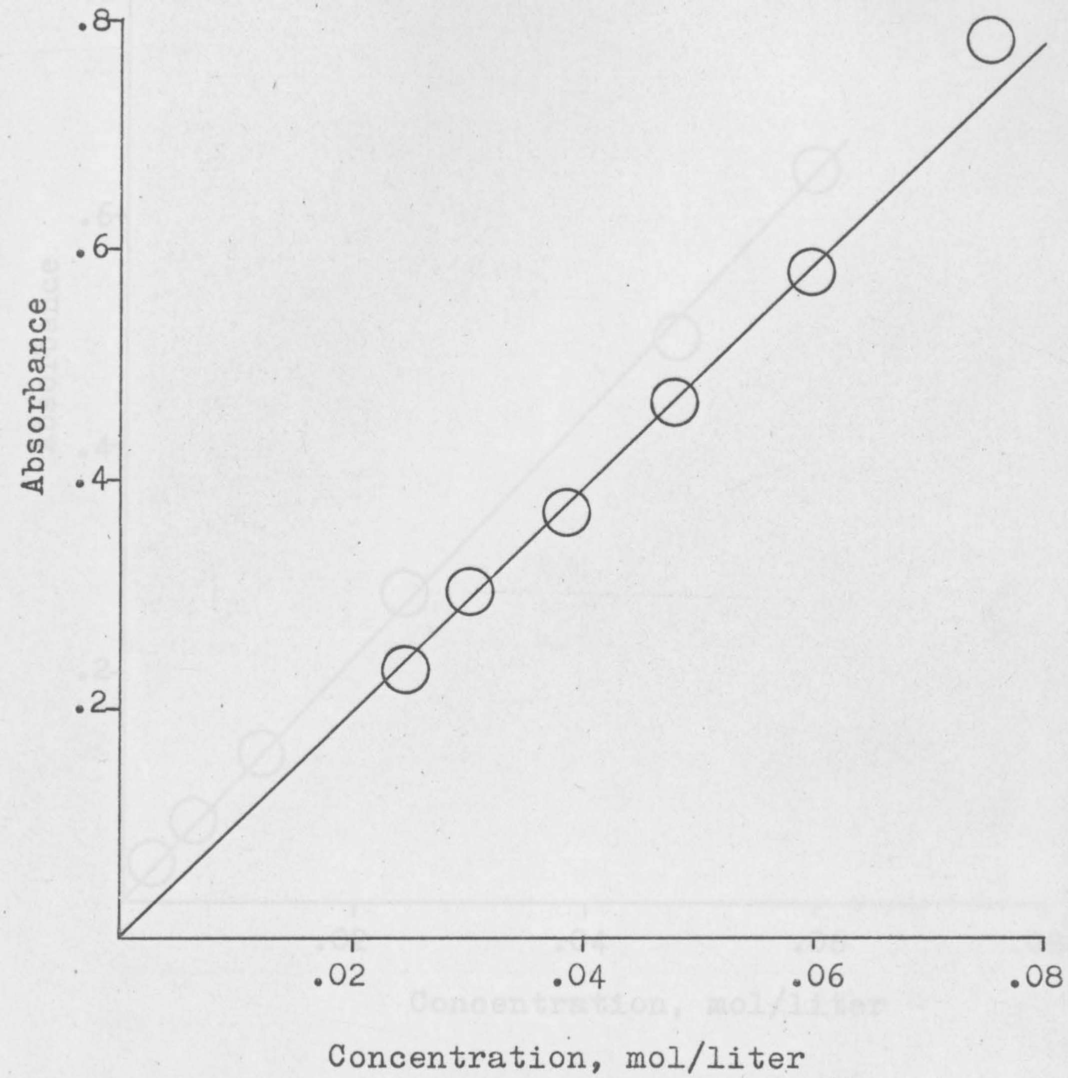


Fig. 5. m-Methoxyphenyl carbanilate in benzene. Infrared absorbance at 1761 cm^{-1} vs. concentration.

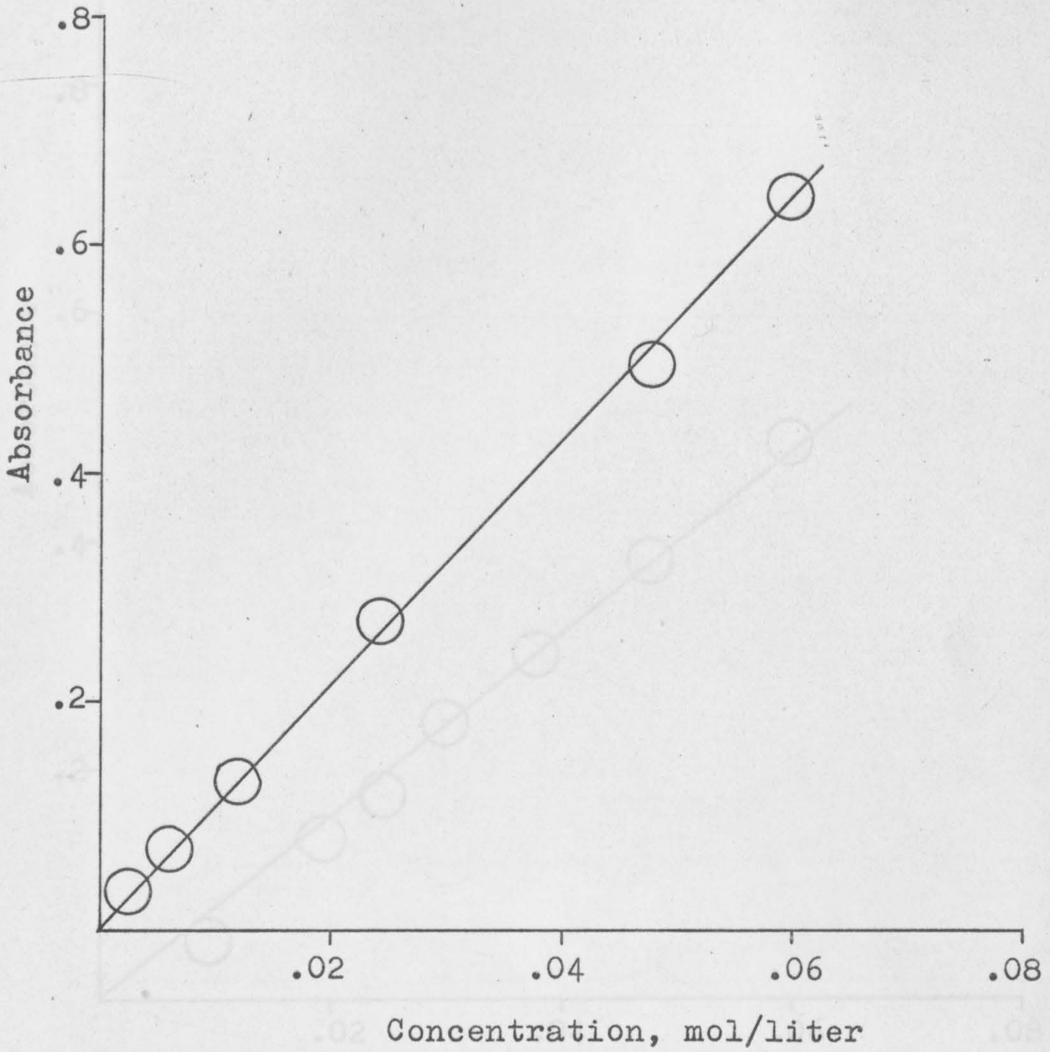


Fig. 6. p̲-Methoxyphenyl carbanilate in benzene. Infrared absorbance at 1759 cm^{-1} *vs*. concentration.

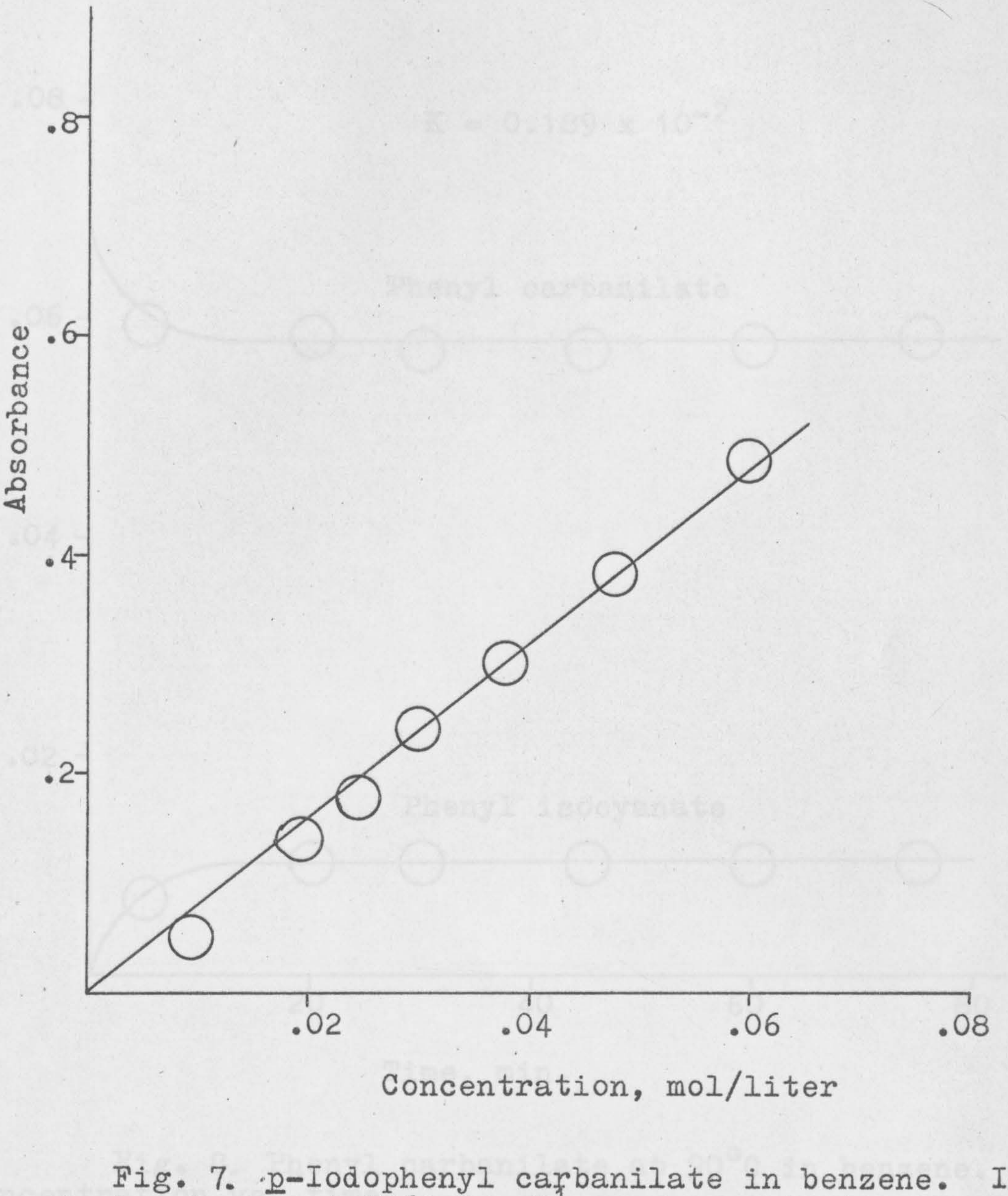


Fig. 7. p-Iodophenyl carbanilate in benzene. Infrared absorbance at 1764.5 cm^{-1} vs. concentration.

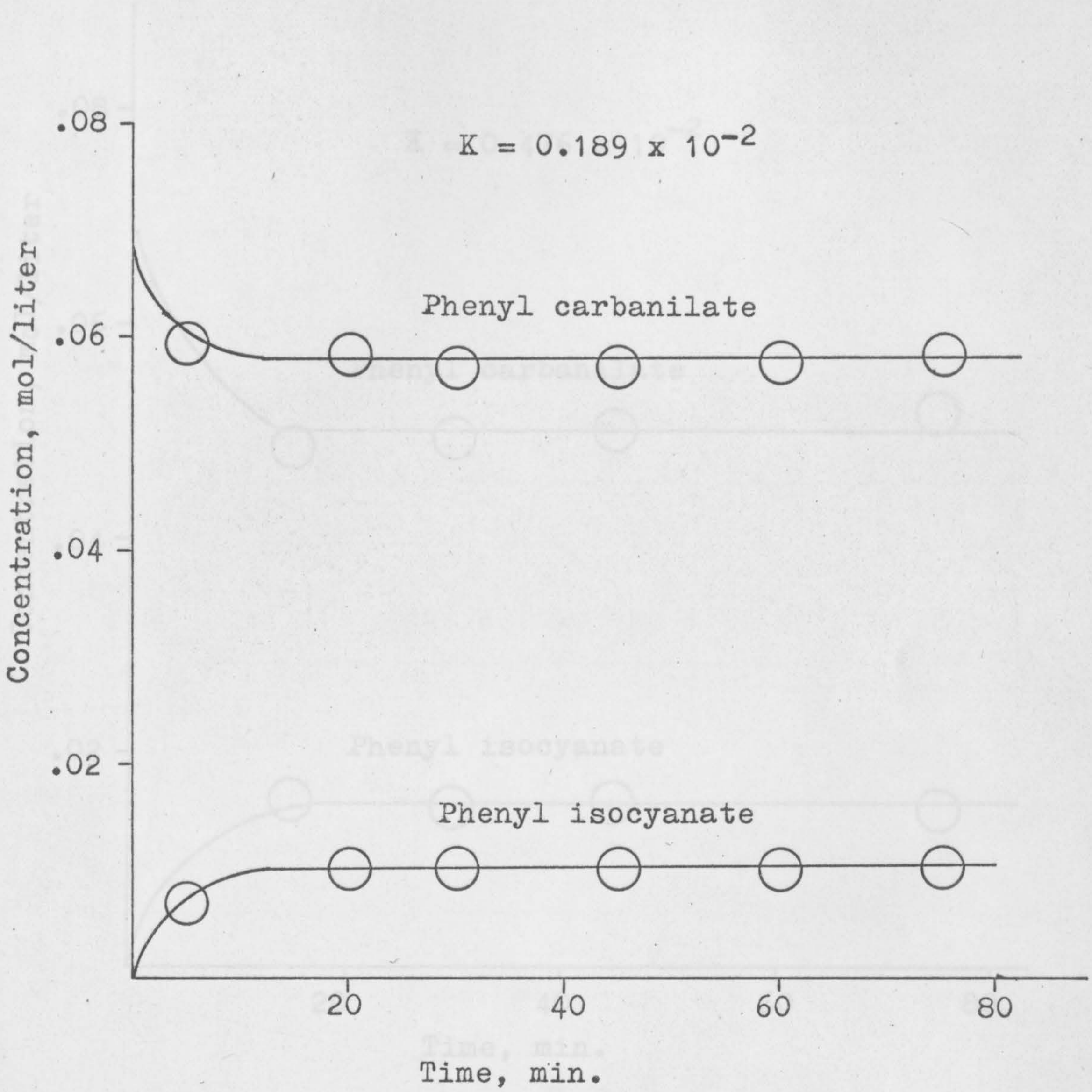


Fig. 8. Phenyl carbanilate at 90°C in benzene. Concentration <u>vs</u>. time.

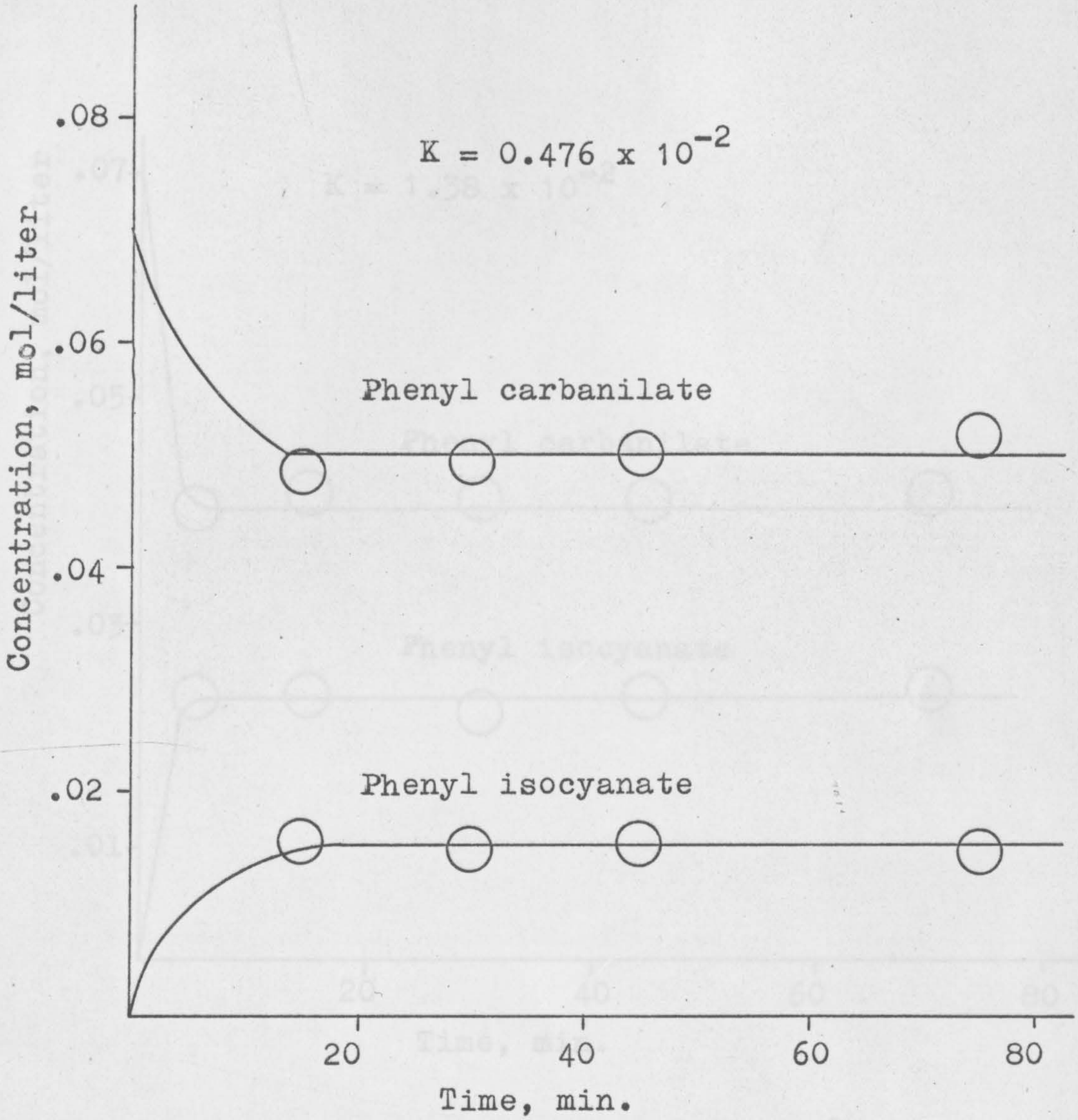


Fig. 9. Phenyl carbanilate at 110°C in benzene. Concentration vs. time.

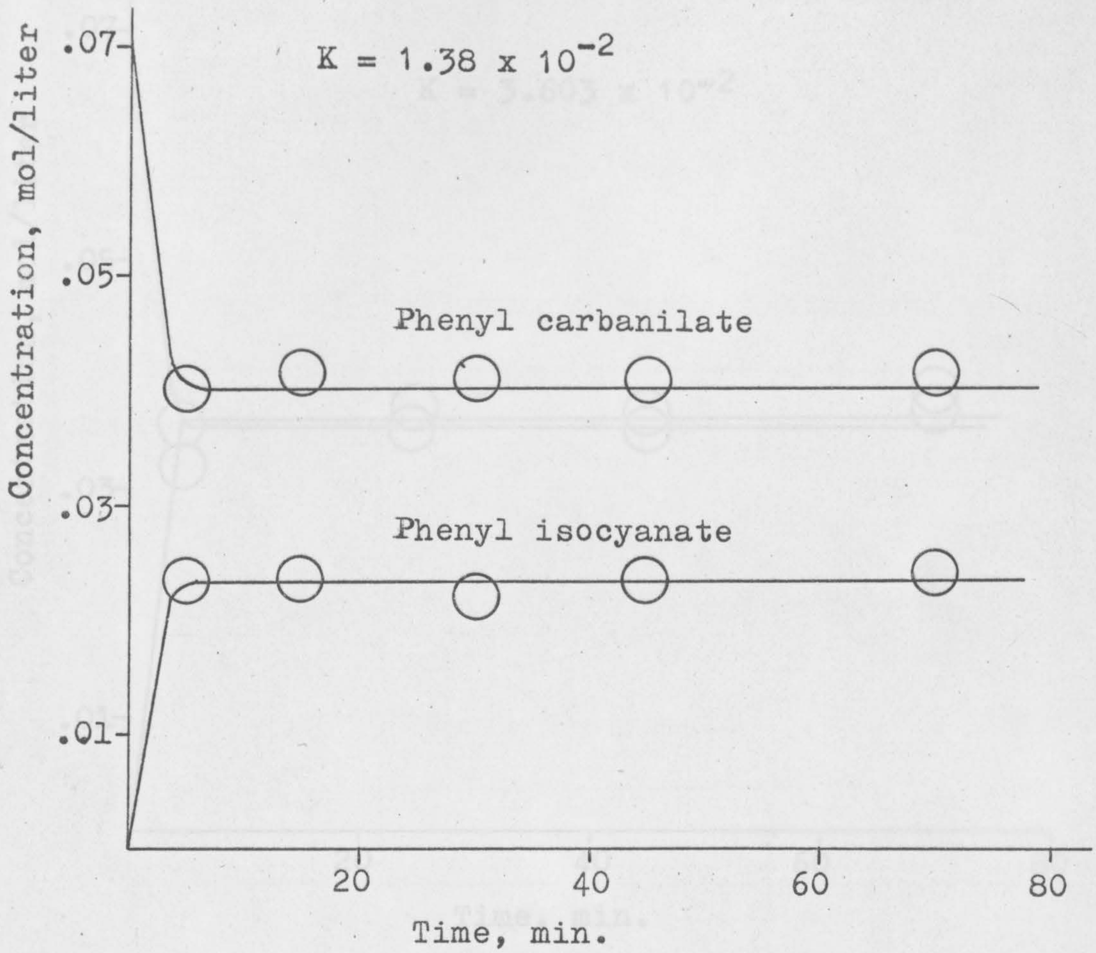


Fig. 10. Phenyl carbanilate at 130°C in benzene. Concentration vs. time.

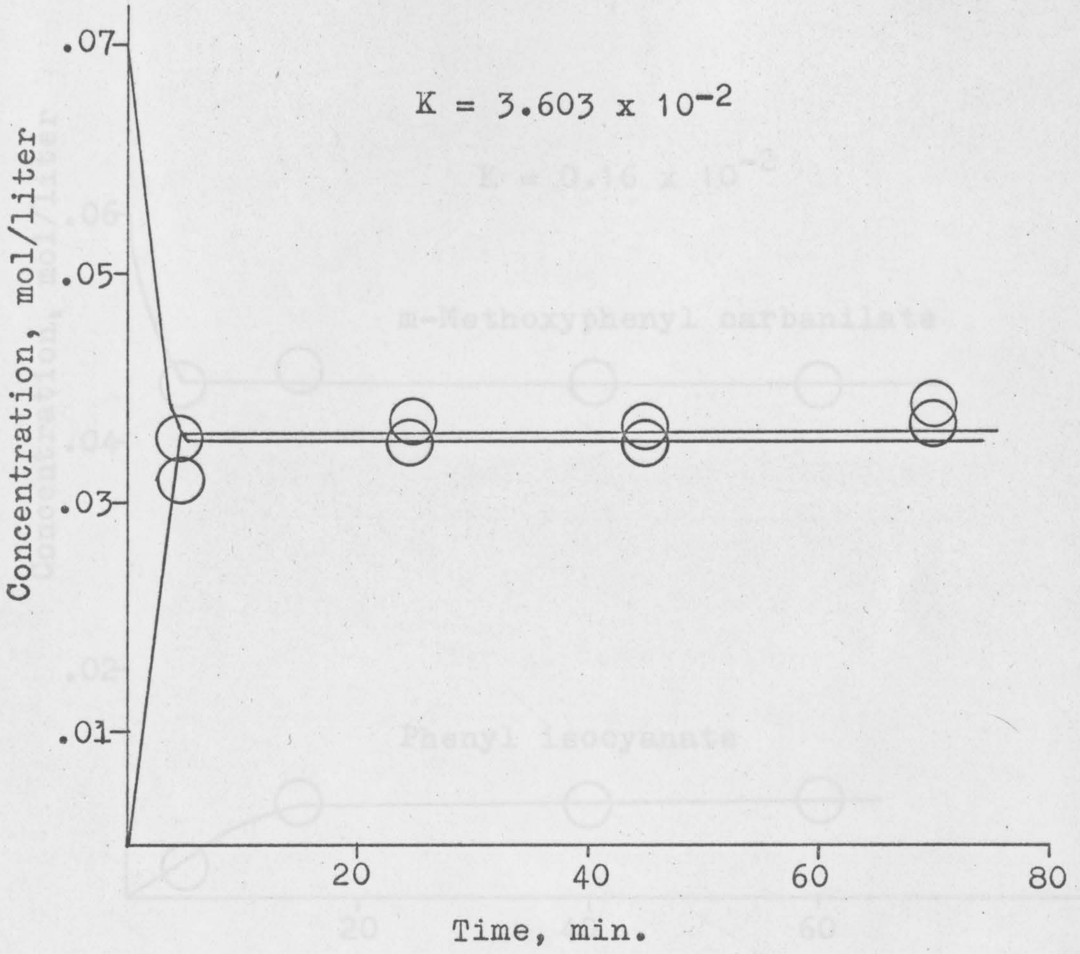


Fig. 11. Phenyl carbanilate at 150°C in benzene. Concentration vs. time.

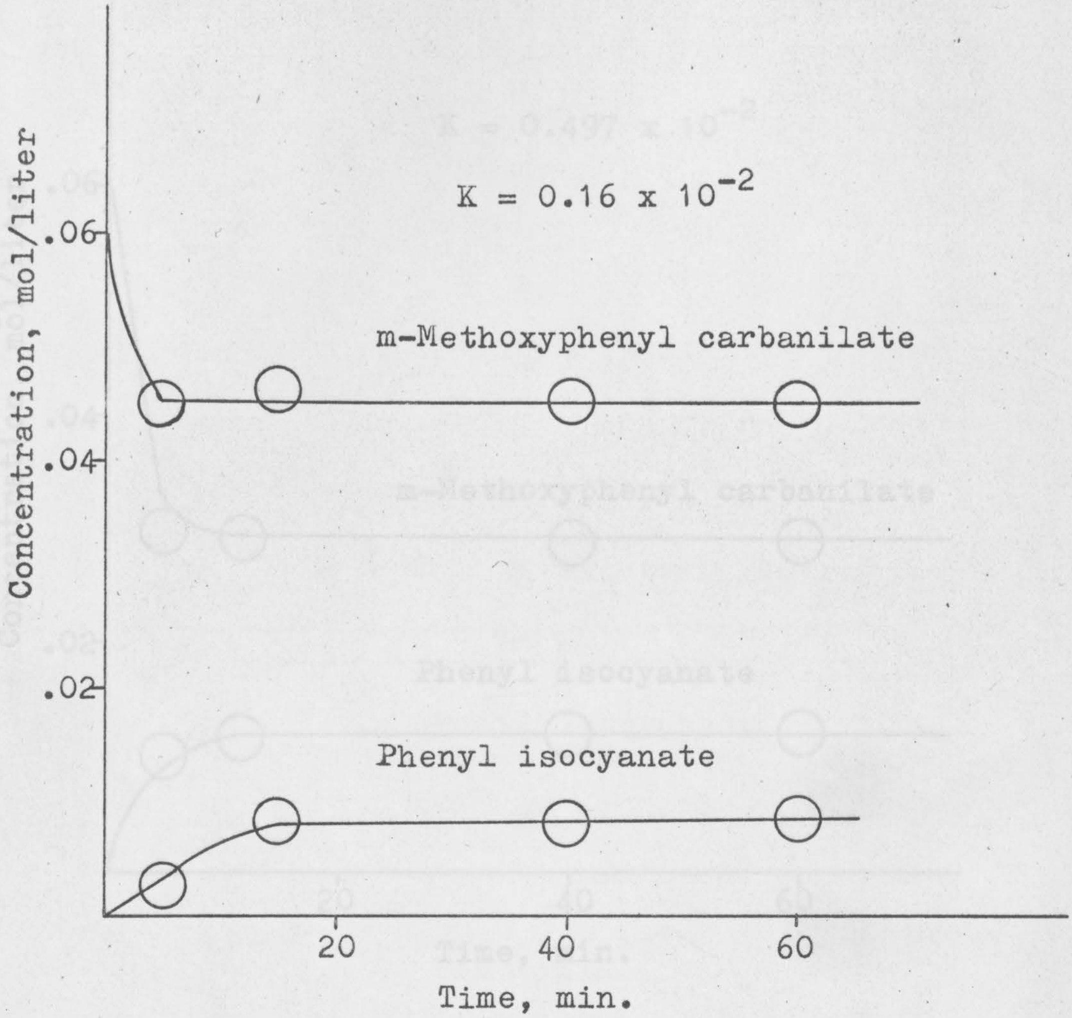


Fig. 12. m-Methoxyphenyl carbanilate at 90°C in benzene. Concentration *vs*. time.

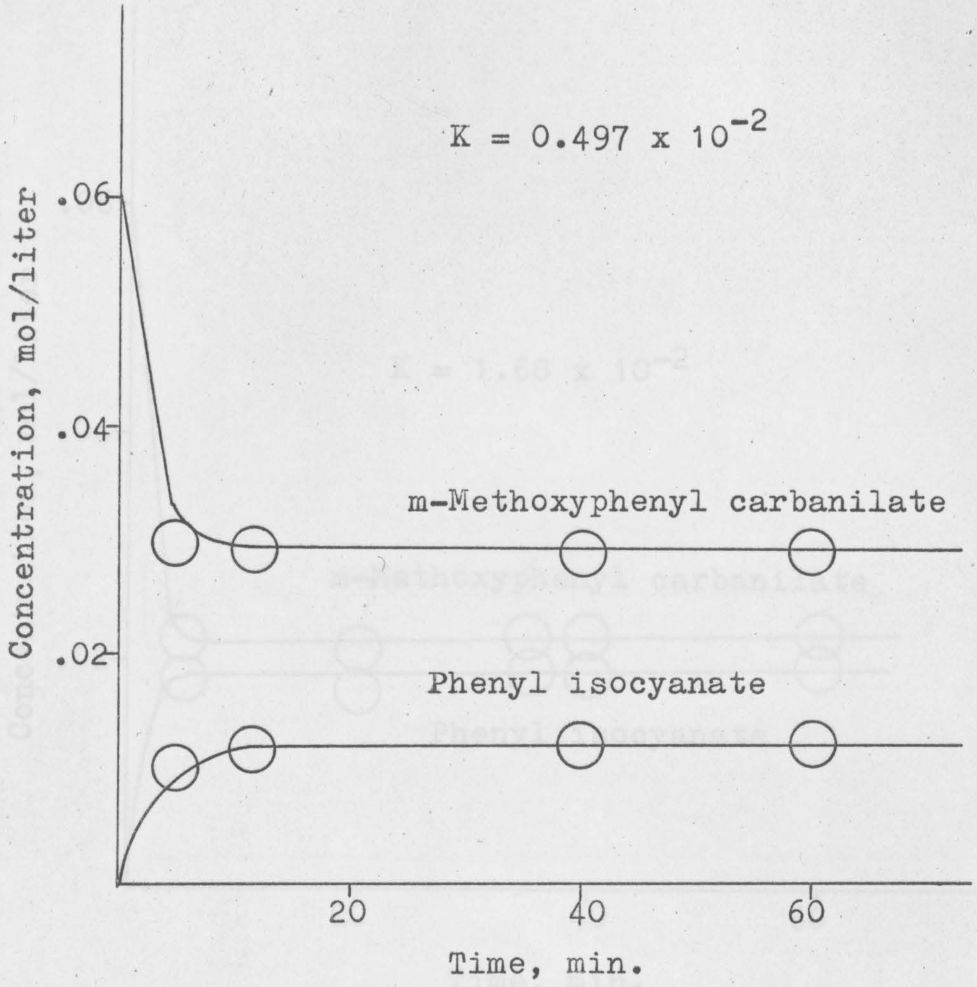


Fig. 13. m-Methoxyphenyl carbanilate at 110°C in benzene. Concentration *vs*. time.

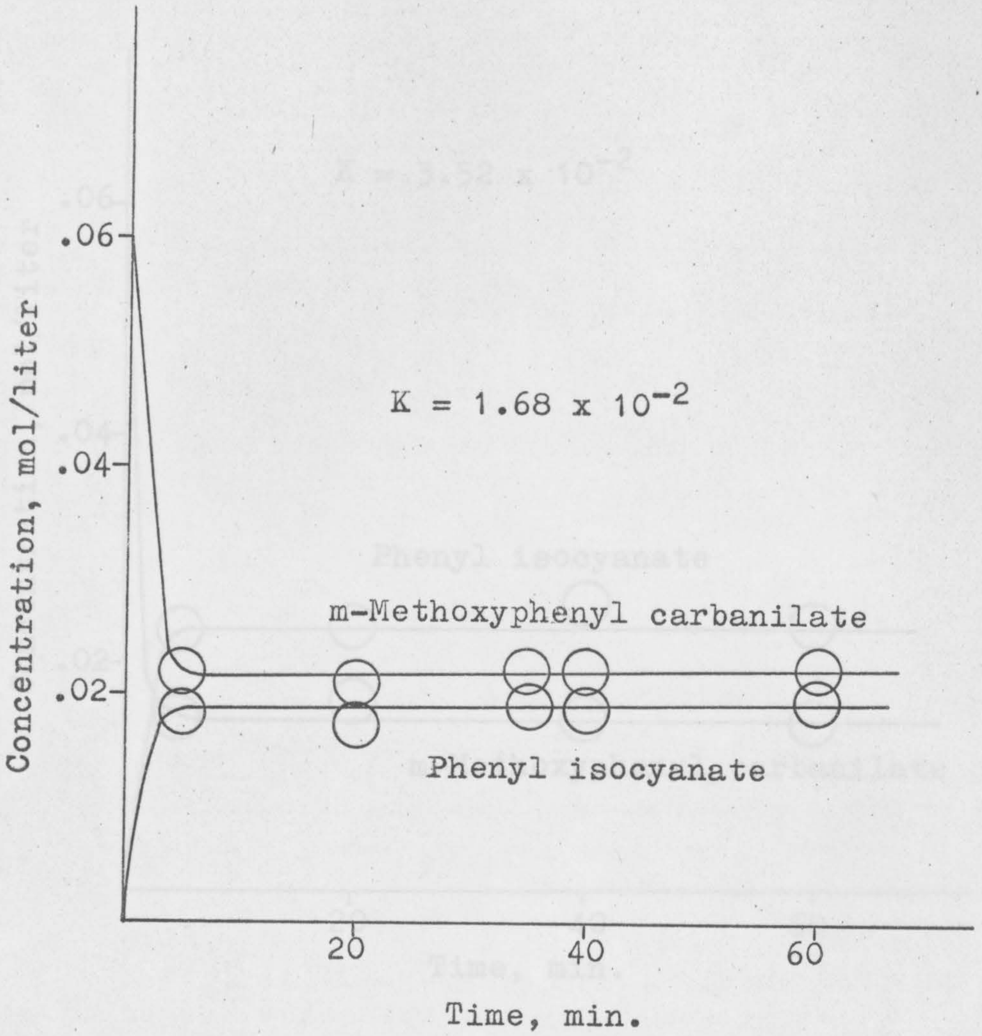


Fig. 14. m-Methoxyphenyl carbanilate at 130°C in benzene. Concentration <u>vs</u>. time.

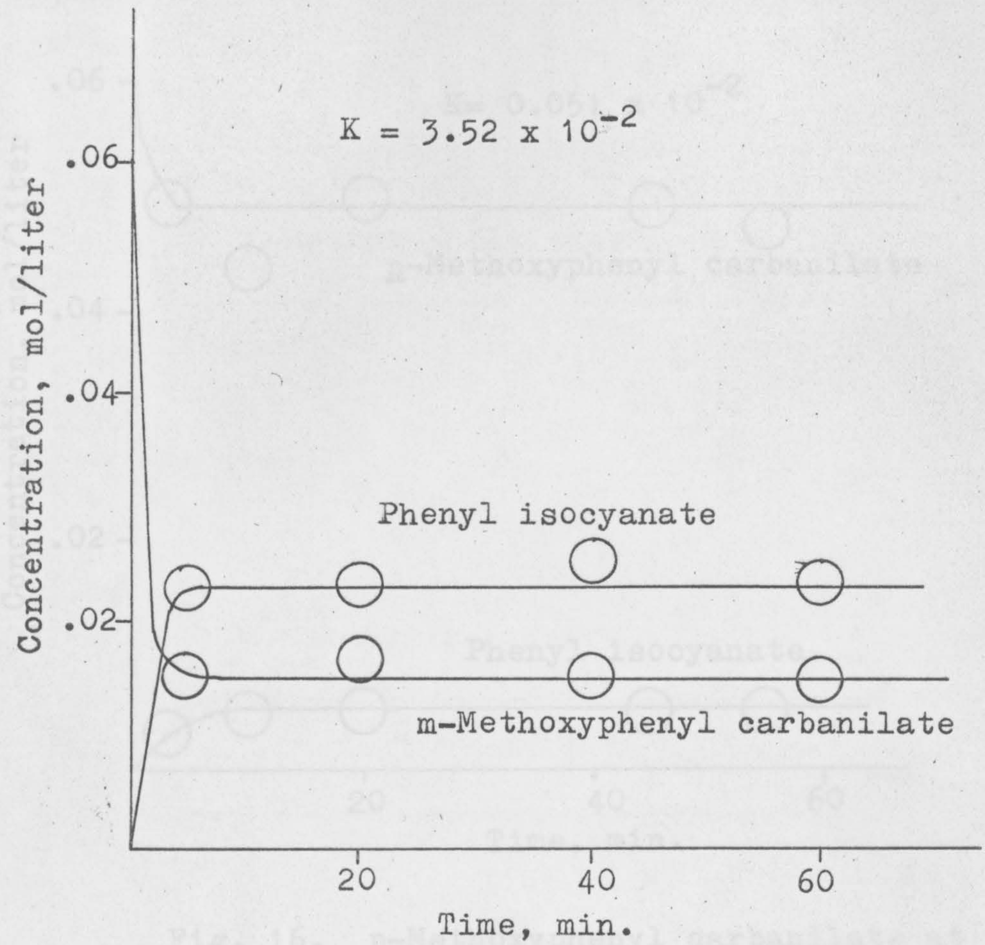


Fig. 15. m-Methoxyphenyl carbanilate at 150°C in benzene. Concentration *vs*. time.

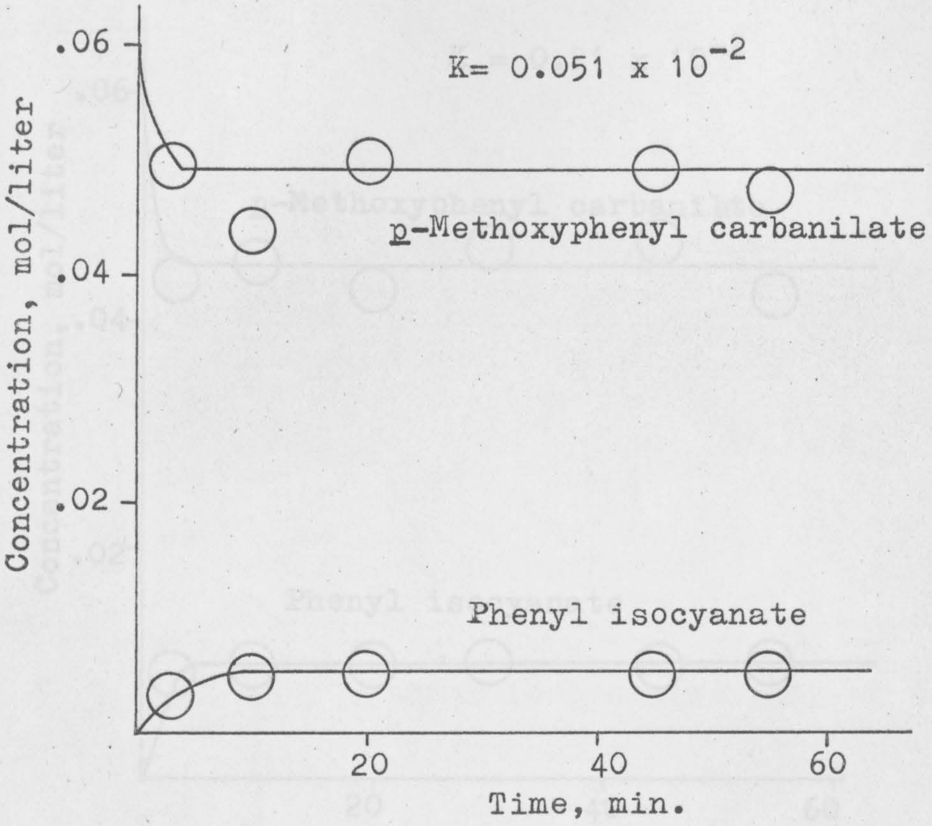


Fig. 16. p-Methoxyphenyl carbanilate at 90°C in benzene. Concentration vs. time.

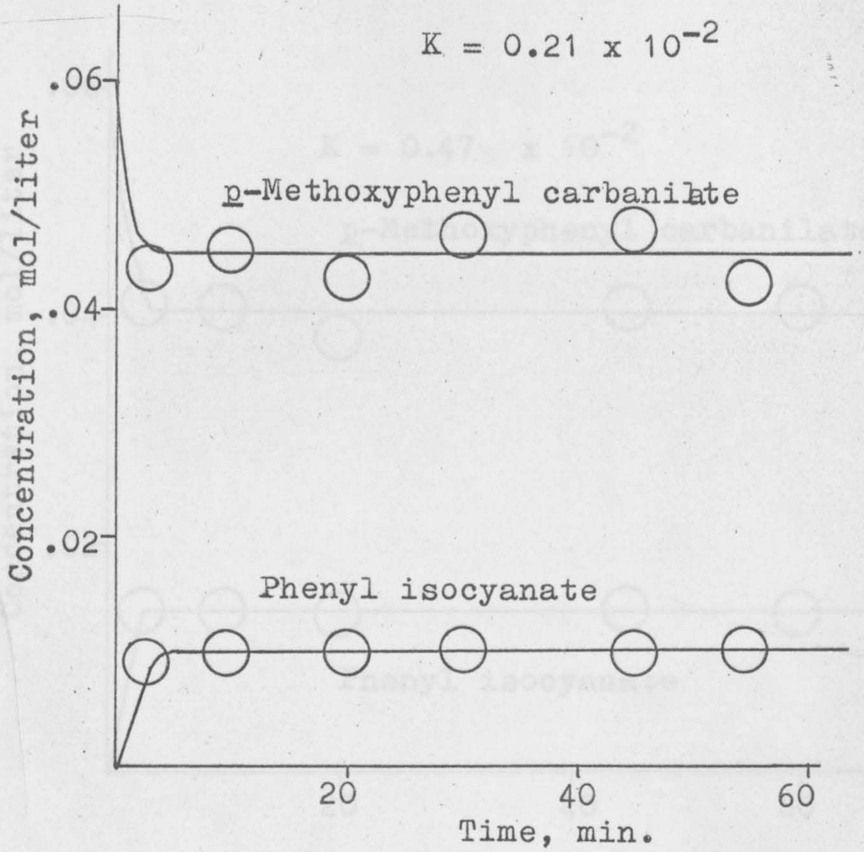


Fig. 17. p-Methoxyphenyl carbanilate at 110°C in benzene. Concentration *vs*. time.

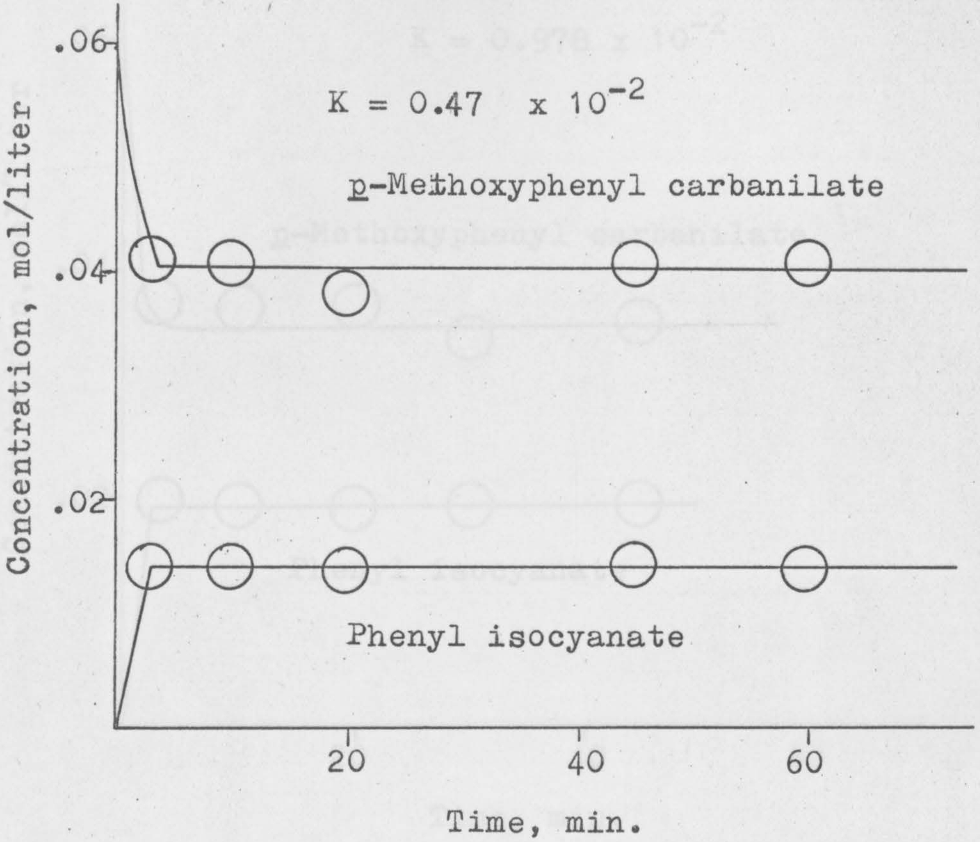


Fig. 18. p-Methoxyphenyl carbanilate at 130°C in benzene. Concentration *vs*. time.

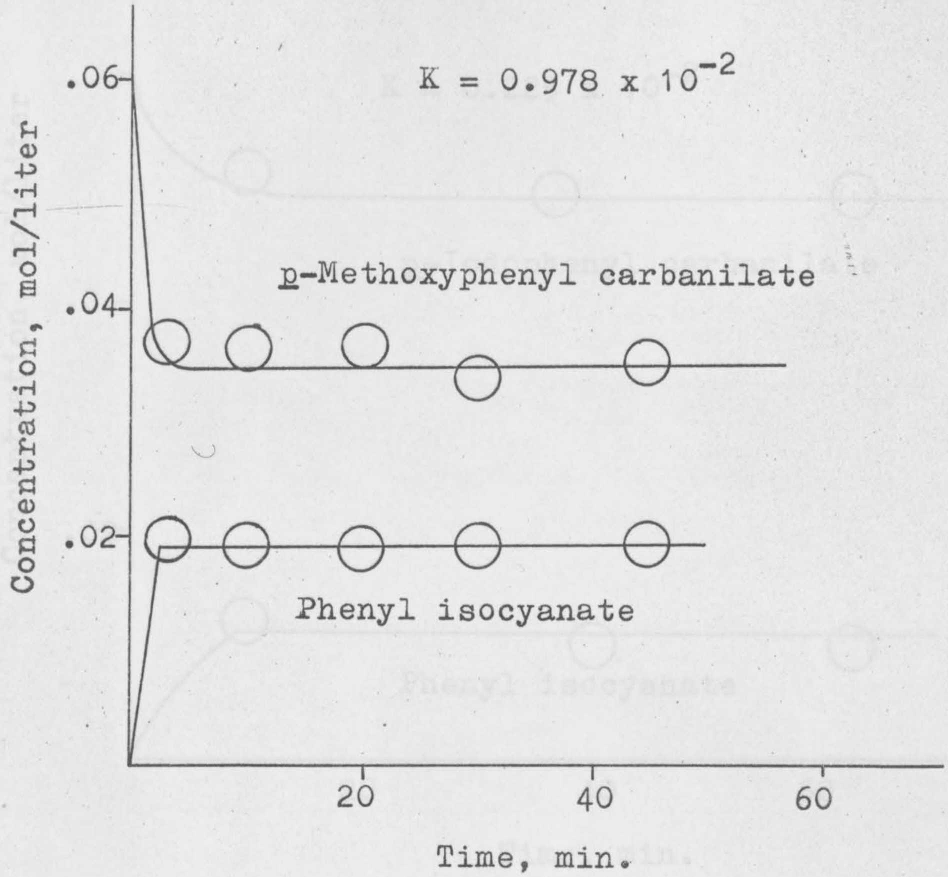


Fig. 19. p-Methoxyphenyl carbanilate at 150°C in benzene. Concentration vs. time.

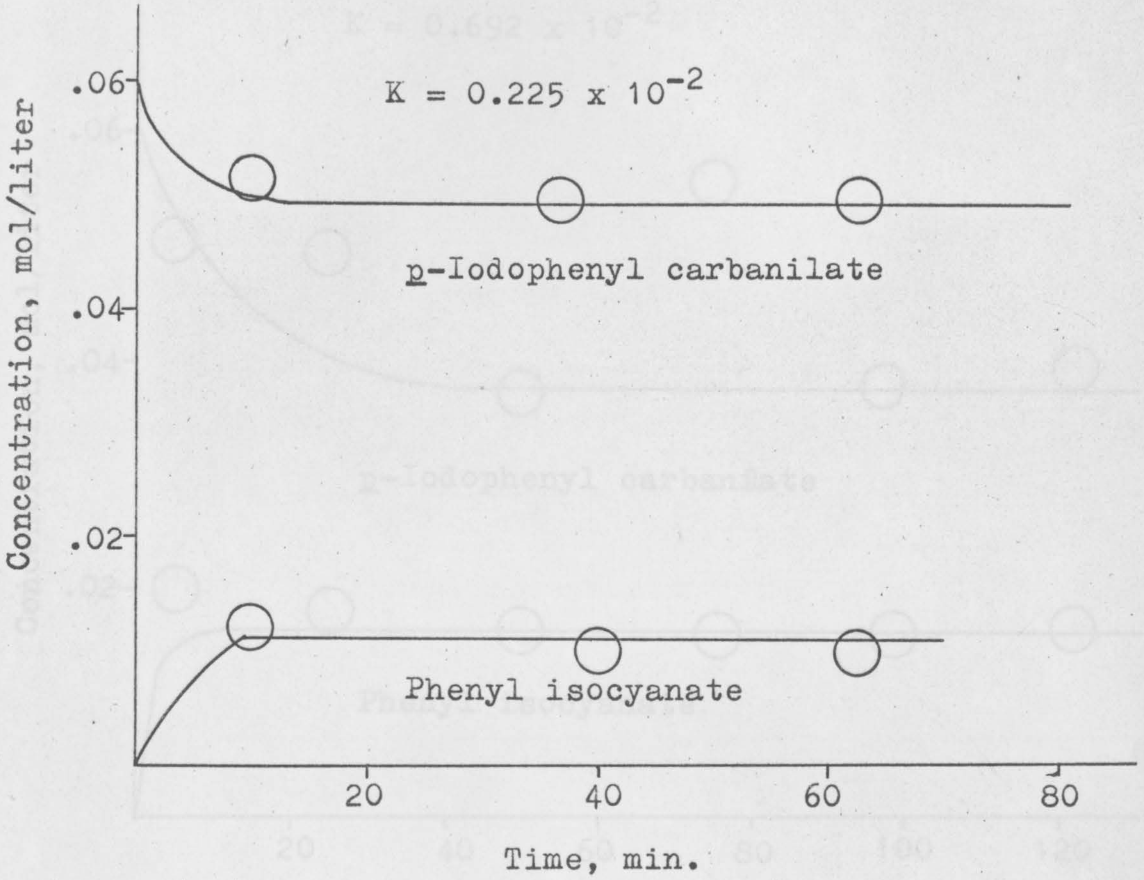


Fig. 20. p-Iodophenyl carbanilate at 90°C in benzene. Concentration vs. time.

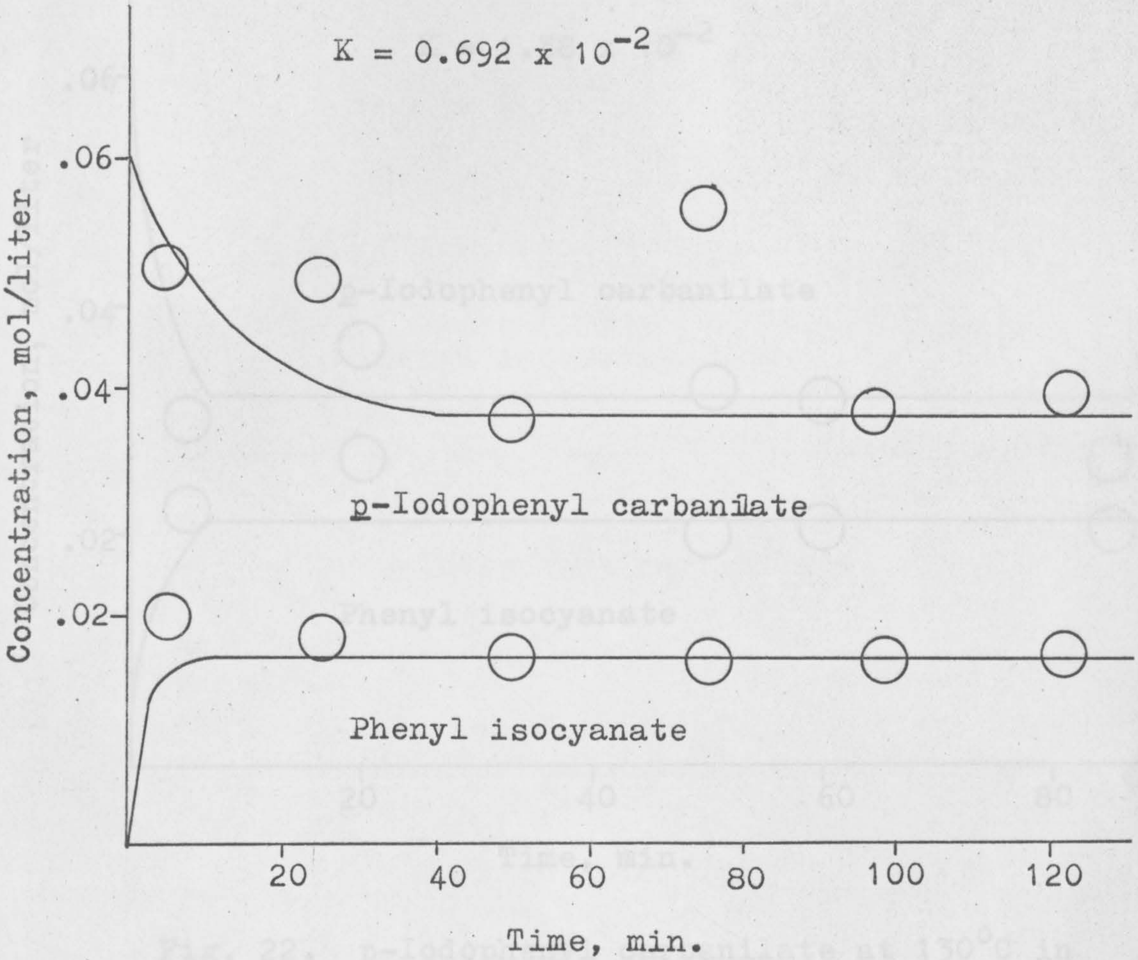


Fig. 21. p-Iodophenyl carbanilate at 110°C in benzene. Concentration vs. time.

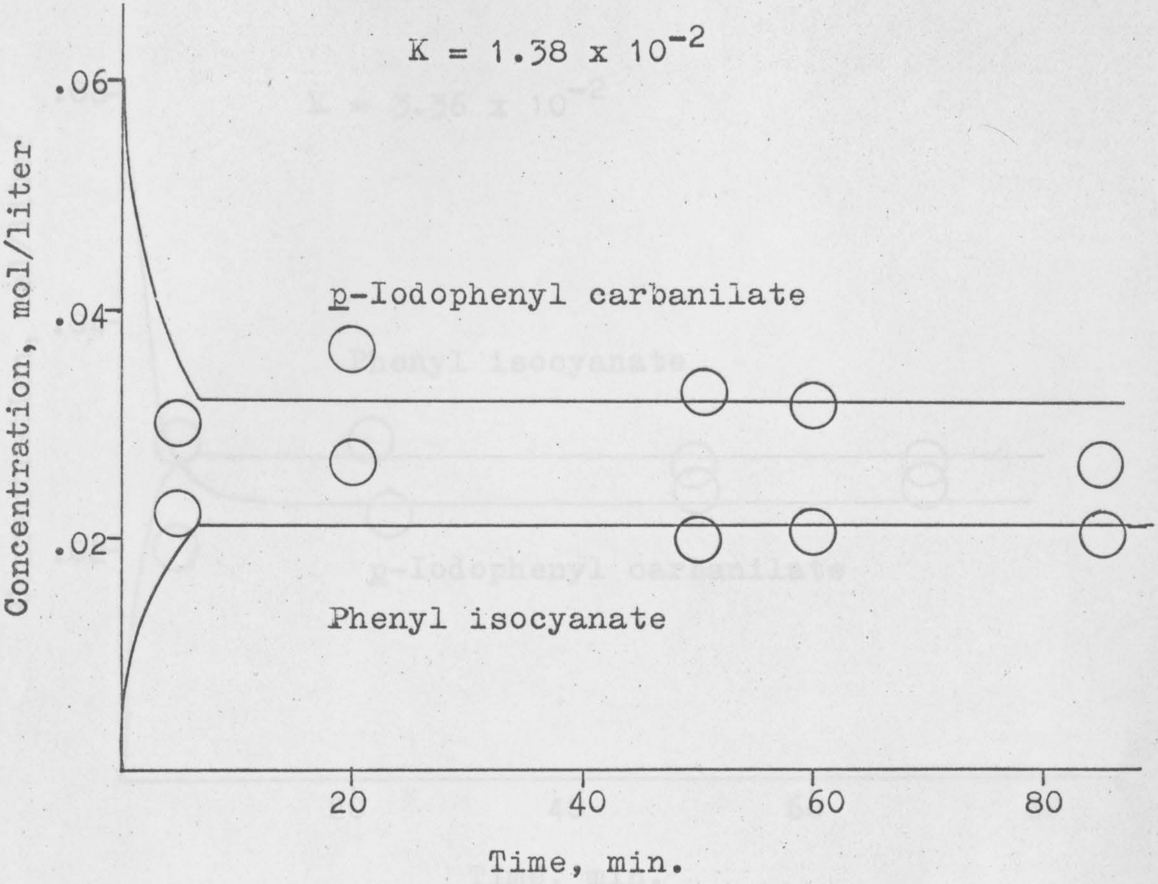


Fig. 22. p-Iodophenyl carbanilate at 130°C in benzene. Concentration *vs*. time.

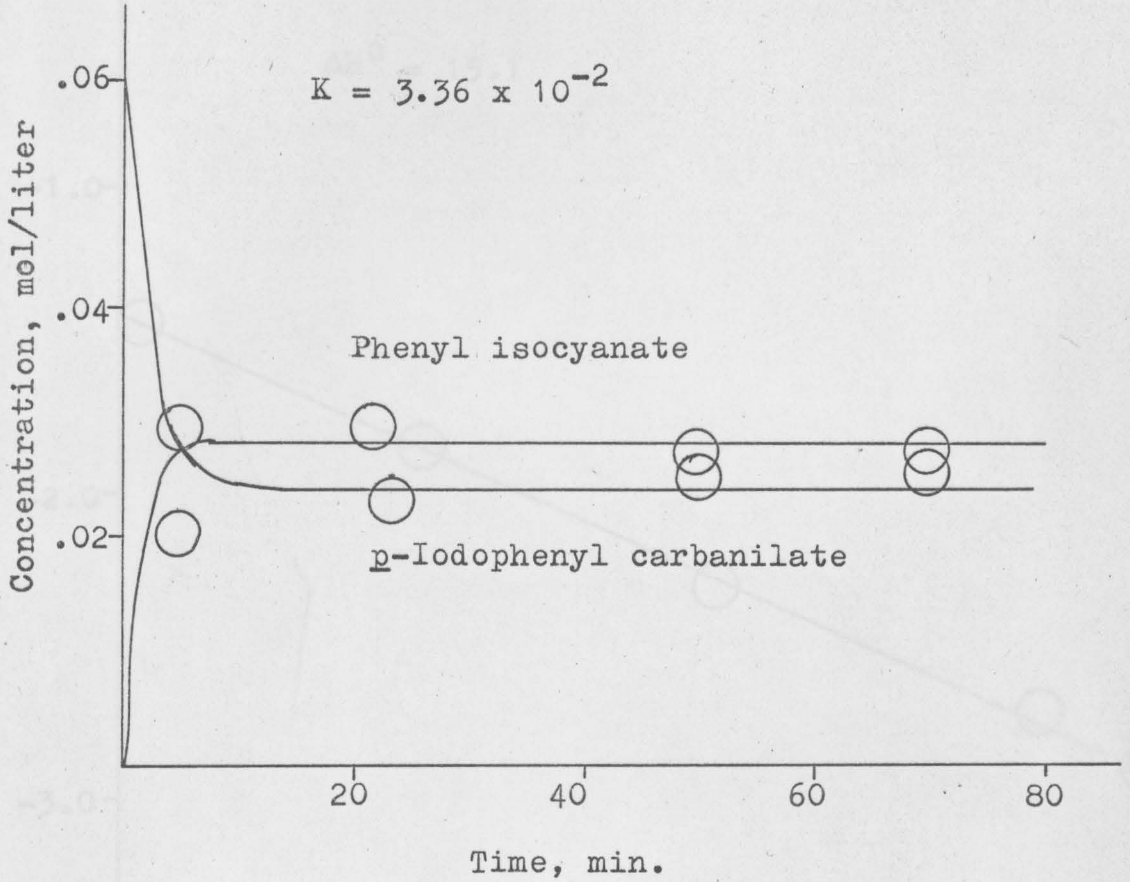


Fig. 23. p-Iodophenyl carbanilate at 150°C in benzene. Concentration *vs*. time.

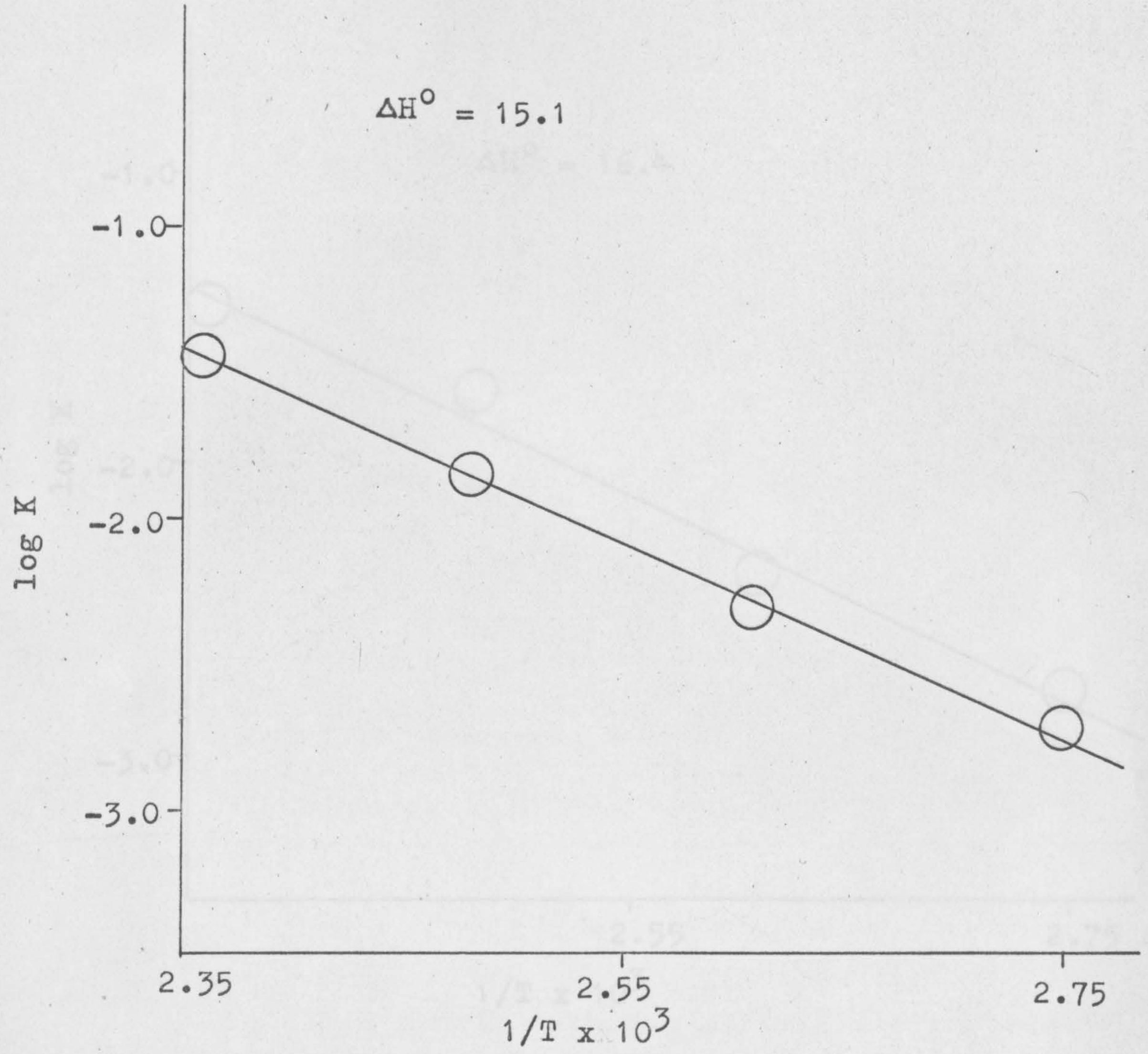


Fig. 24. Phenyl carbanilate in benzene. Log K <u>vs</u>. 1/T.

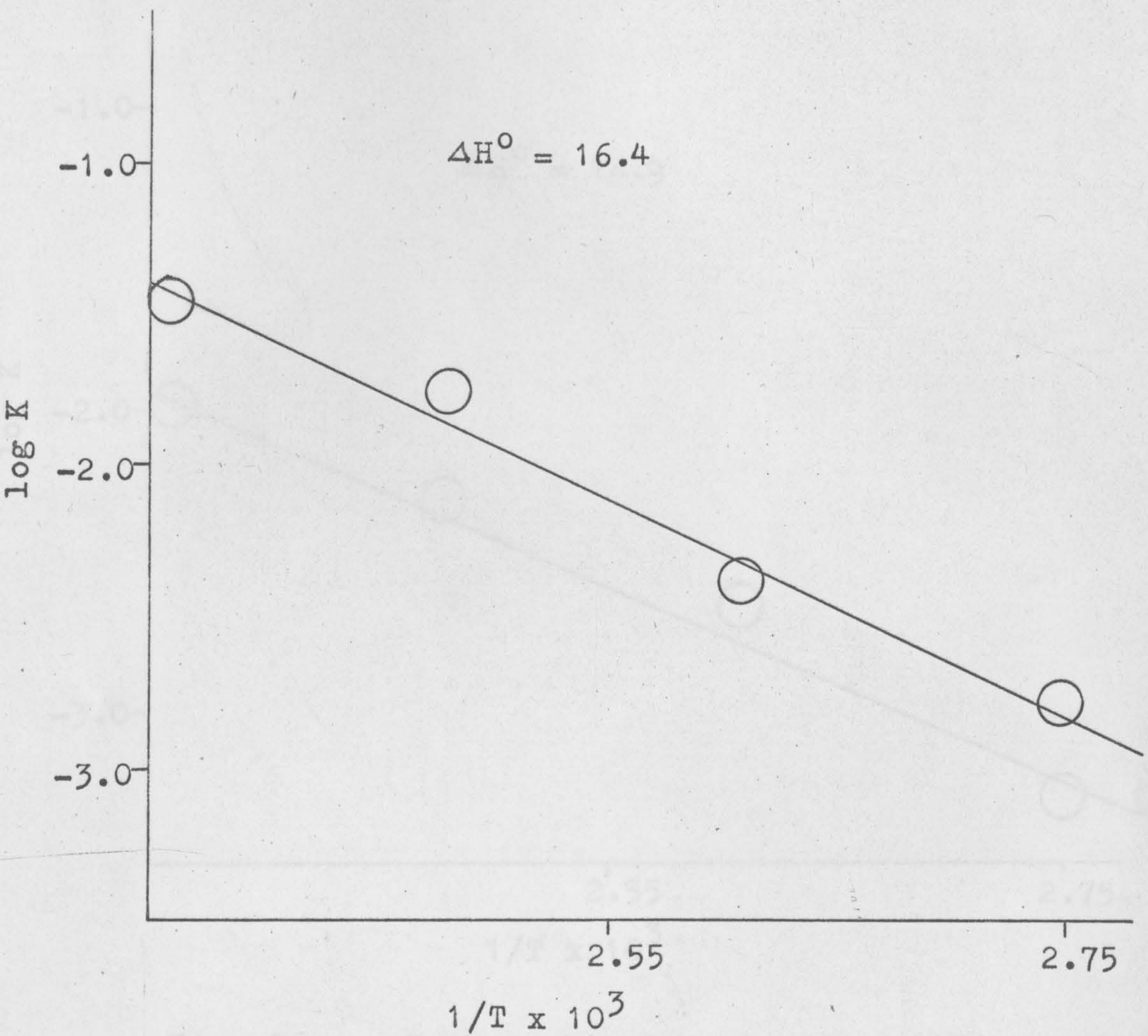


Fig. 25. m-Methoxyphenyl carbanilate in benzene. Log K *vs*. 1/T.

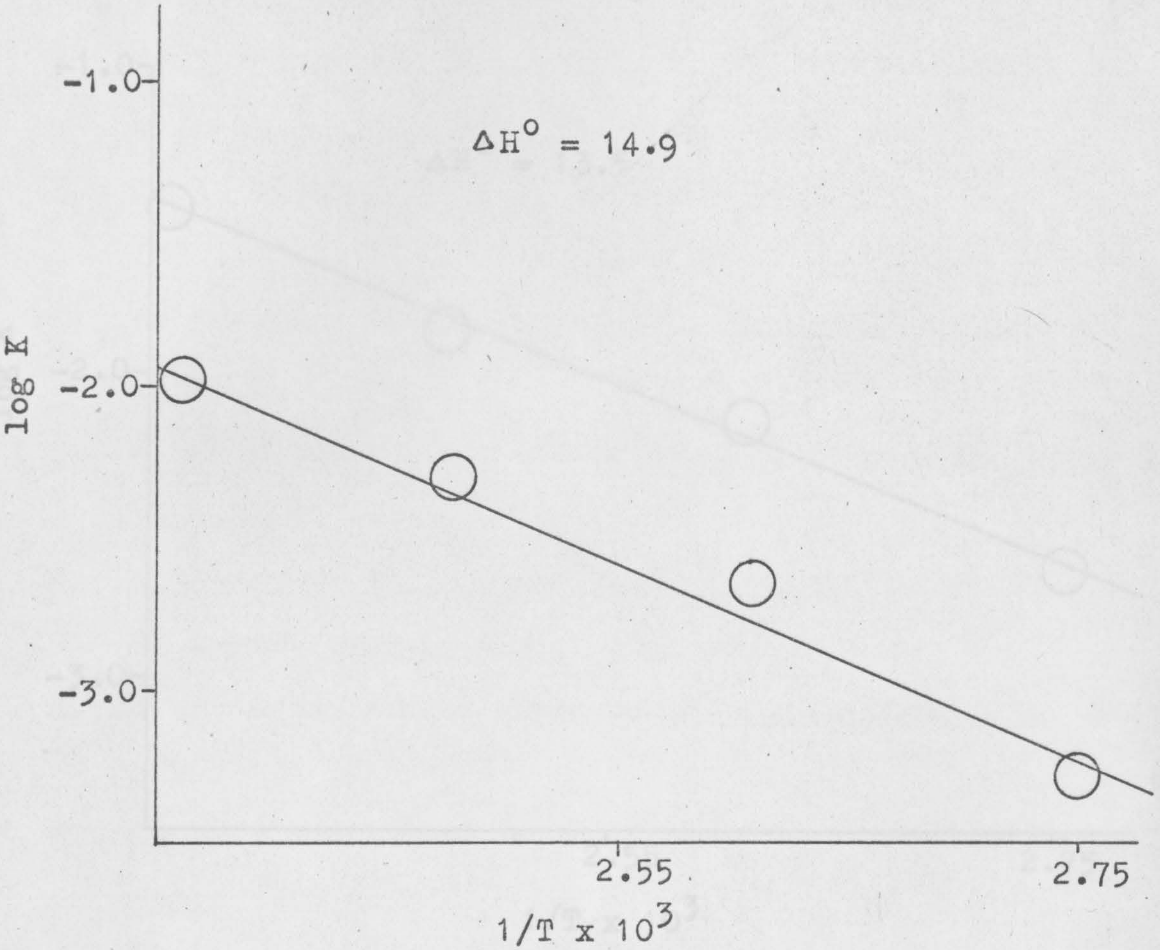


Fig. 26. p-Methoxyphenyl carbanilate in benzene. Log K vs. 1/T.

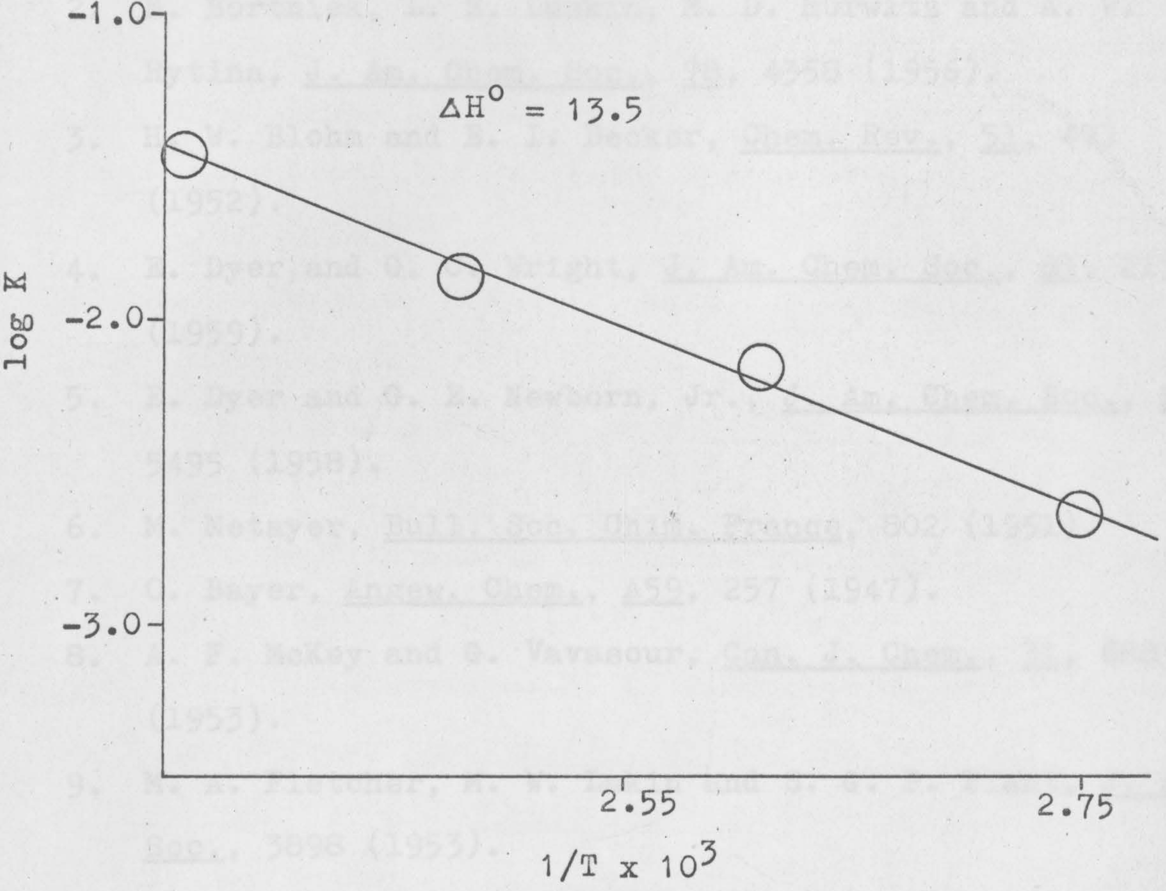


Fig. 27. _p_-Iodophenyl carbanilate in benzene. Log K _vs_. 1/T.

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