

THE KINETICS AND MECHANISMS OF
THE FORMATION OF METAL COMPLEXES
CONTAINING NON-CYCLIC AND
MACROCYCLIC LIGANDS

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
KARIM NAFISI-MOVAGHAR
1974

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ABSTRACT

THE KINETICS AND MECHANISMS OF THE FORMATION OF METAL COMPLEXES CONTAINING NON-CYCLIC AND MACROCYCLIC LIGANDS

By

Karim Nafisi-Movaghar

In this project the reaction of $[\alpha, \alpha'''\text{-[isopropylidenebis(azo)]di-}\alpha\text{-stibenendato}]$ nickel(II), (NiMMK) with ethylenediamine and 1,3 - propanediamine has been investigated in the presence of solvent. NiMMK contains a ligand with cis-oriented CO groups. The reaction of ethylenediamine with NiMMK results in the formation of macrocyclic complex with four nitrogen donors, [3,3,9-trimethyl-6,7,12,13 tetraphenyl-1,2,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenato]nickel(II), (NiMyclo-13). With 1,3-propanediamine, however, only one of the CO groups of NiMMK undergoes condensation producing a complex with a non-cyclic ligand, $[\alpha'[[1-[[2-[(3\text{-aminopropyl})\text{amino}]-1,2\text{-diphenylvinyl}]azo]-1\text{-methyleneethyl}]azo]-\alpha\text{-stibenolato}]$ nickel(II), (NiApSo).

The reactions were followed spectrophotometrically in tetrahydrofuran. The formation of NiApSo is found to involve a single slow step, but the formation of NiMyclo-13 involves two slow steps (XVI). It was also found that the reactions of amines with NiMMK are base catalysed. Kinetics data have been obtained for the reactions. The dependence of the rate of the reactions on the hydroxide concentration and each of the reactants has been

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investigated. A mechanism consistent with all the experimental data is proposed.

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By

Karim Nafisi-Movaghar

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To Terry and Jabbar

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CHAPTER ONE

INTRODUCTION

The ability of transition metal ions to direct the steric course of certain condensation reactions between organic molecules has been recognized for several years. Many of the products of these condensation reactions are natural products, for example, derivatives of porphin or corrin ring systems.

During the past ten years or so there has been considerable interest in the use of transition metal ions for the synthesis of compounds containing macrocyclic ligands which may serve as models for biological processes which are known to require the presence of metal ions. Research into the synthesis and characterization of complexes containing macrocyclic ligands has been extensive, and several reviews which summarize the research in the area have been published¹⁻⁶. The most extensively studied systems are those which lead to the formation of complexes containing macrocyclic ligands with four nitrogen donors. Condensation reactions between carbonyl compounds and primary amines have been extensively employed for the formation of these new macrocyclic ligands. The groups of Busch and Curtis have been particularly active in this area (see reference 5) although significant contributions have been made by other workers including Jager⁷⁻¹⁰, Black¹¹, Cummings¹²⁻¹⁴, Green and Tasker¹⁵, and Bamfield¹⁶. Recently Kerwin and Melson reported some reactions between amines and ligands derived from hydrazones¹⁷. The research group of Holm has carried out extensive studies of the synthesis, characterization and reactions of complexes of this type, although

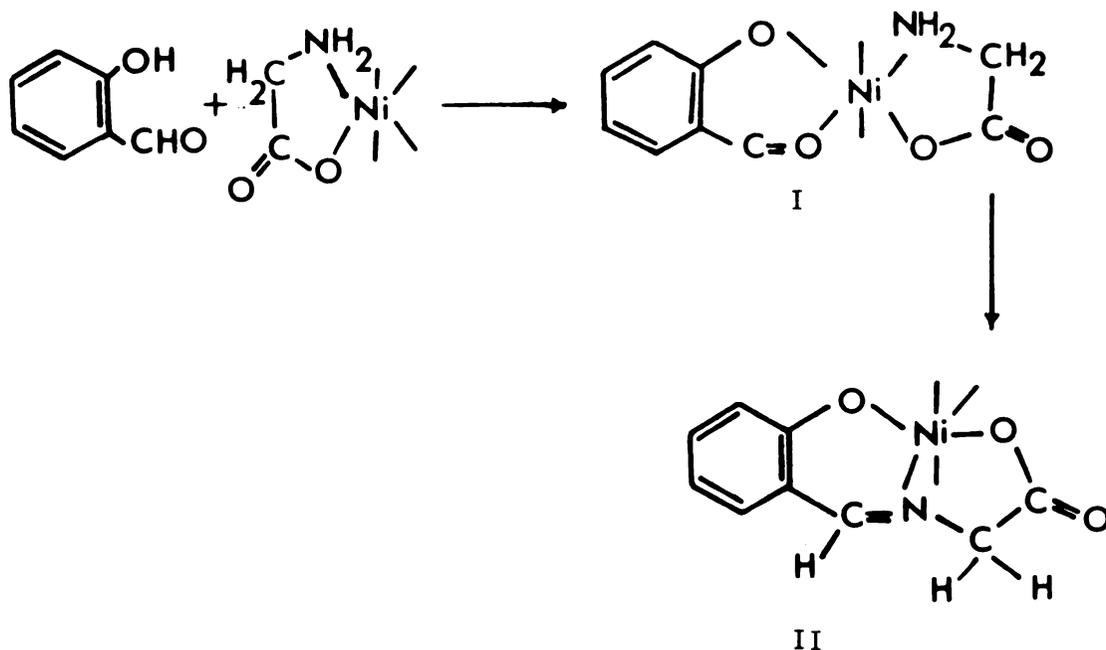
their syntheses have been accomplished by direct reaction between the free organic macrocycle and the metal ion rather than by "in situ" reactions which are governed more directly by template effects¹⁸⁻²⁰. While recognizing the significant results of Holm's research, we shall concentrate this discussion on "in situ" process; i.e., those processes in which the reactants are brought together by coordination to the same metal ion. The proximity of the reactive sites then promotes a reaction that would take place much less readily, if at all, in the absence of the metal ion.

In spite of the wealth of data on the synthesis and characterization of metal complexes containing macrocyclic ligands with nitrogen donors, there is little information on the factors that are important in controlling the reactions or on the role that the metal ion plays in the "in situ" condensations. Indeed Lindoy and Busch in their article⁵ concerning complexes of macrocyclic ligands comment:

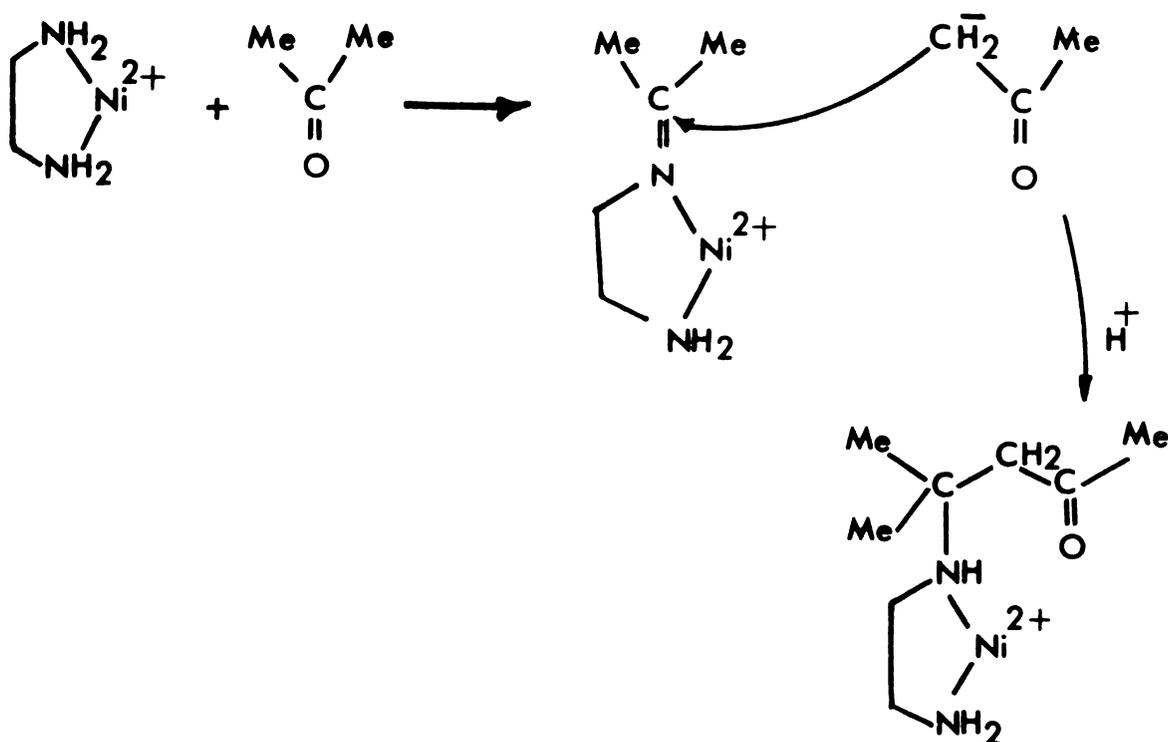
Unfortunately the principles underlying some of the synthetic procedures are yet little understood, and in addition to its contribution to fundamental understanding, the elucidation of the mechanisms of the formation of macrocyclic complexes will undoubtedly be of great benefit in the design of new syntheses.

Metal-ion control in the synthesis of Schiff base complexes has been the subject of a recent review²¹ although reactions of salicylaldehyde complexes with amines have been discussed earlier^{22,23}. The nature of both the metal ion and the ligand is an important criterion to be considered in planning the synthesis of a Schiff base complex. Nunez and Eichhorn²⁴ reported one of the early studies on the kinetics of formation of metal complexes containing Schiff bases. The reactions of nickel(II) and copper(II) with salicylaldehyde and glycine were investigated and it was found that the nature

of participation of the metal ion in Schiff base formation is dependent on the metal ion and on the order of mixing of the reactants. The proposed mechanism involves the formation of an intermediate, I, followed by reaction to produce the Schiff base complex, II.

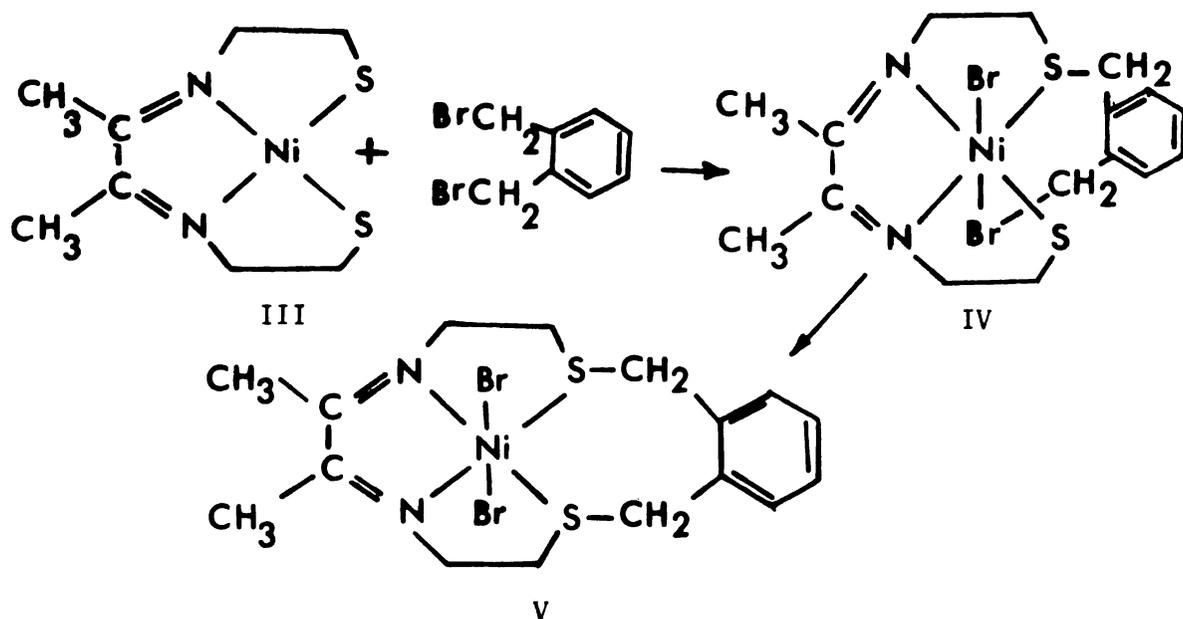


Leussing and co-workers²⁵ have studied the formation of Schiff bases in the presence of metal ions in aqueous media, and the effects of metal ions on the rates of formation have been discussed²⁶. Recently, Curtis^{27,28} proposed the following mechanism for reactions between metal-amine complexes and carbonyl compounds:



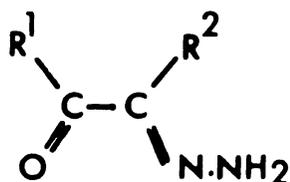
With the exception of the above work of Curtis and the report on the stepwise formation of phthalocyanine²⁹, no detailed studies related to the formation of complexes containing macrocyclic ligands with nitrogen donors have been reported.

In 1968, Blinn and Busch described the only study of the kinetics of macrocycle formation³⁰. This involved the reaction between 2,3 pentanedione-bis (mercaptoethylimino) nickel(II) and α, α' -dibromo-*o*-xylene. The "kinetic coordination template effect" was demonstrated by following the reaction spectrophotometrically in dichloroethane at 25^o. A two-step mechanism was proposed; the first being slow, (III,IV) and the second ring closure step (IV-V) very rapid.

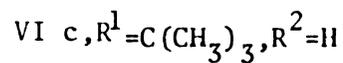
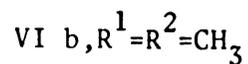
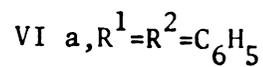


Since this report, other studies of reactions of the mercaptide function of complexes containing mercaptoamines with alkyl and aryl halides have been reported³¹⁻³⁴ although no further studies of macrocycle formation have appeared in the literature.

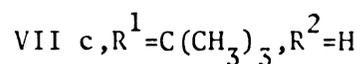
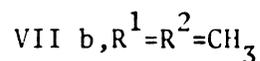
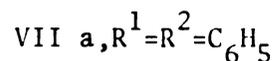
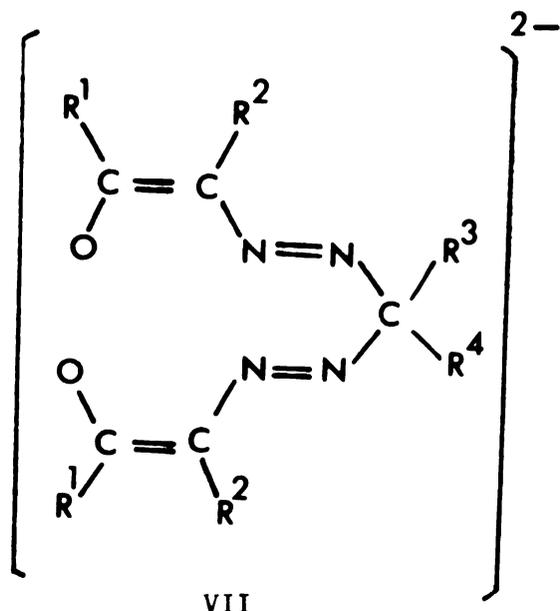
Reactions between some monohydrazones, VI and ketones, $R^3R^4C=O$ in the presence of nickel (II) ions have been reported recently by Melson and et al.



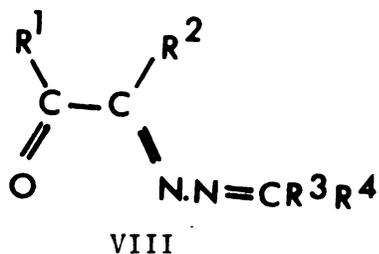
VI



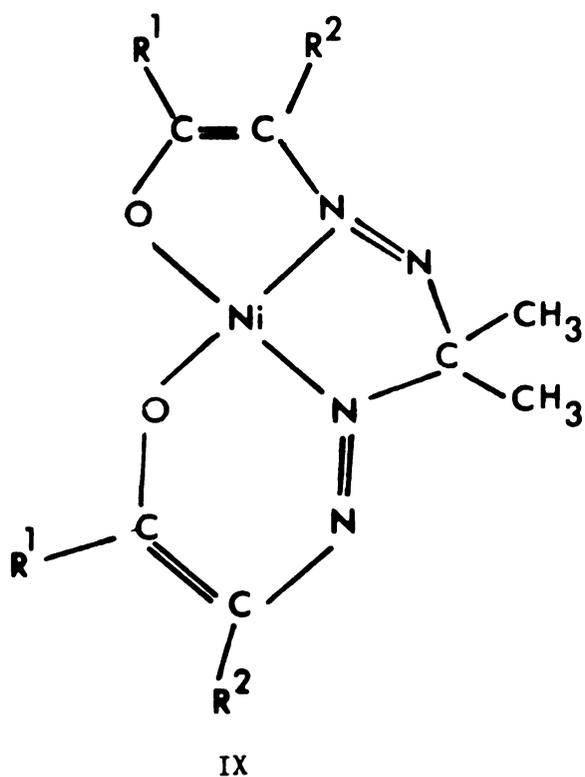
In all cases, nickel(II) complexes which contain ligands derived from two monohydrazones and one ketone, VII, are obtained³⁵⁻³⁷.



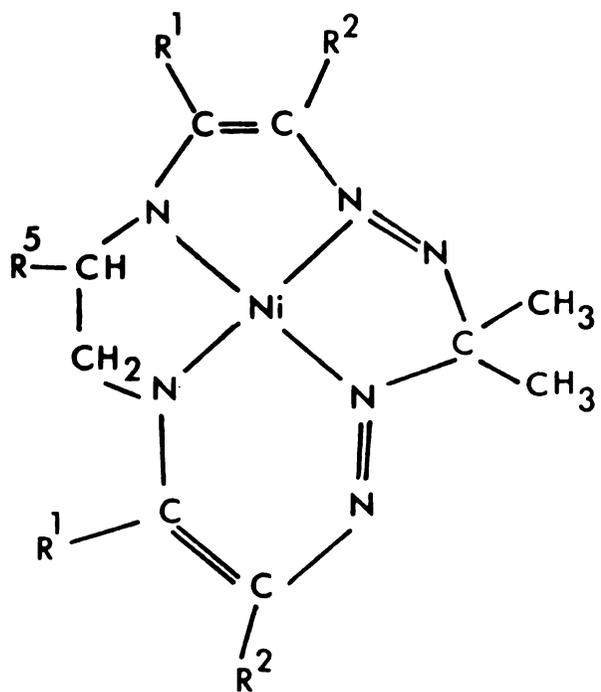
In the absence of nickel (II) ions, VIII is obtained.



Thus the nickel (II) ions control the condensation reactions with the result that products are formed which are not obtained in the absence of the metal ions. The mode of coordination of the ligands with $R^3 = R^4 = CH_3$, and $R^1 = R^2 = CH_3$ (VII^b) and $R^1 = C(CH_3)_3, R^2 = H$, (VII^c) has been established from ¹H nmr spectra³⁸ and it is assumed that ligands derived from (VII^a) coordinate in a similar manner, as in IX.



The reactivity of the coordinated CO groups of these ligands towards amines has been investigated. Since they are oriented in a cis configuration in the nickel complex, reaction with a suitable diamine would be expected to result in a complex with a macrocyclic ligand containing four nitrogen donors. In the presence of diamines, the species X have been obtained¹⁷. The mode of coordination and conformation of the new chelate ring has been established from ¹H nmr and circular dichroism spectra³⁹.



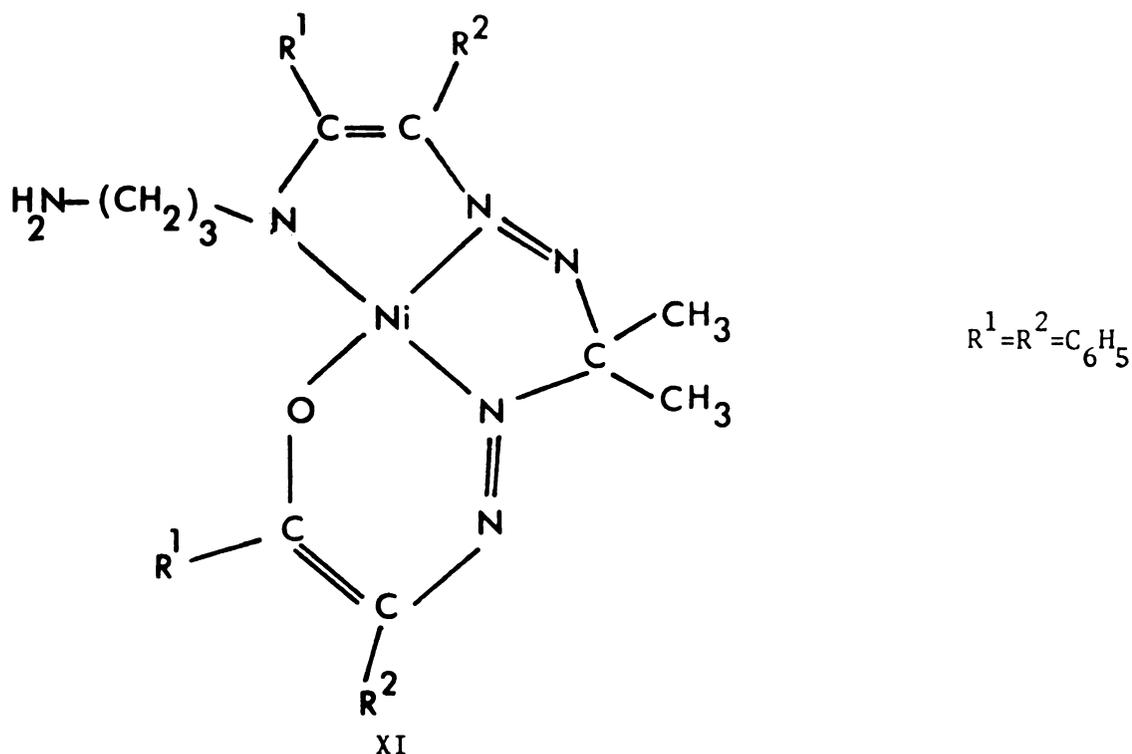
X

X a, $R^1=R^2=C_6H_5$, $R^5=H$

X b, $R^1=R^2=C_6H_5$, $R^5=CH_3$

X c, $R^1=R^2=CH_3$, $R^5=H$

With 1,3 diaminopropane, replacement of only one of the coordinated oxygens occurs¹⁷, producing a complex containing a non-cyclic, potentially pentadentate ligand XI.



It is interesting to note that the complex with ligand VII^c does not react with diamines, even under forcing conditions³⁷. Obviously the nature of the group attached to the coordinated CO has a marked influence on the reactivity of the carbonyl.

It is appropriate at this time to determine the mechanisms of reactions which lead to the formation of complexes containing macrocyclic ligands. This dissertation is a report on the kinetics and mechanism of ring closure reactions between IX, $R^1 = R^2 = C_6H_5$ and some diamines such as ethylenediamine, 1,2-propanediamine and 1,3-propanediamine in solution. (The preparative reactions were carried out in the absence of solvent). It is anticipated that this study should lead to a more complete understanding of the mechanism of macrocycle formation and may lead to the development of new and more effective synthetic procedures.

CHAPTER TWO
EXPERIMENTAL

1. Preparation of Materials

A. Nickel Complexes

$[\alpha, \alpha'']$ [Isopropylidenebis(azo)di- α stibenendato]nickel(II), (NiMMK), [3,3-Dimethyl-6,7,12,13-tetraphenyl-1,2,4,5,9,11-hexaazacyclo-trideca-1,4,6,12-tetraenato] nickel(II), (NiHcyclo-13), [3,3,9-Trimethyl-6,7,12,13 tetraphenyl-12,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenato] nickel(II), (NiMycyclo-13) and $[\alpha'[[1-[[2-[(3-Aminopropyl)amino]-1,2-diphenylvinyl]azo]-1-methylethyl]azo]-\alpha$ -stibenolato] nickel(II), (NiApSo) were prepared as previously described³²⁻³⁴. NiMMK, NiHcyclo13 and NiMycyclo13 were recrystallized from acetone and NiApSo was recrystallized from tetrahydrofuran.

B. Amines

Ethylenediamine, 1,2-propanediamine and 1,3-propanediamine were distilled from sodium hydroxide under nitrogen, collected over sodium hydroxide and stored in a dry box.

C. Solvents

1. Tetrahydrofuran (Mallinckrodt) was refluxed and distilled from sodium to remove water, benzophenone was added as an indicator. (Water content of the solvent after distillation was 60 μ l per ml).

2. Acetonitrile (Baker analyzed reagent) was refluxed and then distilled from calcium hydride. Other solvents used were dichloroethane, dimethyl sulfoxide, dimethylformamide, dioxane and pyridine.

They were all reagent grade or equivalent and used as supplied.

D. Sodium Hydroxide

Stock solutions of sodium hydroxide were prepared by dissolving solid sodium hydroxide in absolute ethanol, and standardized with a standard solution of potassium hydrogen phthalate (Fisher scientific Company) using either phenolphthalein or pH meter for determination of end point.

Note: All other chemicals used were reagent grade or equivalent.

2. Physical Measurements

All visible and ultraviolet spectra were obtained between 600-275 nm by use of a Unicam SP800 B spectrophotometer. Kinetics data were obtained from a Beckman model Du spectrophotometer. Both Unicam and Beckman spectrophotometers were calibrated for absorption with a standard solution of potassiumdichromate in sulfuric acid and for wavelength with a didymium filter. The base lines of the spectra were obtained via air vs. air.

Mass spectra were determined with a Hitachi-Perkin-Elmer RMU-60 mass spectrometer. A pH meter model LS S-30005 (Sargent) was used for preparation of the standard sodium hydroxide solution.

3. General Procedure for Obtaining Kinetics Data

A weighed amount of MiMMK was dissolved in a known quantity of tetrahydrofuran (concentration approximately 2×10^{-3} - 8×10^{-3} M) in a 50 ml round bottom flask filled with a reflux condenser, and

stopcock. The stopcock was closed with a serum cap. The solution was stirred with a magnetic stirrer. To the solution was added 0.5-2ml of ~ 1.5 M alcoholic solution of sodium hydroxide. The solution was warmed to $\sim 60^{\circ}\text{C}$ and the diamine (approximately .3 M - .6 M) was injected into the mixture with a syringe, and within seconds the solution started to reflux. At this time (zero time for reaction) 0.2 - 0.5 ml of sample (depending on the original concentration of NiMMK) was removed with a microsyringe from the flask through the serum cap of the side arm. The sample was diluted with tetrahydrofuran to approximately 8×10^{-5} M in complex, and then transferred to a spectrophotometer cell, with a 1 Cm. path length, placed into the spectrophotometer, and the spectrum recorded (Unicam) or absorption at 500, 400, 385, 360 and 340 nm. measured (Beckman). Total run times ranged from 18 hours at high diamine concentration to ~ 24 hours at low diamine concentration.

CHAPTER THREE

KINETICS AND DATA TREATMENT

I. The Kinetics of the Reactions of NiMMK

with 1,3 Propanediamine

The experimental procedure outlined for following the reaction between NiMMK and 1,3-propanediamine in tetrahydrofuran solution at 66°C results in a series of spectra (Figure I). Over a period of time the decrease in absorbance at 385 nm is larger than that at other wavelengths and the rate of reaction of NiMMK with 1,3-propanediamine may be followed at this point, (a typical data set is shown in Table I), however, choosing any point between each two isosbestic points is expected to show similar results, and they do. The change of the spectra of the reactants as the reaction progresses produces several sharp isosbestic points at 325, 418, 464 and 526 nm (see Figure I). These isosbestic points are coincident to those obtained experimentally from the spectra of the NiMMK and pure NiApSo (Figure II). This suggests a simple reaction between NiMMK and 1,3-propanediamine. Reactions were run under pseudo first-order conditions (\approx 1:200 NiMMK to 1,3-propanediamine) and therefore 1,3-propanediamine concentration can be considered to be constant. With this assumption, the data are fitted to pseudo first-order rate equation of the form $(A_{\infty} - A_t / A_{\infty} - A_0) = e^{-kt}$, where k is rate constant and A_{∞} , A_t and A_0 are the observed absorbances at infinite, t and zero time (few seconds after mixing the reactants) respectively. By using this equation rate constants were calculated by the curve fitting program of Dye and Nicely⁴⁰. By feeding rate constant, time and absorbance to the computer the computer adjusts them until the

calculated constant agrees with the experimental one. The calculated and experimental data should nearly coincide if the form of the equation being used in the curve fitting program is correct. A sample plot of absorption vs. time, from the reaction between NiMMK and 1,3-propanediamine is shown in Figure III.

FIGURE I

Absorption Spectrum for Reaction of NiMMK with 1,3-Propanediamine

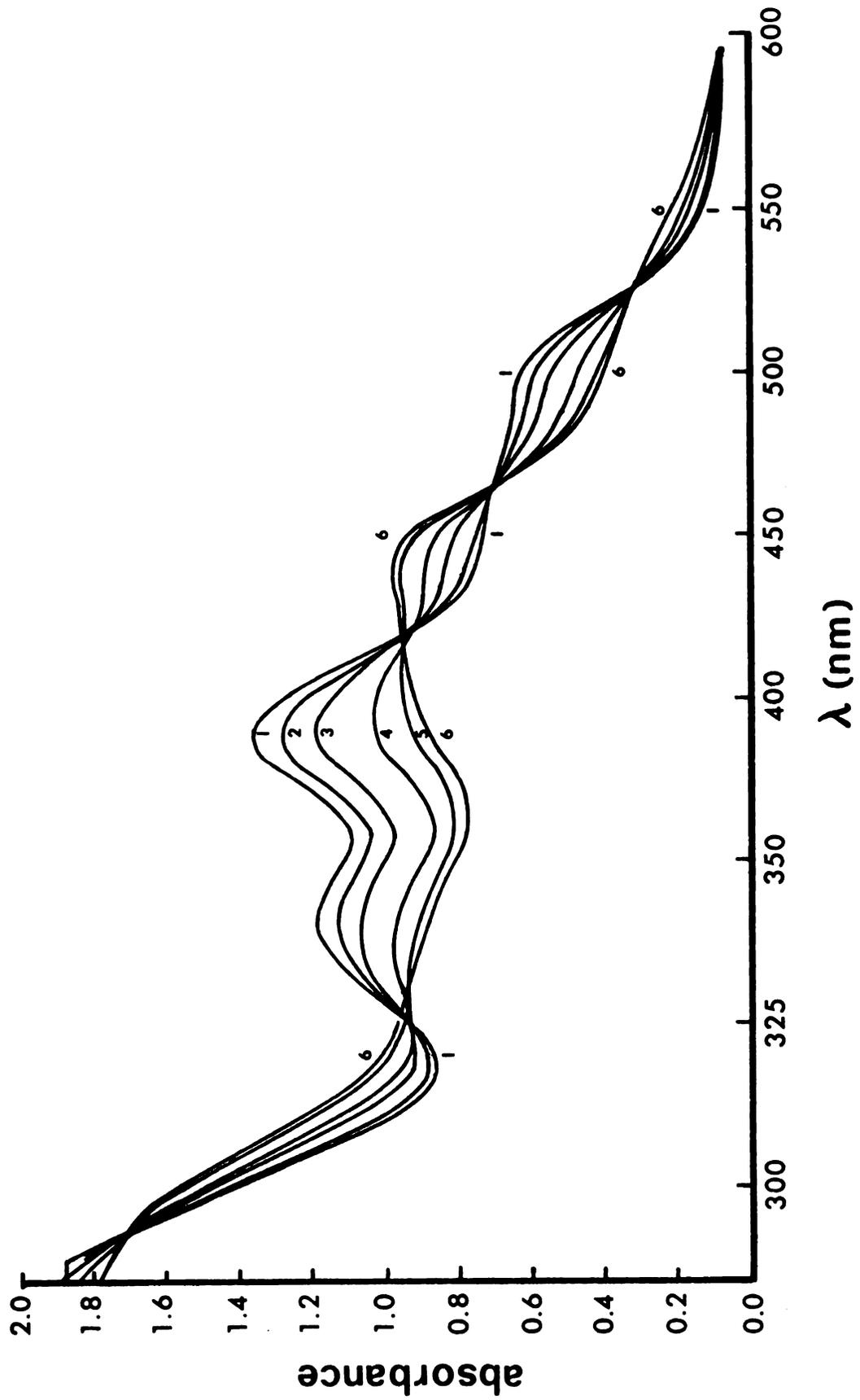


TABLE I

A Set of Kinetics Data for the Reaction
between NiMMK and 1,3-Propanediamine

λ_{nm}	340		385		440		500	
Time/Min	A	T%	A	T%	A	T%	A	T%
0.0	1.075	8.75	1.280	5.35	0.668	21.75	0.521	30.18
14.66	1.015	8.90	1.232	6.00	0.692	20.25	0.493	32.10
28.83	0.987	10.28	1.175	6.90	0.713	19.50	0.469	34.10
42.16	0.958	11.10	1.120	7.90	0.734	18.75	0.451	35.70
53.83	0.942	11.50	1.080	3.50	0.752	17.90	0.435	35.95
68.50	0.938	11.90	1.050	9.10	0.772	17.00	0.419	38.20
85.16	0.910	12.38	1.008	9.98	0.790	16.25	0.399	40.80
110.16	0.878	13.50	0.962	11.00	0.802	15.90	0.375	42.10
140.16	0.842	14.45	0.910	12.40	0.828	15.00	0.355	44.10
175.16	0.812	15.60	0.865	13.80	0.842	14.70	0.336	46.20
213.83	0.800	16.00	0.838	14.80	0.862	13.92	0.324	47.50
255.50	0.817	15.35	0.817	15.30	0.878	13.40	0.315	48.70
325.50	0.779	16.80	0.797	16.10	0.886	13.10	0.302	50.10
508.83	0.768	17.10	0.772	17.00	0.897	12.90	0.291	51.20
1255.50	0.768	17.10	0.769	17.10	0.897	12.90	0.211	51.20

FIGURE II
Absorption Spectrum of Equal Concentrations
of NiMMK, (a) and NiApSo, (b)

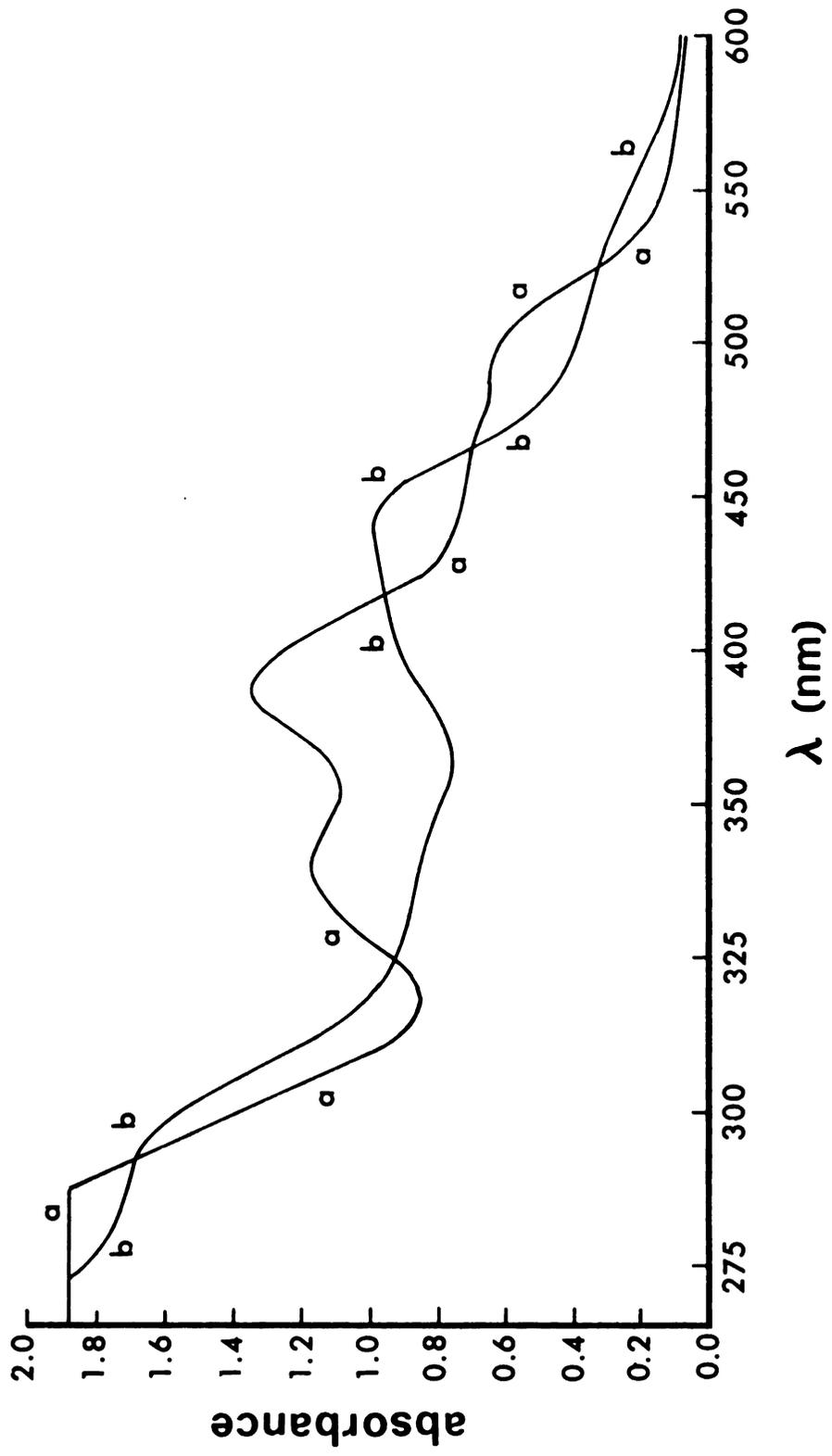
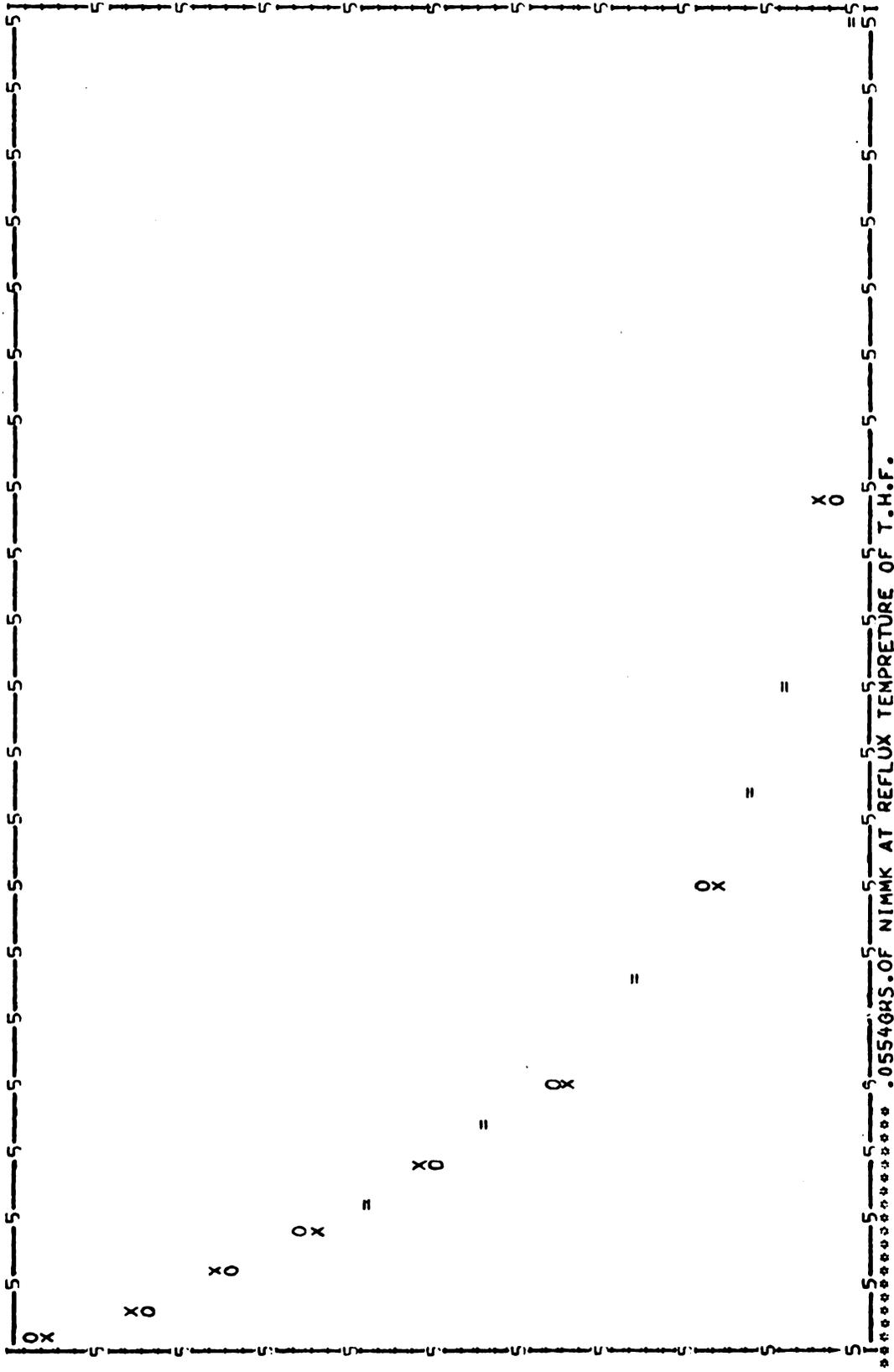


FIGURE III

A Computer Plot of Absorbance vs. Time of the Reaction
between NiMMK and 1,3-Propanediamine

X IS AN EXPERIMENTAL POINT. O MEANS A CALCULATED POINT (ONLY = IS USED WHEN RESID IS PLOTTED)
 = IS AN EXPERIMENTAL AND CALCULATED POINT ARE IN THE SAME DELTA X BY DELTA Y



***** .0554GRS.OF NIMMK AT REFLUX TEMPRETURE OF T.H.F. X O

A. 1,3-Propanediamine Dependence of the Rate

The reaction procedure has been outlined previously. Table II records the rate constants that are obtained with different concentrations of 1,3-propanediamine.

TABLE II

1,3-Propanediamine Dependence of the Rate

<u>[1,3-propanediamine]mole lit⁻¹</u>	<u>k_{obs} (min⁻¹)</u>	<u>standard deviation %</u>
0.53	0.327	<u>+5</u>
0.663	0.510	<u>+3</u>
0.796	0.532	<u>+6</u>
0.884	0.713	<u>+4</u>

In Figure IV a plot of 1,3-propanediamine concentration vs. k_{obs} is shown. This suggests a first order reaction with respect to amine.

B. NiMMK Dependence of the Rate

The rate constants obtained in differenc concentrations of NiMMK are shown in Table III.

FIGURE IV
A Plot of k_{obs} vs. 1,3-Propanediamine Concentration
for the Reaction between NiMMK and 1,3-Propanediamine

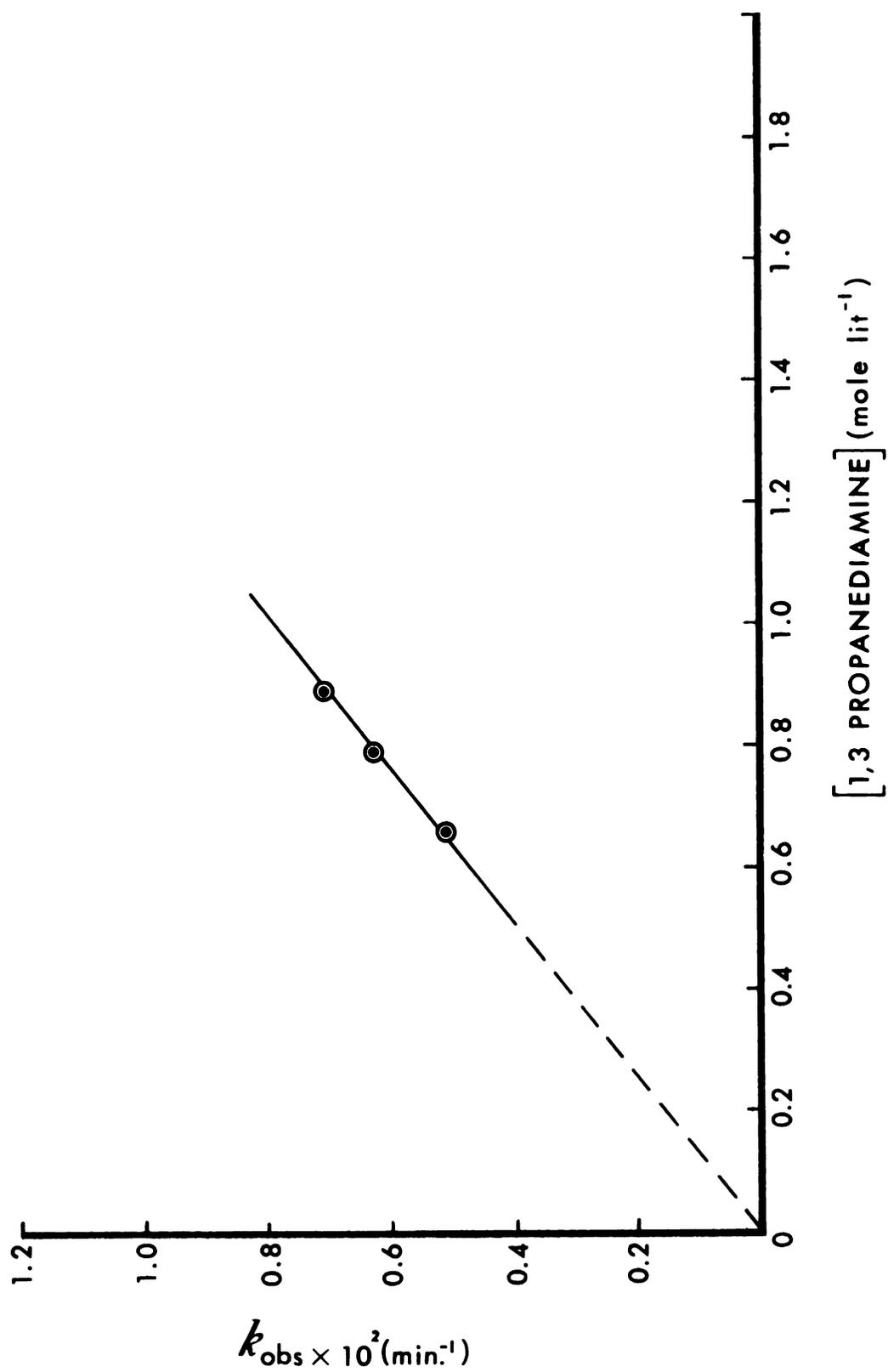


TABLE III

NiMMK Dependence of the Rate

<u>[NiMMK] x 10² (mole lit⁻¹)</u>	<u>k_{obs} x 10² (min⁻¹)</u>	<u>standard deviation %</u>
0.185	0.89	<u>+2.0</u>
0.370	0.89	<u>+3.0</u>
0.740	0.89	<u>+2.0</u>

Since the calculation of k_{obs} includes the concentration of NiMMK, the above data suggest an order of one with respect to the NiMMK concentration.

C. Sodium Hydroxide Dependence of the Rate

During the experiment it was found that the rate of the reaction is dependent on the sodium hydroxide concentration. The experimental results are shown in Table IV.

TABLE IV

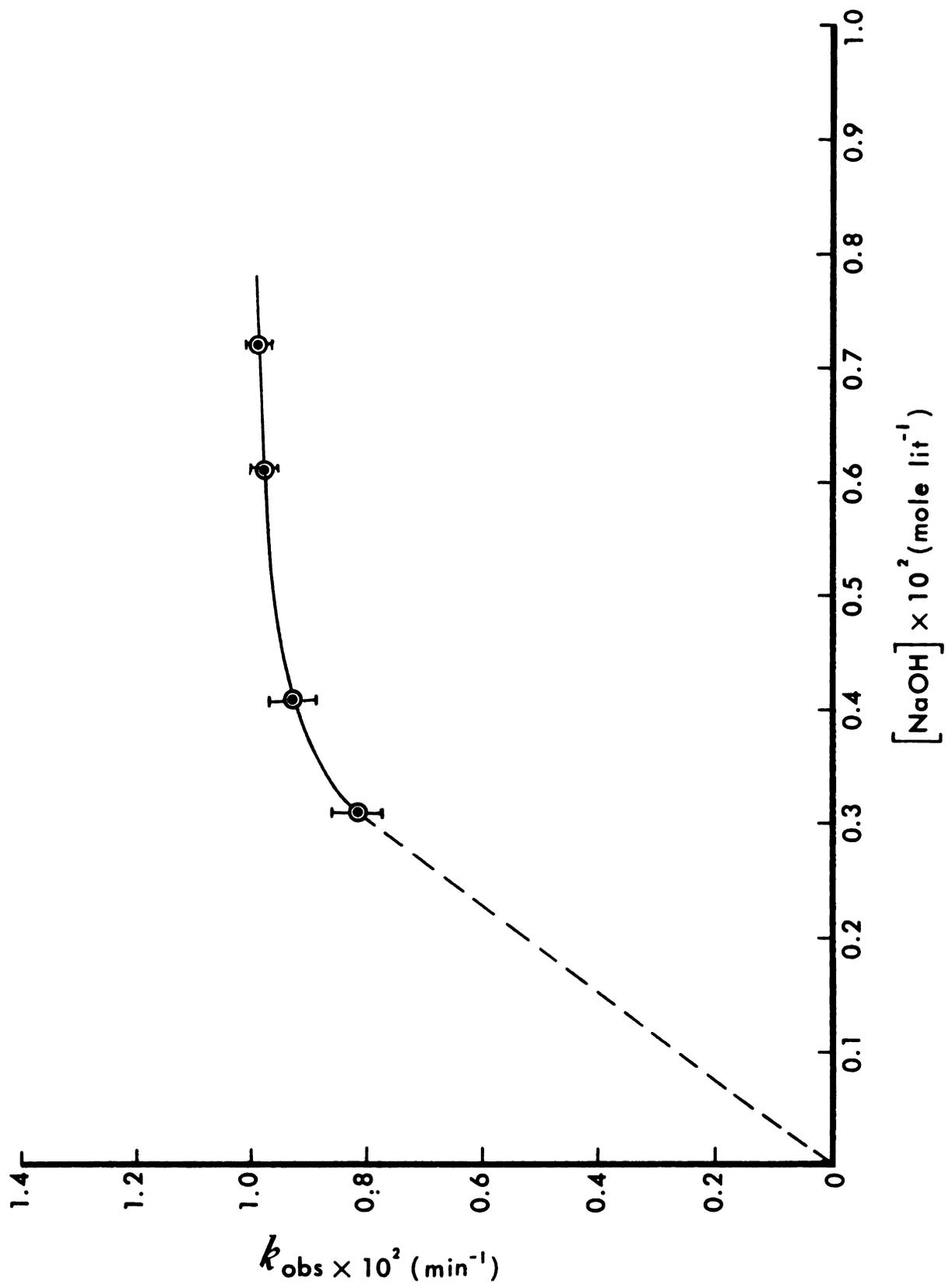
Sodium Hydroxide Dependence of the Rate

<u>[NaOH] x 10² (mole lit⁻¹)</u>	<u>k_{obs} x 10² (min⁻¹)</u>	<u>standard deviation %</u>
0.30	0.820	<u>+4.0</u>
0.41	0.934	<u>+4.0</u>
0.51	0.980	<u>+2.0</u>
0.62	0.989	<u>+2.0</u>
0.72	0.990	<u>+4.0</u>

A plot of observed rate constant vs. sodium hydroxide concentration is shown in Figure V. The rate initially increases as sodium hydroxide concentration increases, however, at higher concentrations of sodium hydroxide the rate stays almost constant. More experimental results have shown that this is due to an inhibitory effect of the ethanol in which the sodium hydroxide is dissolved. By increasing the sodium hydroxide concentration, consequently the concentration of ethanol increases and therefore the rate decreases. A third order rate constant calculated from the slope of the hydroxide dependence is $1.72 \text{ lit}^2 \text{mole}^{-2} \text{min}^{-1}$.

FIGURE V

A Plot of k_{obs} vs. Sodium Hydroxide Concentration
for the Reaction between NiMMK and 1,3-Propanediamine



2. Kinetics of the Reaction of NiMMK with Ethylenediamine

The reaction of NiMMK with ethylenediamine in tetrahydrofuran produces a series of spectra (a typical sample is shown in Figure VI). There are three important pieces of information that may be obtained from this series:

i. The absorbance at 360 nm initially decreases and is then followed by the appearance of an isosbestic point (see Figure VI and Table V at 360 nm).

ii. The absorbance at 340 nm initially decreases (spectra 1,2,3 and 4 of Figure VI) and then increases as the reaction proceeds.

iii. Reaction of NiMMK with ethylenediamine does not produce the predicted isobestic points at 299, 360, 422, 476 and 519 nm based on spectra of NiMMK and NiMcylo-13 (see Figure VII).

These phenomena were not observed in the reaction of NiMMK with 1,3-propanediamine and are thus evidence for greater complexity of this reaction compared with the simple reaction with 1,3-propanediamine. Similar to the spectrum number five of figure VI is spectrum number six from Figure I, which is the final product in reaction of NiMMK with 1,3-propanediamine. The spectra suggest that the reaction of NiMMK with ethylenediamine occurs via a two step process in which a significant concentration of the "intermediate" builds up as the reaction proceeds.

Reactions were run under pseudo first-order conditions (by making ethylenediamine concentrations approximately 200 fold larger than NiMMK concentrations). A typical set of data is in Table V. The two steps were treated separately and each step was fitted to a pseudo first-order rate equation by the procedure

previously mentioned. Figures VIII and IX show the computer plot of absorbance vs. time for the first and second steps respectively.

TABLE V
 A Set of Kinetics Data of the Reaction
 of NiMMK with Ethylenediamine

λ_{nm}	340		360		385		440		500	
Time/Min	A	T%	A	T%	A	T%	A	T%	A	T%
0.0	1.048	9.10	0.962	11.00	1.200	5.15	0.648	22.90	0.505	31.30
16.0	0.999	10.10	0.917	12.10	1.140	7.45	0.671	21.20	0.468	34.10
27.66	1.000	10.00	0.885	13.00	1.018	8.90	0.694	20.25	0.448	36.00
39.33	1.015	9.90	0.8810	13.11	1.000	10.00	0.723	19.00	0.435	37.00
52.33	1.038	9.50	0.860	14.00	0.936	11.90	0.735	18.60	0.418	38.60
66.0	1.050	9.00	0.868	13.80	0.878	13.25	0.762	17.45	0.411	39.00
78.66	1.072	8.70	0.860	14.00	0.819	15.10	0.769	17.10	0.397	40.10
91.66	1.110	7.92	0.863	13.90	0.790	16.30	0.795	16.10	0.392	40.16
108.33	1.150	7.10	0.866	13.60	0.739	18.45	0.810	15.70	0.391	40.90
125.16	1.190	7.50	0.850	14.10	0.671	21.40	0.796	16.10	0.384	42.70
141.83	1.220	6.10	0.865	13.90	0.661	21.90	0.837	14.90	0.379	41.50
161.83	1.240	5.92	0.866	13.85	0.619	24.10	0.842	14.30	0.371	41.90
183.5	1.245	5.90	0.866	13.85	0.588	25.92	0.878	14.10	0.372	42.80
208.5	1.290	5.10	0.866	13.85	0.561	27.65	0.859	14.00	0.373	42.60
258.5	1.310	5.00	0.890	13.00	0.530	29.80	0.879	13.25	0.366	42.60
316.83	1.340	4.90	0.890	13.00	0.510	31.75	0.862	13.90	0.371	43.00
386.83	1.350	4.75	0.890	13.00	0.491	32.10	0.882	13.10	0.369	42.50
685.16	1.351	4.60	0.900	12.80	0.477	33.72	0.883	13.00	0.371	42.90
1298.5	1.370	4.40	0.900	12.80	0.473	33.90	0.898	12.90	0.366	42.50
1570.16	-	-	0.900	12.80	0.471	34.00	-	-	-	-

FIGURE VI

Absorption Spectrum of the Reaction of NiMMK with Ethylenediamine

FIGURE VII
Absorption Spectrum of Equal Concentrations
of NiMMK(a) and MiMcylo-13(b)

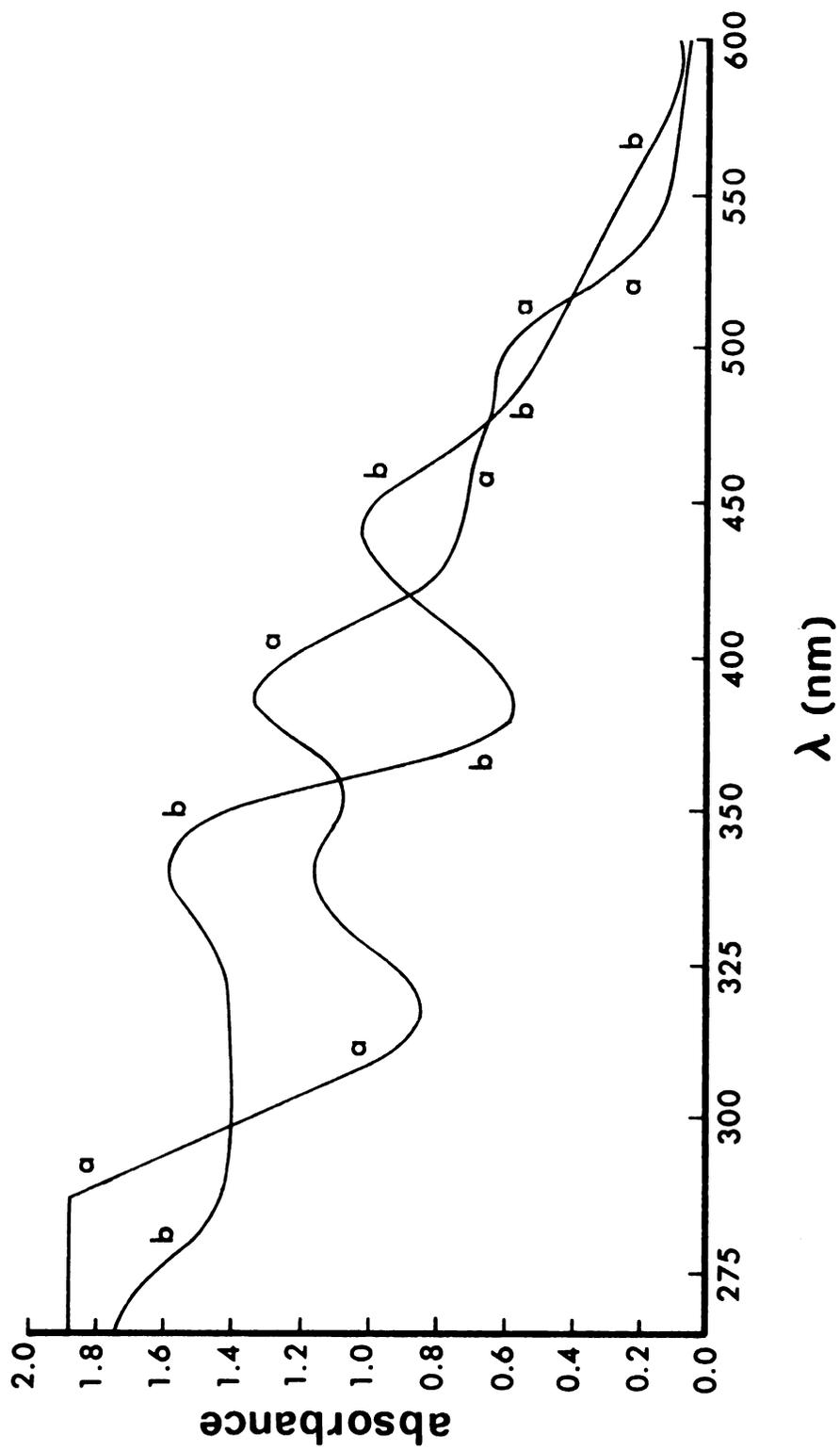
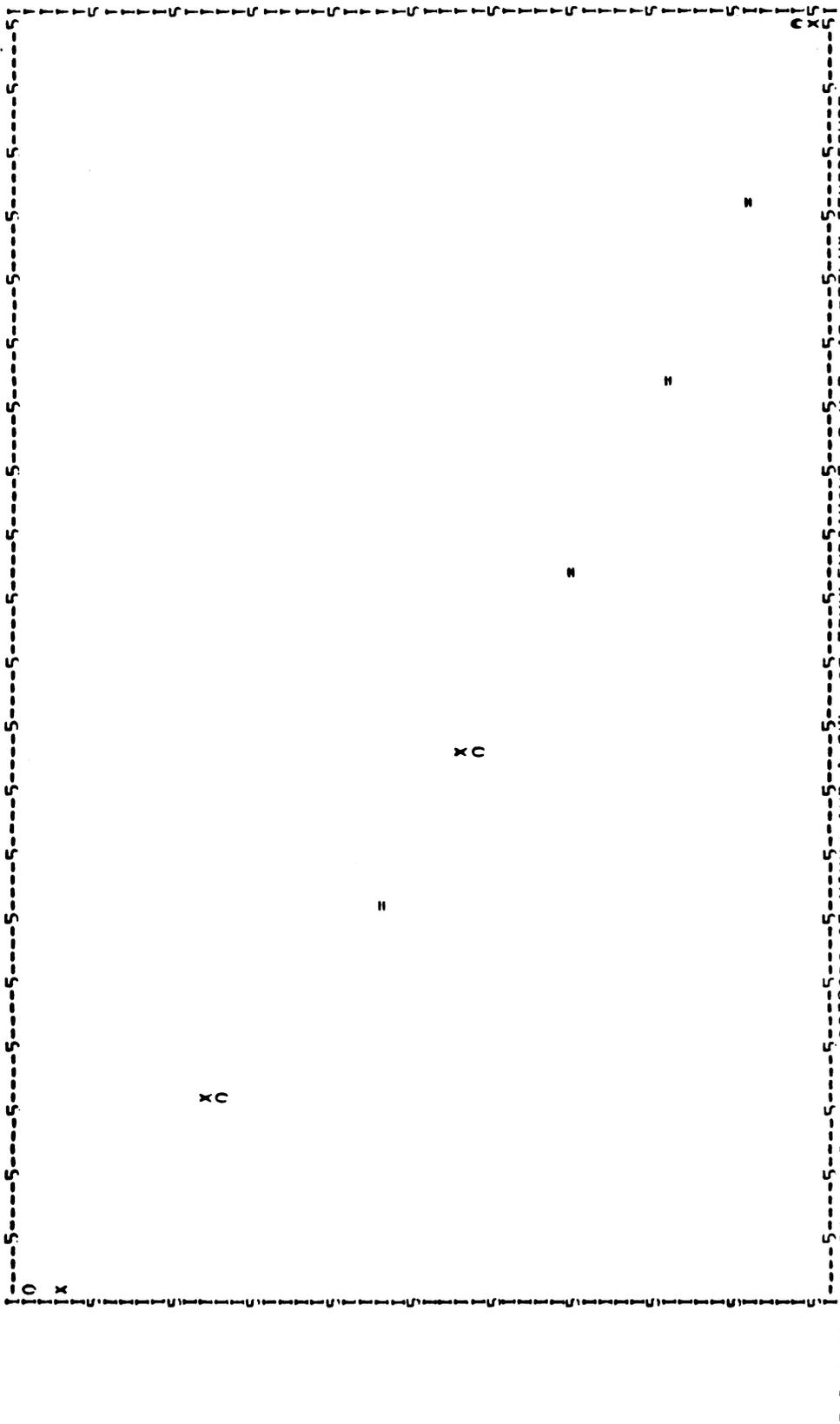


FIGURE VIII
A Computer Plot of Absorbance vs. Time
for the First Step of the Reaction
of NiMMK and Ethylenediamine

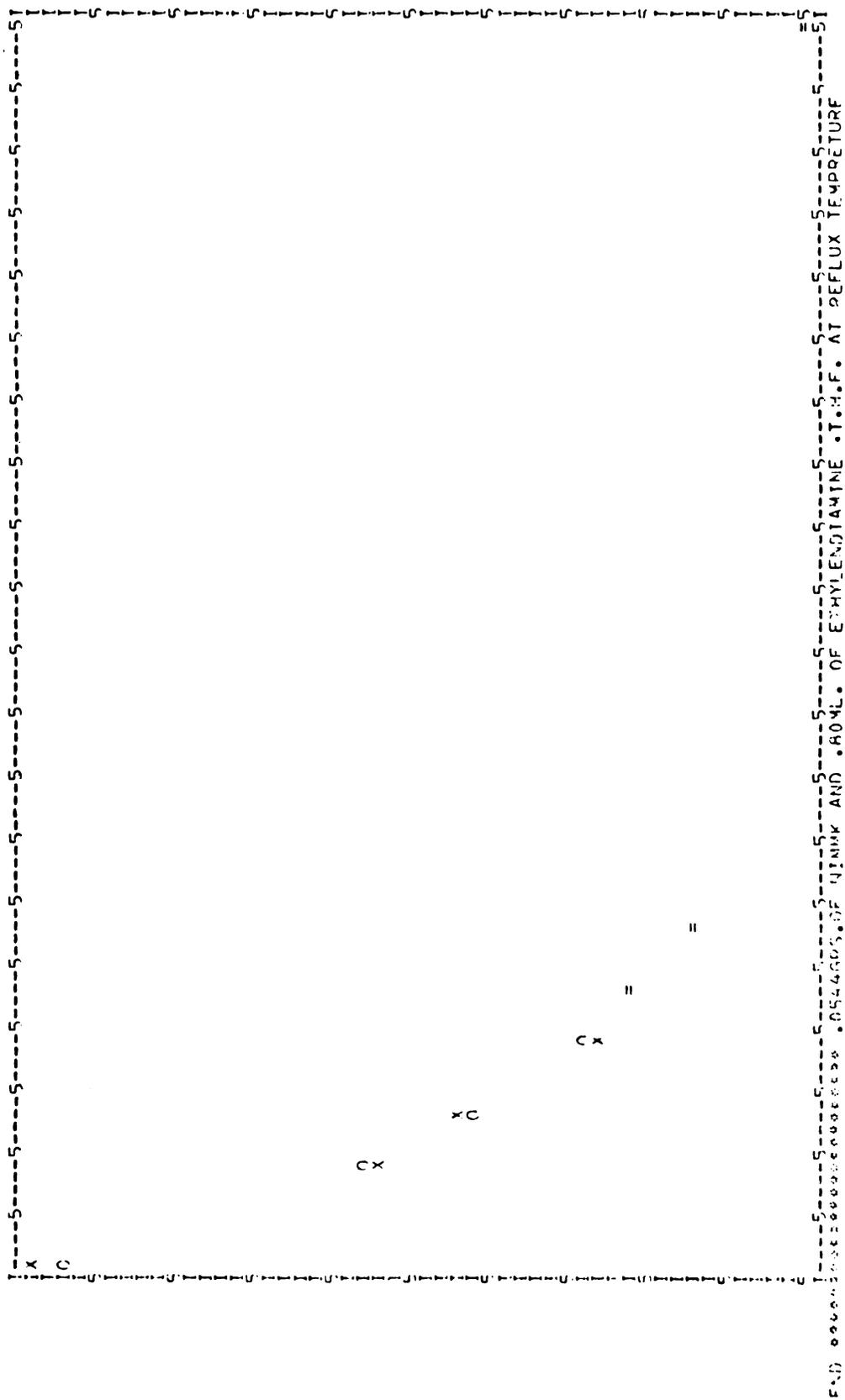
X MEANS AN EXPERIMENTAL POINT; O MEANS A CALCULATED POINT (ONLY = IS USED WHEN RESID IS PLOTTED)
= MEANS AN EXPERIMENTAL AND CALCULATED POINT ARE IN THE SAME DELTA X BY DELTA Y



END 0.072695 OF NIMMK AND 1.24L. OF ETHYLENDIAMINE .T.M.F. AT REFLUX TEMPERATURE

FIGURE IX
A Computer Plot of Absorbance vs. Time
for the Second Step of the Reaction
of NiMMK and Ethylenediamine

X MEANS AN EXPERIMENTAL POINT, O MEANS A CALCULATED POINT (ONLY = IS USED WHEN RESID IS PLOTTED)
 = MEANS AN EXPERIMENTAL AND CALCULATED POINT ARE IN THE SAME DELTA X BY DELTA Y



A. Ethylenediamine Dependence of the Reaction Rate

The experimental data for ethylenediamine dependence of the first and second steps are tabulated in Table VI. The second order rate constants are obtained by plotting observed rate constants vs. ethylenediamine concentrations (Figures X and XI). Their values are 0.19×10^{-1} liters mole⁻¹ min⁻¹ and 0.16×10^{-1} liters mole⁻¹ min⁻¹ respectively.

B. NiMMK Dependence of the Reaction Rate

By holding ethylenediamine and sodium hydroxide concentrations constant the following results have been obtained by varying the NiMMK concentration (the results are shown in Table VI).

TABLE VI

[Ethylenediamine] Dependence of the First and Second Steps

a. First Stage

<u>[en] mole lit⁻¹</u>	<u>k_{obs} x 10² (min⁻¹)</u>	<u>standard deviation %</u>
0.38	0.90	±7.0
0.47	1.16	±7.0
0.57	1.44	±4.0
0.66	1.68	±6.0

b. Second Stage

0.38	0.70	±5.0
0.47	0.79	±3.0
0.57	1.07	±9.0
0.66	1.14	±10.0

TABLE VII

[NiMMK] Dependence of the First and Second Step

a. First Stage

<u>[NiMMK] x 10²M</u>	<u>k_{obs} x 10¹ (min⁻¹)</u>	<u>standard deviation %</u>
0.159	0.142	± 3.0
0.318	0.144	± 4.0
0.477	0.141	± 6.0
0.636	0.143	± 5.0

b. Second Stage

0.159	0.108	± 3.0
0.318	0.107	± 8.0
0.477	0.107	± 4.0
0.636	0.107	± 4.0

FIGURE X

Ethylenediamine Dependence of the Rate of the First Step

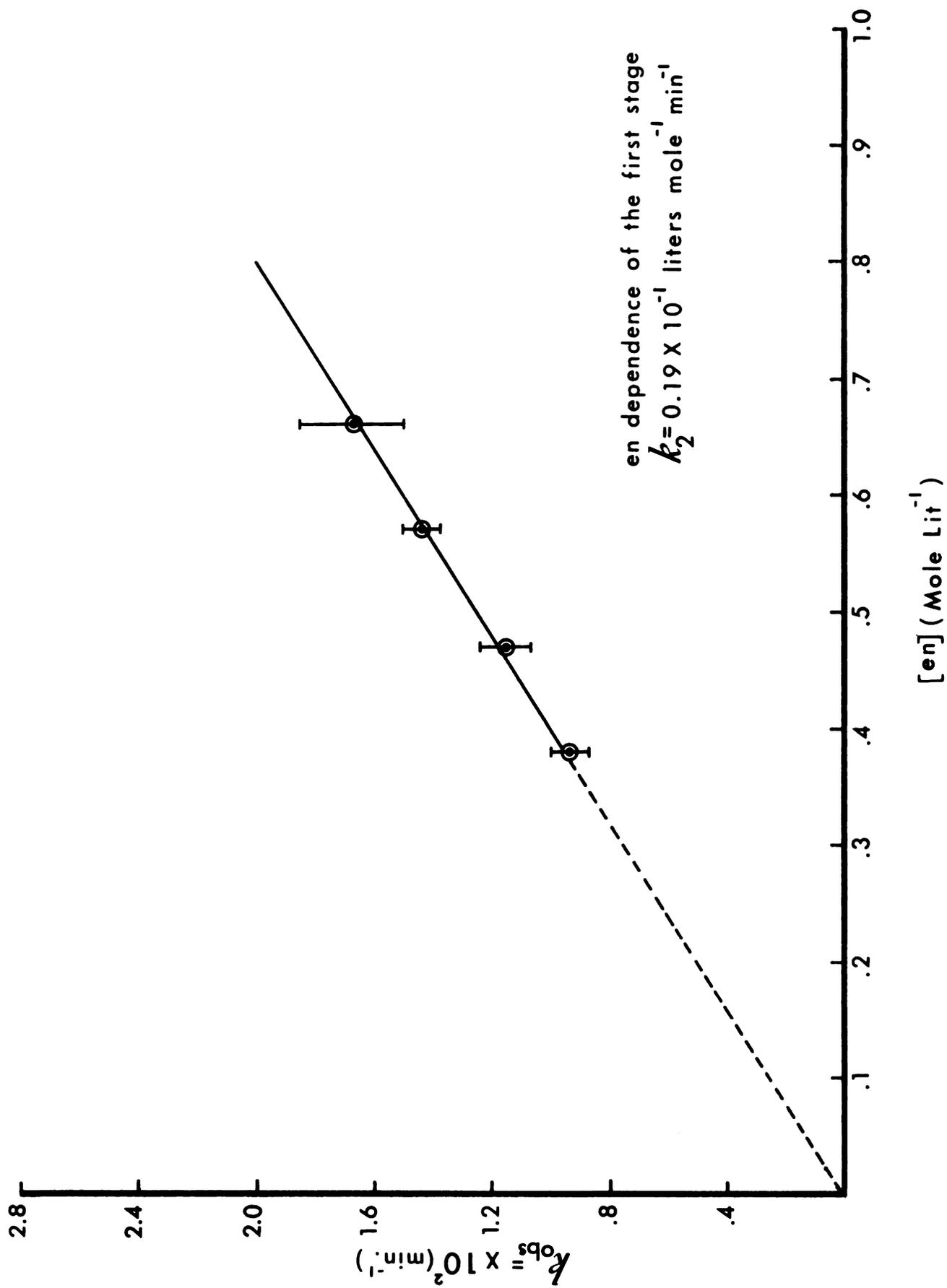
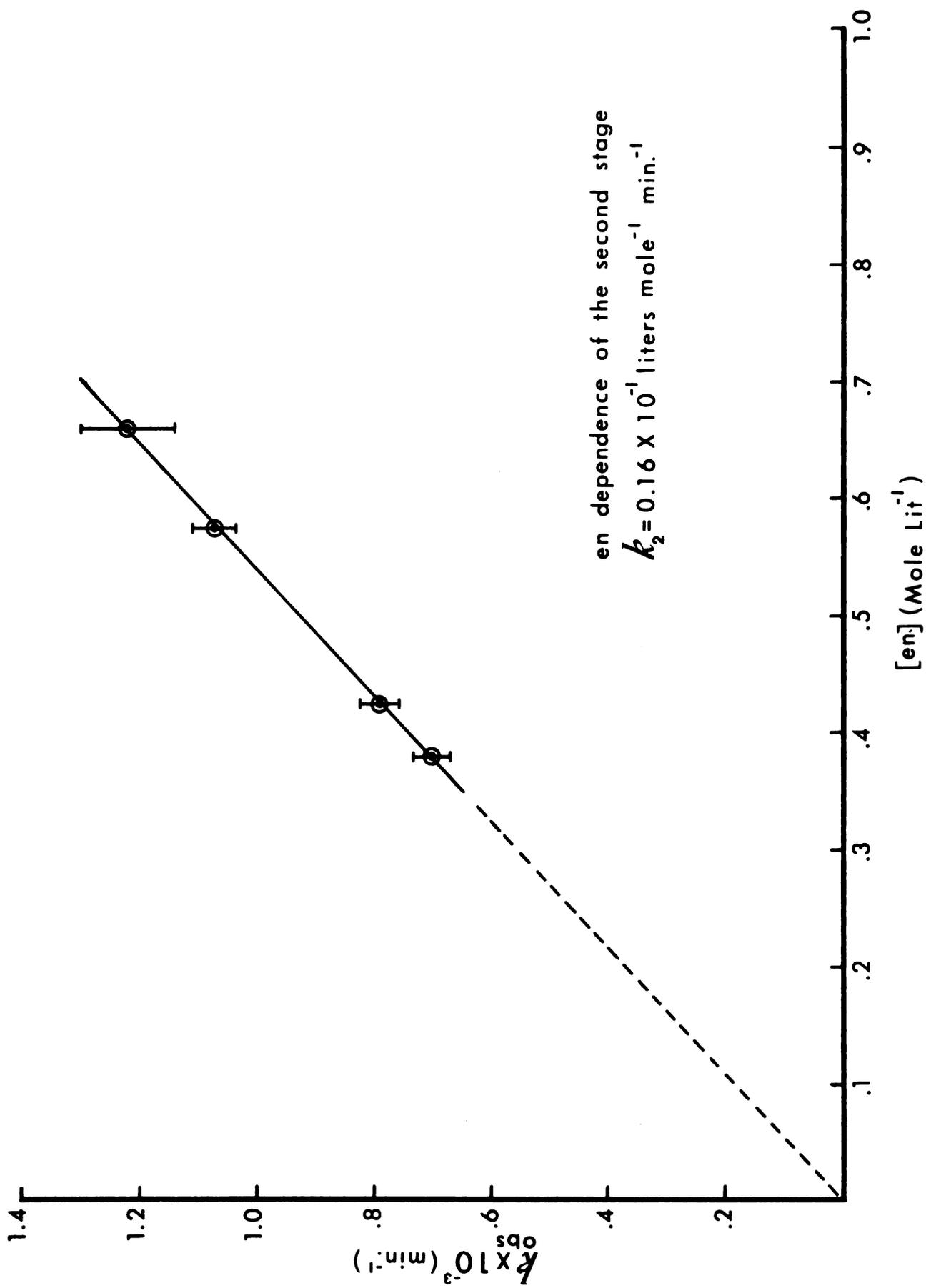


FIGURE XI

Ethylenediamine Dependence of the Rate of the Second Step



C. Sodium Hydroxide Dependence of the Reaction Rate

The rates of both the first and the second steps are dependent on the sodium hydroxide concentration, similar to that found for the reaction between NiMMK and 1,3-propanediamine; the rate stays constant at higher hydroxide concentration. The resulting rate constants are tabulated in Table VIII a and b. Figure XII shows the plot of $\ln(A_{\infty} - A_t/A_{\infty} - A_0)$ vs. time. The slope of these lines are pseudo first-order rate constants at different concentrations of sodium hydroxide. A plot of the observed rate constant vs. sodium hydroxide concentration for both steps are shown in Figures XII and XIV.

As was mentioned earlier, by increasing the sodium hydroxide concentration, the concentration of the ethanol in the reaction mixture increases, and due to its inhibitory property, rate decreases (as is shown in Figures XIII and XIV). The estimated third order rate constants for the first and the second stage are $32.93 \text{ lit}^2 \text{ mole}^{-2} \text{ min}^{-1}$ and $11.65 \text{ lit}^2 \text{ mole}^{-2} \text{ min}^{-1}$ respectively.

TABLE VIII

[Sodium Hydroxide] Dependence of the First and Second Step

a. First Stage

<u>[OH] x 10²M</u>	<u>k_{obs} x 10²min⁻¹</u>	<u>standard deviation %</u>
0.092	2.95	+ -3.0
0.123	3.60	+ -4.0
0.185	3.70	+ -4.0
0.246	3.70	+ -5.0
0.308	3.80	+ -4.0

b. Second Stage

0.092	0.43	+ -6.0
0.123	0.66	+ -3.0
0.185	1.05	+ -3.0
0.308	1.26	+ -3.0
0.401	1.29	+ -2.0

FIGURE XII

Sodium Hydroxide Dependence of the Rate for the Second Step

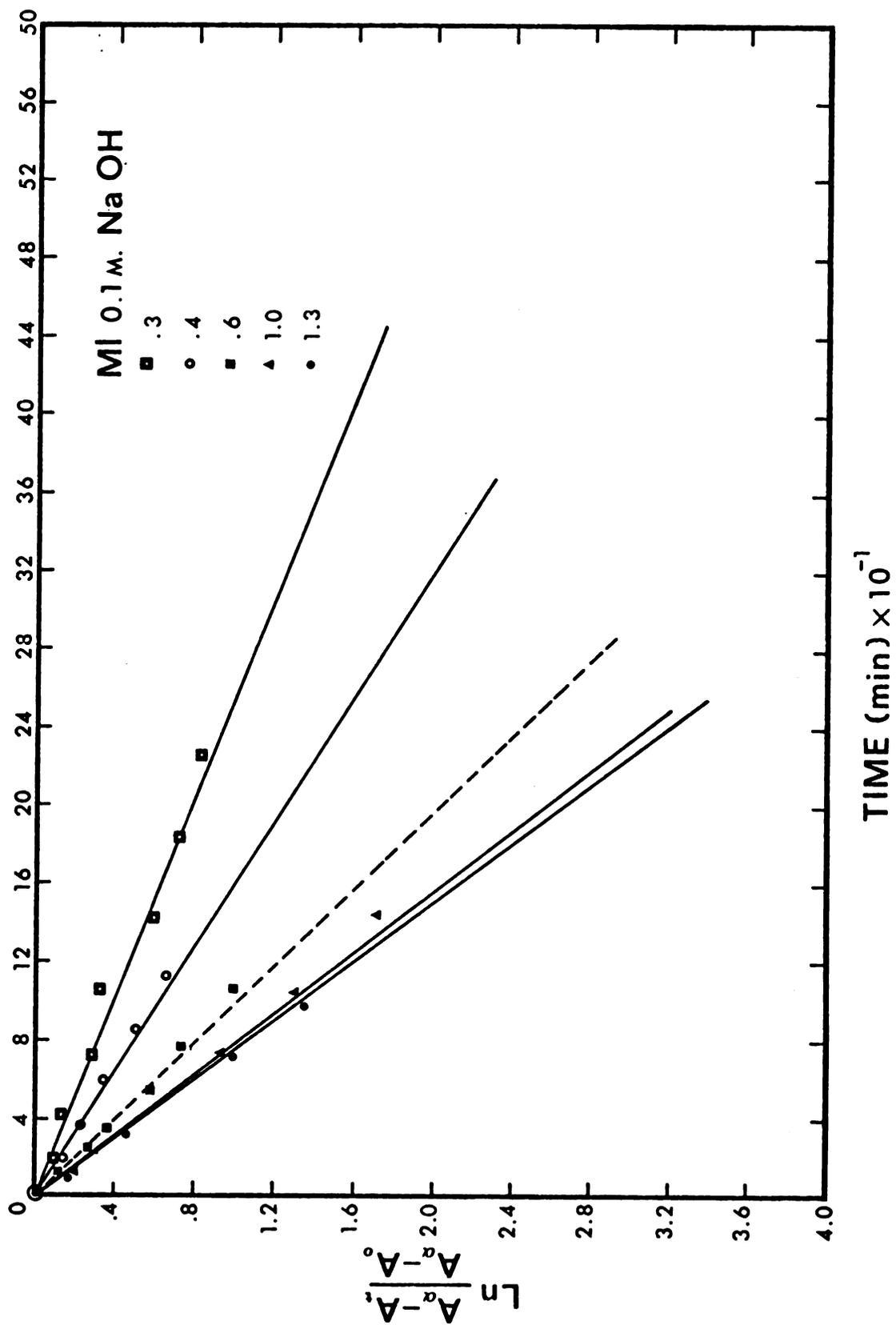


FIGURE XIII
Sodium Hydroxide Dependence of the First Step
for the Reaction between NiMMK and Ethylenediamine

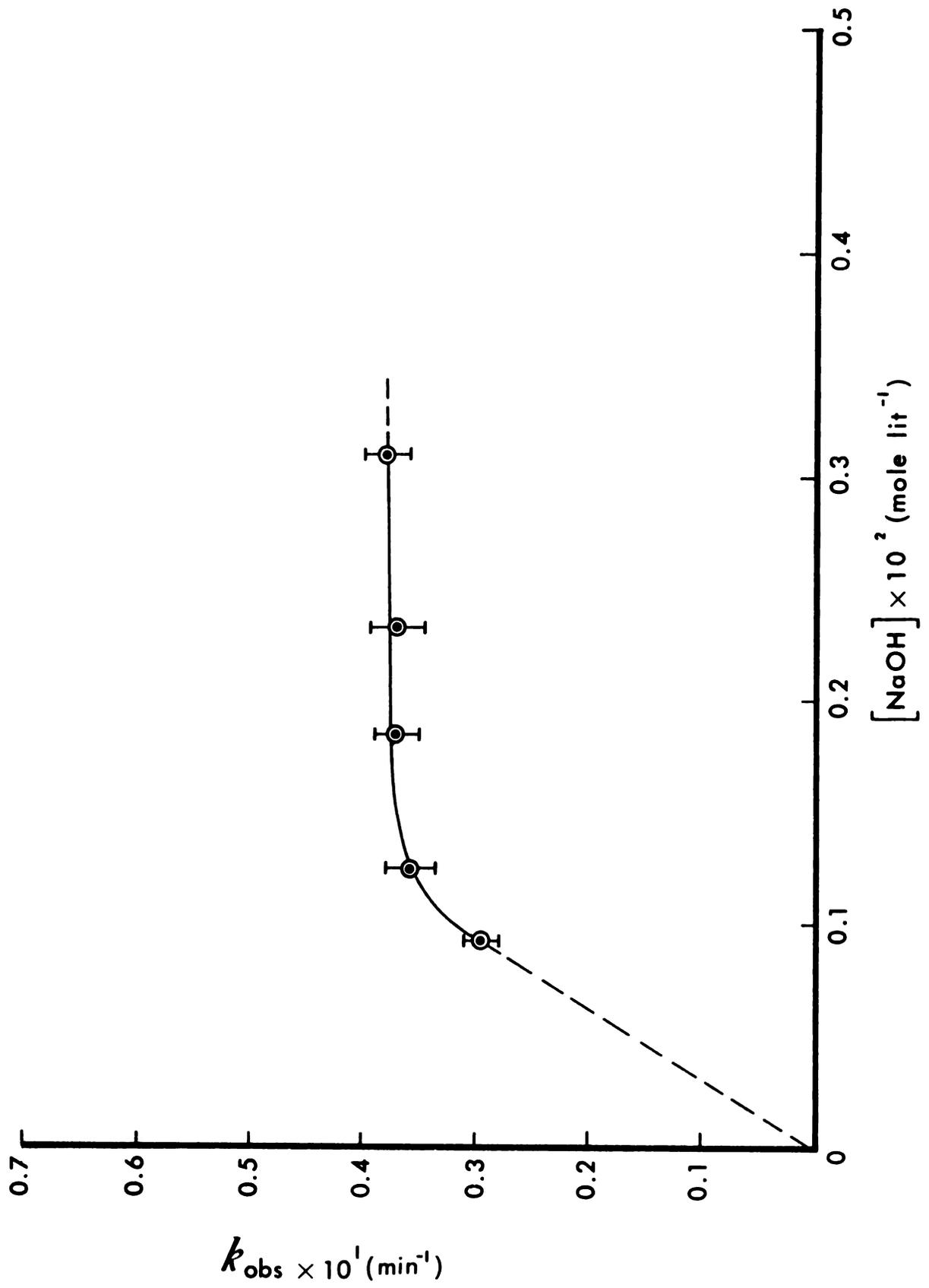
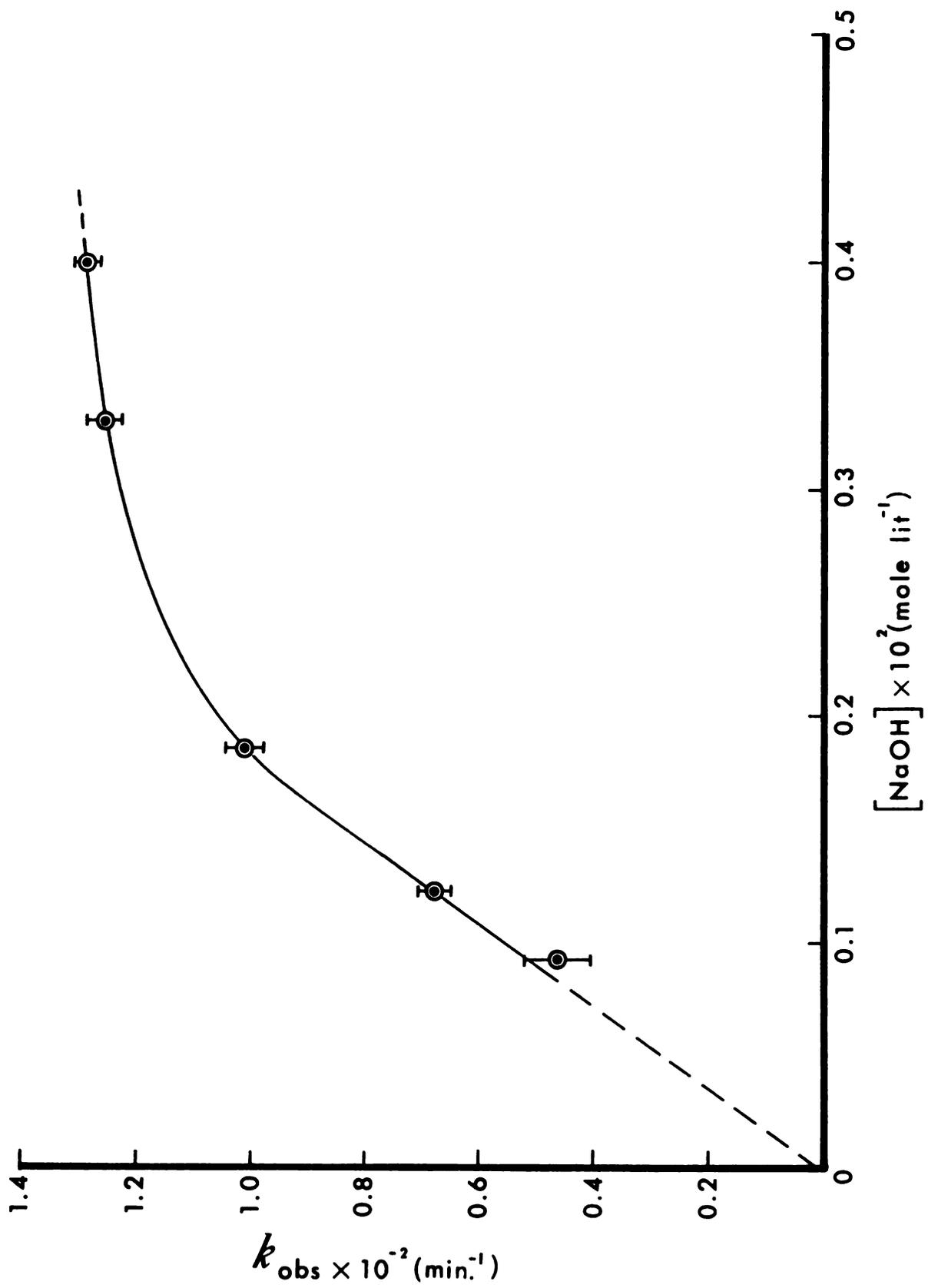


FIGURE XIV
Sodium Hydroxide Dependence of the Second Step
for the Reaction between NiMMK and Ethylenediamine

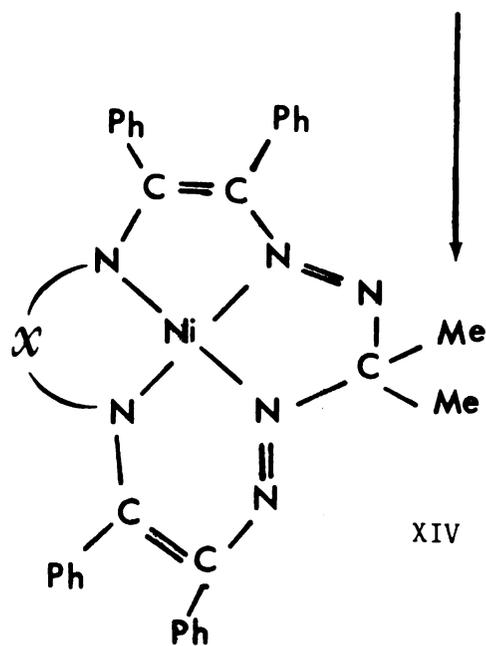
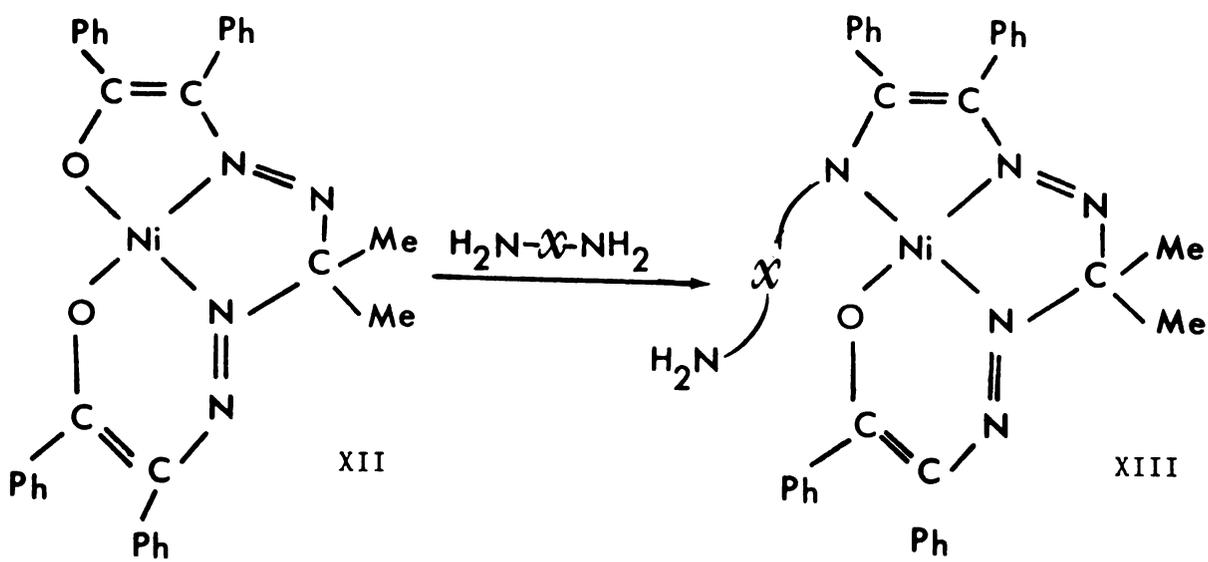


CHAPTER FOUR

MECHANISM OF THE REACTIONS

The reaction of NiMMK with amines results in the formation of two types of complexes, the macrocycle (X) and non-cyclic (XI) complexes. These compounds are obtained by the condensation of the CO group(s) of NiMMK with one or two amine groups and the elimination of one or two molecules of water^{35,36}.

With 1,3-propanediamine, only one of the CO groups has undergone condensation, whereas with ethylenediamine both of the CO groups have taken part in the condensation reaction (compare Figures I and VI). It thus appears that the ring closure reaction proceeds via a stepwise process in which the coordinated CO groups react successively.



Since the CO groups are of different types, one is part of a five membered chelate ring; the other part of a six-membered ring their reactivities may be different. By study of the fragmentation pattern of the mass spectrum of NiApSo it seems that the fragments of the six-membered ring predominates (see Table IX), and thus we conclude that the CO groups of the five membered ring preferentially reacts faster. The data obtained from the fragmentation pattern of this compound are shown in Table IX.

Although attempts to isolate the intermediate species in the ring closure reaction have not been successful, there are indications for the existence of intermediate in the reaction mixture.

Benzoyl Derivative of the Intermediate

100 ml. of $\approx 3.3 \times 10^{-3}$ M solution of NiMMK in acetonitrile and ethylenediamine (0.6M) were mixed, and refluxed. The reaction was followed by Unicam spectrophotometer until the spectrum of the reaction mixture was close to the spectrum of the NiApSo (see spectrum number 5 of Figure VI). At this time the reaction mixture was cooled to prevent the progress of the reaction. 1.5 ml of benzoyl chloride was added to a solution of 15 ml chloroform and 60 ml of a 5% solution of sodium hydroxide. This mixture was then added to the quenched solution of the reaction mixture. The solution was stirred for about twenty minutes at room temperature and then allowed to stand for twelve hours in a separatory funnel. The higher level of separatory funnel was evaporated and then introduced to the mass spectrometer. The spectra showed a benzoyl derivative of the dangling complex (XV, M.W = 690).

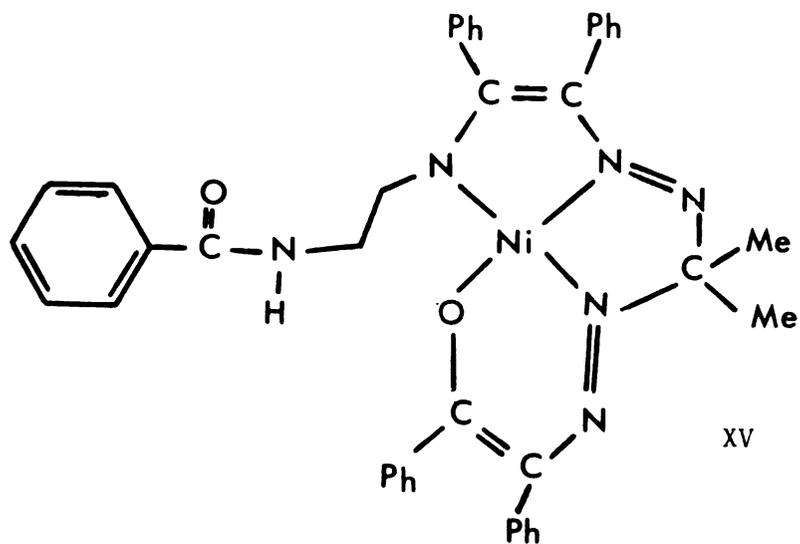
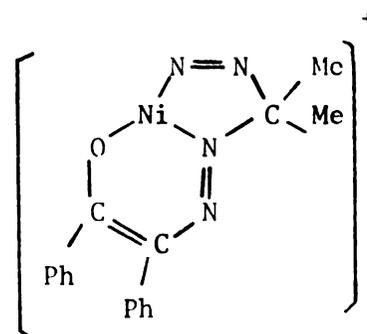


TABLE IX
Mass Spectrum of NiApSo

m/e^a	Assignment Leaving Group	Assignment Residue
p-15	$-\text{CH}_3$	
p-28	N_2	
p-56	$\text{NC}(\text{CH}_3)_2$	
p-84	$\text{N}=\text{N}-\underset{\text{N}}{\text{C}}(\text{CH}_3)_2$	
p-159	$\text{Ph}-\text{C}-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2$	
p-187	$\text{Ph}-\text{C}-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2-\text{N}=\text{N}$	
p-250 ^b	$\text{Ph}-\text{C}=\text{C}(\text{Ph})-\text{N}-(\text{CH}_2)_3-\text{NH}_2^b$	
p-276	$\text{Ph}-\text{C}=\text{C}(\text{Ph})\text{N}=\text{N}-\text{C}(\text{CH}_3)_2$	
p-290	$\text{Ph}-\text{C}(\text{N})=\text{C}(\text{Ph})\text{N}=\text{N}-\text{C}(\text{CH}_3)_2$	

350



308

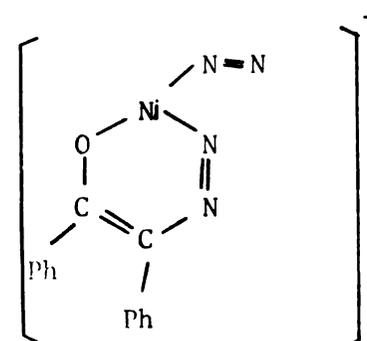


TABLE IX
Continued

m/e	Assignment Leaving Group	Assignment Residue
294		
280		
236		$[\text{Ni-N-C(Ph)-C(Ph)}]^+$
222		$[\text{O-C(Ph) = C(Ph)-N = N}]^+$
202		
178		$[\text{PhC(NH)CPh}]^+$
77		$[\text{Ph}]^+$

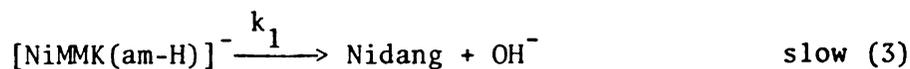
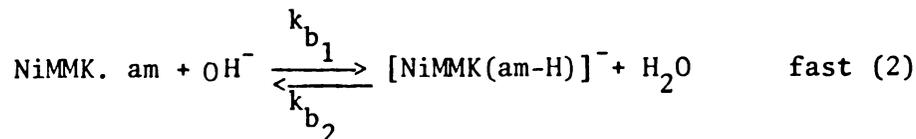
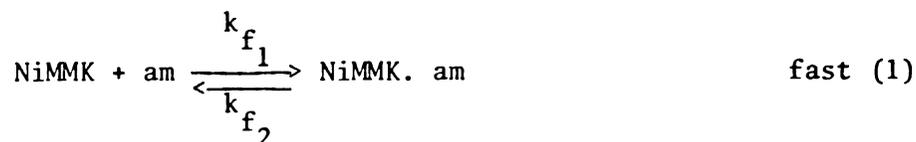
a. for nickel containing species the value for ^{58}N is given

b. for dangling compounds only

The experimental results (based on the dependence of the rate of the reaction on the concentration of amines, NiMMK and sodium hydroxide) have shown that for each stage the overall reaction is a third order, and is first order with respect to each of the reactants.

A mechanism consistent with the observed results and a derivation of the rate equation is suggested as follows:

a. For 1,3-propanediamine and NiMMK reactions:



$$\frac{d(\text{Nidang})}{dt} = k_1 [\text{NiMMK}(\text{am-H})]^-$$

from 2

$$K_b = \frac{[\text{NiMMK}(\text{am-H})]^- [\text{H}_2\text{O}]}{[\text{NiMMK} \cdot \text{am}] [\text{OH}^-]}$$

$$[\text{NiMMK}(\text{am-H})]^- = K_b \frac{[\text{OH}^-]}{[\text{H}_2\text{O}]} \cdot [\text{NiMMK} \cdot \text{am}]$$

$$\frac{d(\text{Nidang})}{dt} = k_1 K_b \frac{[\text{OH}^-]}{[\text{H}_2\text{O}]} \cdot [\text{NiMMK} \cdot \text{am}]$$

from 1

$$[\text{NiMMK. am}] = K_f [\text{NiMMK}] [\text{am}]$$

$$\frac{d(\text{Nidang})}{dt} = k_1 K_b K_f \frac{[\text{OH}^-]}{[\text{H}_2\text{O}]} \cdot [\text{NiMMK}] [\text{am}]$$

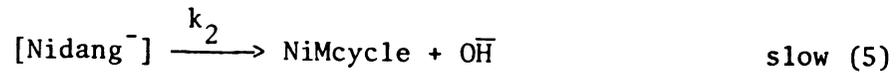
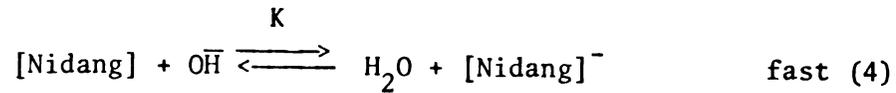
assume

$$k_3 = k_1 K_b K_f$$

Therefore

$$\frac{d(\text{Nidang})}{dt} = k_3 [\text{OH}^-] [\text{NiMMK}] [\text{am}] / \text{H}_2\text{O}$$

b. For ethylenediamine and NiMMK reaction:



$$\frac{d(\text{NiMcycle})}{dt} = k_2 [\text{Nidang}]^-$$

But

$$K = \frac{[\text{H}_2\text{O}] [\text{Nidang}]^-}{[\text{OH}^-] [\text{Nidang}]}$$

$$[\text{Nidang}]^- = \frac{K [\text{OH}^-] [\text{Nidang}]}{\text{H}_2\text{O}}$$

$$\text{Therefore } \frac{d(\text{NiMcycle})}{dt} = k_2 K \frac{[\text{OH}^-] [\text{Nidang}]}{\text{H}_2\text{O}}$$

CHAPTER FIVE

SUGGESTIONS FOR FUTURE WORK

In addition to the determination of the activation energy, entropy and enthalpy of the reaction of diamines with NiMMK, there are several other areas that should be investigated.

Fragmentation pattern of NiApSo in mass spectrometer shows that the site of the first condensation is the five-membered chelate ring, rather than the six-membered ring (see Table IX). Work has to be done on the crystal structure of NiApSo to support the idea; we are in the process of doing this.

We have also examined successfully reactions of 1,2-propanediamine with NiMMK and ethylenediamine with NiDMK (VII where R³ and R⁴ are methyl groups) in tetrahydrofuran. Their absorption spectra are shown in Figures XV and XVI respectively. Understanding their mechanism of the reaction needs more kinetics data; however reactions of NiMMK with 1,2 propanediamine shows very similar paths to those of NiMMK with ethylenediamine (compare Figures VI and XV).

FIGURE XV

Absorption Spectrum for Reaction of NiMMK with 1,2-Propanediamine

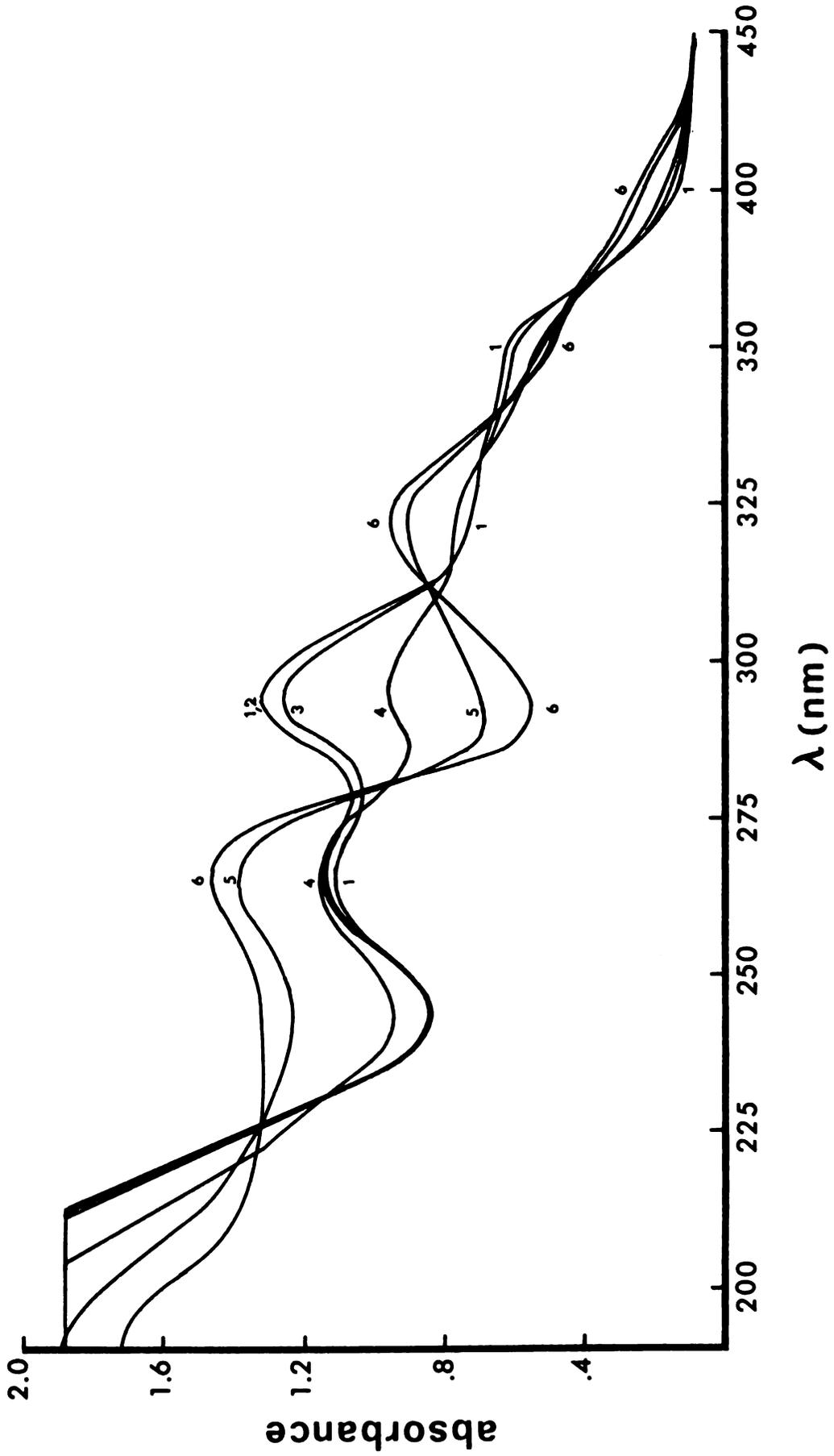
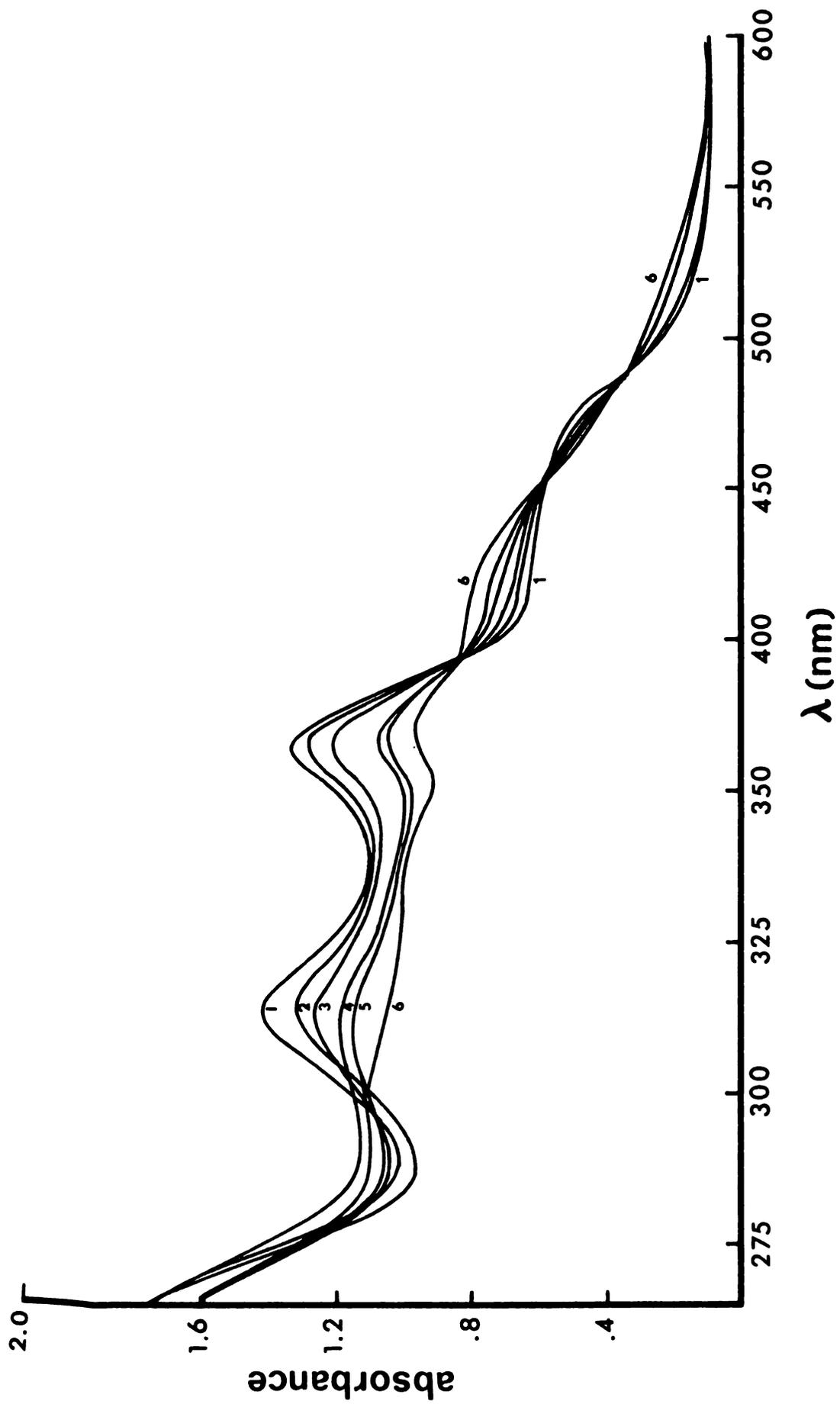


FIGURE XVI

Absorption Spectrum for Reactions of NiDMK with Ethylenediamine



APPENDIX

APPENDIX

During the preparation of this thesis we became aware of the Tektronix 4012 graphics terminal.* Reexamination of the kinetics data was carried out. The resulting plots obtained from the plotter are shown in Figures XVII-XX.** The program used for the plots is also included.

Figure XVII [NiMMK] Dependence for the Reaction between
1,3-Propanediamine and NiMMK

Figure XVIII [Sodium Hydroxide] Dependence for the First
Step of the Reaction between NiMMK and Ethylenediamine

Figure XIX [NiMMK] Dependence for the Second Stage of the
Reaction between NiMMK and Ethylenediamine

Figure XX [Sodium Hydroxide] Dependence for the Reaction
between NiMMK and 1,3-Propanediamine

*Special thanks to Lawrence Pachla for this information.

**The dotted line indicates the theoretical values; the triangles indicate the experimental values.

FIGURE XVII

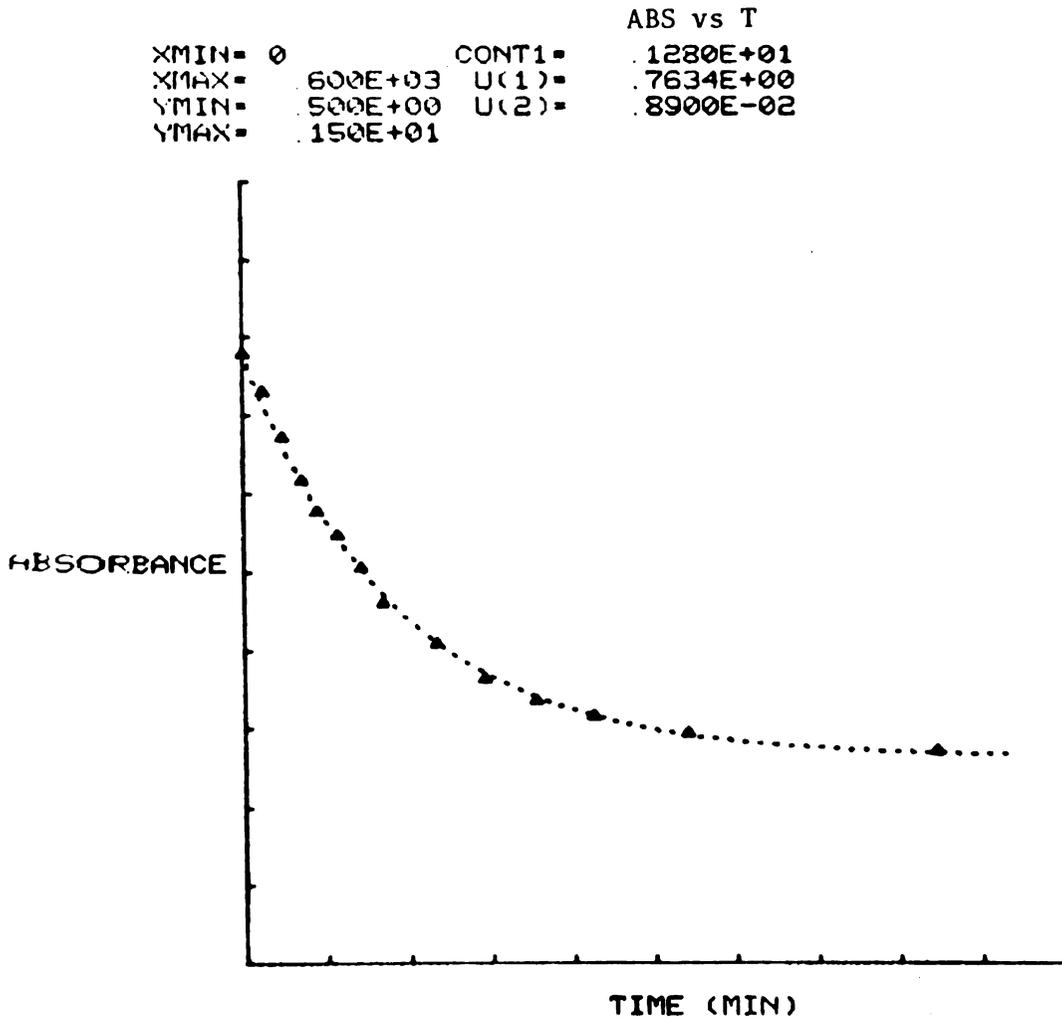


FIGURE XVIII

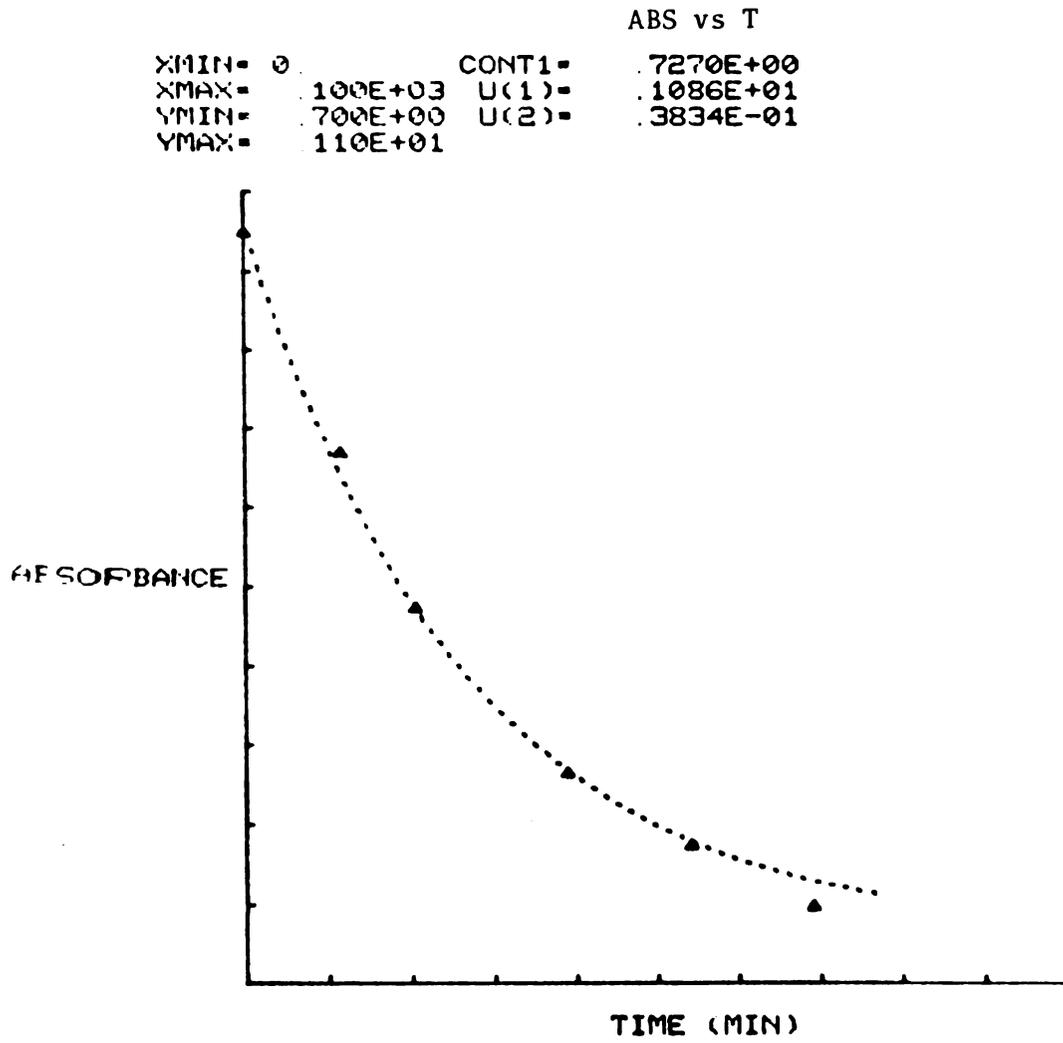


FIGURE XIX

XMIN=	0	CONT1=	.6630E+00
XMAX=	380E+03	U(1)=	.4260E+00
YMIN=	.400E+00	U(2)=	.1082E-01
YMAX=	.700E+00		

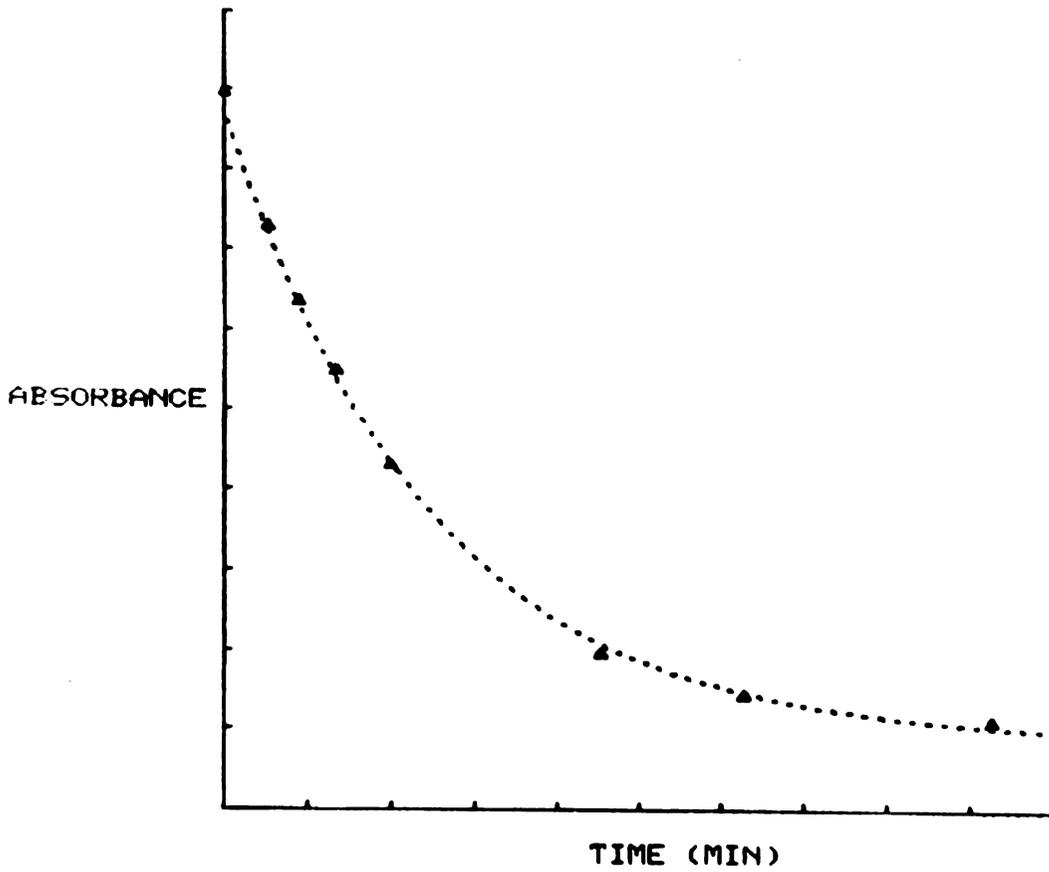
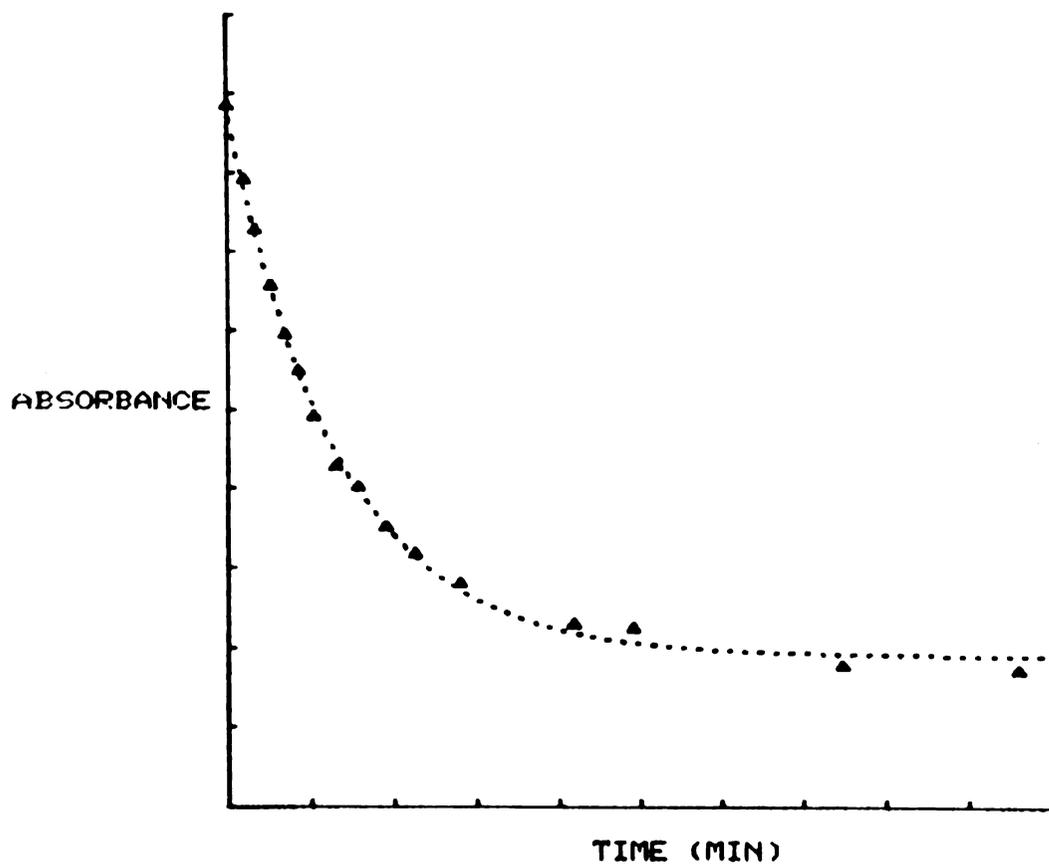


FIGURE XX

XMIN= 0	CONT1=	ABS VS T
XMAX= .780E+03	U(1)=	.1320E+01
YMIN= 700E+00	U(2)=	.8335E+00
YMAX= .140E+01		.9844E-02



PROGRAM PLOTT CALL EXECIT
235 64 CALL FINIT (500,400)
CDC 4500 FIN V3.0-P376 OPT=1 07/24/74 .00.36.47. PAGE 4

PAGE 1

CUC 4500 FTN V3.0-4376 OPT=1 07/24/74 .00.16.47.

SUBROUTINE TP=CI

```

SUBROUTINE TP=CI, TXNGI(K,XX,YY)
DIMENSION XX(20),YY(20)
DO 100 J=1,K
CALL POINTA (XX(J),YY(J))
CALL POINTB (0,J)
CALL POINTC (-4,-4)
CALL POINTD (8,0)
100 CALL DRWDEL (-4,4)
RETURN
END

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5

10

EXECUTIVE REFERENCE TABLE.

CCBUF	8	PROGRAM
CPE	17	EXTERNAL
EXECIT	16	PROGRAM
PARM		PROGRAM

2/05 L	2/14	2/16	07/24/76	00.36.53.	PAGE
2/07 L	2/12 L	2/22			3
2/11 F	2/16	2/19 S			
2/10 I		2/22			

CRIBASS - VER 2.

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