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## Reaction kinetics for the synthesis of benzyl benzoate from benzyl chloride and the triethylamine salt of benzoic acid

Michael A. Kolakowski  
*New Jersey Institute of Technology*

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REACTION KINETICS FOR THE SYNTHESIS  
OF BENZYL BENZOATE FROM BENZYL CHLORIDE  
AND THE TRIETHYLAMINE SALT OF BENZOIC ACID

BY

MICHAEL A. KOLAKOWSKI

A THESIS  
PRESENTED IN PARTIAL FULFILLMENT OF  
THE REQUIREMENTS FOR THE DEGREE  
OF  
MASTER OF SCIENCE IN CHEMICAL ENGINEERING  
AT  
NEW JERSEY INSTITUTE OF TECHNOLOGY

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Newark, New Jersey  
1976

APPROVAL OF THESIS  
REACTION KINETICS FOR THE SYNTHESIS  
OF BENZYL BENZOATE FROM BENZYL CHLORIDE  
AND THE TRIETHYLAMINE SALT OF BENZOIC ACID  
BY  
MICHAEL A. KOLAKOWSKI  
FOR  
DEPARTMENT OF CHEMICAL ENGINEERING  
NEW JERSEY INSTITUTE OF TECHNOLOGY  
BY  
FACULTY COMMITTEE

APPROVED:

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NEWARK, NEW JERSEY

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ABSTRACT

The reaction kinetics for the synthesis of benzyl benzoate from benzyl chloride and the triethylamine salt of benzoic acid has been studied over the temperature range of 70-105°C and a mole ratio of benzyl chloride to triethylamine of 0.5 - 10.0.

A reaction mechanism which is consistent with the experimental data has been derived. The experimental data was analyzed by means of the integral method of analysis. The temperature dependency of the reaction was determined from Arrhenius' Law and the activation energy was calculated to be 15,064 cal/g-mole. An empirical equation which explains the effects of the reactant mole ratio was derived.

The reaction under study turned out to be a pseudo first order reaction dependent upon the concentration of benzyl chloride. The observed first order reaction rate constant is a function of the initial mole ratio of triethylamine to benzyl chloride. The reaction occurs mainly by the  $S_N2$  mechanism.

The reaction kinetics studies should provide a useful tool in the evaluation of benzyl benzoate manufacturing processes.

### ACKNOWLEDGEMENTS

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## INTRODUCTION

Benzyl benzoate is considered an extremely useful material by perfumers, namely as a solvent and fixative. Benzyl benzoate is found in balsams of tolu and Peru, and in such oils as jasmin, ylang yland, and hyacinth. Synthetic musks, vanillin, and heliotropin are the major materials listed by trade that make use of benzyl benzoate as a solvent. In floral odors it is used as a fixative.

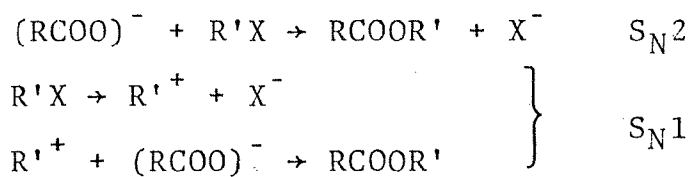
Its main contribution as a solvent is particularly noted for musks, many of which are not readily soluble in alcoholic solutions. Benzyl benzoate's odorless and high molecular weight characteristics are noted as its chief fixative values.

U.S. production statistics in 1972 show an annual production of 408,000 pounds with an annual growth rate of 12%. In 1972 benzyl benzoate was selling for 78 cents per pound. Today it is selling for \$1.25 per pound.

Manufacturing methods have reportedly improved over the years. Esterification of benzyl alcohol and benzoic acid was a comparatively costly process, and less expensive procedures have been found. There are three manufacturing procedures presently being used to produce

benzyl benzoate: by reacting sodium benzoate with benzyl chloride, by the condensation of benzaldehyde, or by the "transesterification" of benzyl alcohol with a suitable ester of benzoic acid. However these procedures give low yields and conversions along with competing side reactions.

In 1961 Merker and Scott prepared benzyl benzoate through the reaction of the triethylamine salt of benzoic acid with benzyl chloride. After washing with water, drying over anhydrous sodium sulfate, and distillation they report a 79% yield. The reaction is as follows:  $\text{RCOOH} + \text{R}'\text{X} + \text{R}''_3\text{N} \rightarrow \text{RCOOR}' + \text{R}''_3\text{NHX}$ . Merker and Scott suggest that ester formation appears to proceed by typical nucleophilic replacement mechanisms. They offer two possible mechanisms:



The degree to which the reaction occurs by the  $\text{S}_\text{N}1$  mechanism would be expected to increase with increasing electron repulsion of  $\text{R}'$  and increasing ionizing power of the solvent medium. They suggest kinetic studies to elucidate these factors.

An extensive literature search showed that no one has attempted this kinetic study.

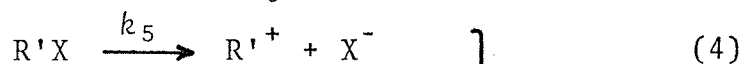
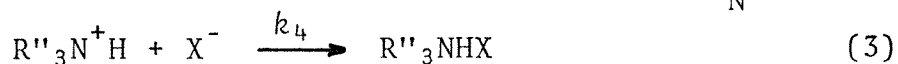
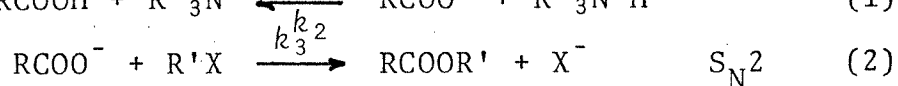
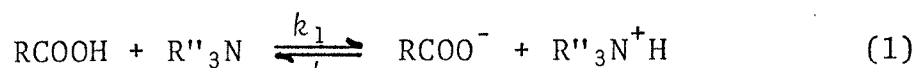
The purpose of this present work is to conduct a kinetic study of this reaction in xylene so that a thorough understanding of the reaction can be attained. The following information will be obtained in this study:

1. The effects of temperature on the reaction
2. The effects of mole ratio of reactants on the reaction
3. The actual mechanism of the reaction

No kinetic data are available in the literature.

# THEORY

A reaction mechanism has been established which explains a pseudo first order reaction. The steps involved in this reaction are:



The solution to the reaction rate expression based on this mechanism is:

$$-r_\text{A} = [k_3(\text{C}^*) + k_5] (\text{R}'\text{X}) \quad (6)$$

where the observed pseudo first order rate constant is equal to  $[k_3(\text{C}^*) + k_5]$ . This rate expression is derived in the appendix.

The symbols  $\text{S}_\text{N}2$  and  $\text{S}_\text{N}1$ , used to describe these processes are abbreviations:  $\text{S}_\text{N}1$  means substitution, nucleophilic, unimolecular, and  $\text{S}_\text{N}2$  means substitution, nucleophilic, bimolecular. The stereochemistry of the  $\text{S}_\text{N}1$  reaction is not as straightforward as that of the  $\text{S}_\text{N}2$  process, for the intermediate carbonium ion is not constrained to accept the nucleophile only at the opposite



side to the departing group: it can, and often does, accept the nucleophile at the same side of the carbon atom at which the departing group was attached. This difference between the  $S_N2$  and  $S_N1$  reactions can be understood when it is recalled that in the  $S_N2$  reaction the nucleophile is partly bonded before the displaced group is fully departed. In  $S_N1$ , on the other hand, the carbonium ion can have an existence that is independent of X and Y and thus can suffer attack by a nucleophile on two sides<sup>1</sup>.

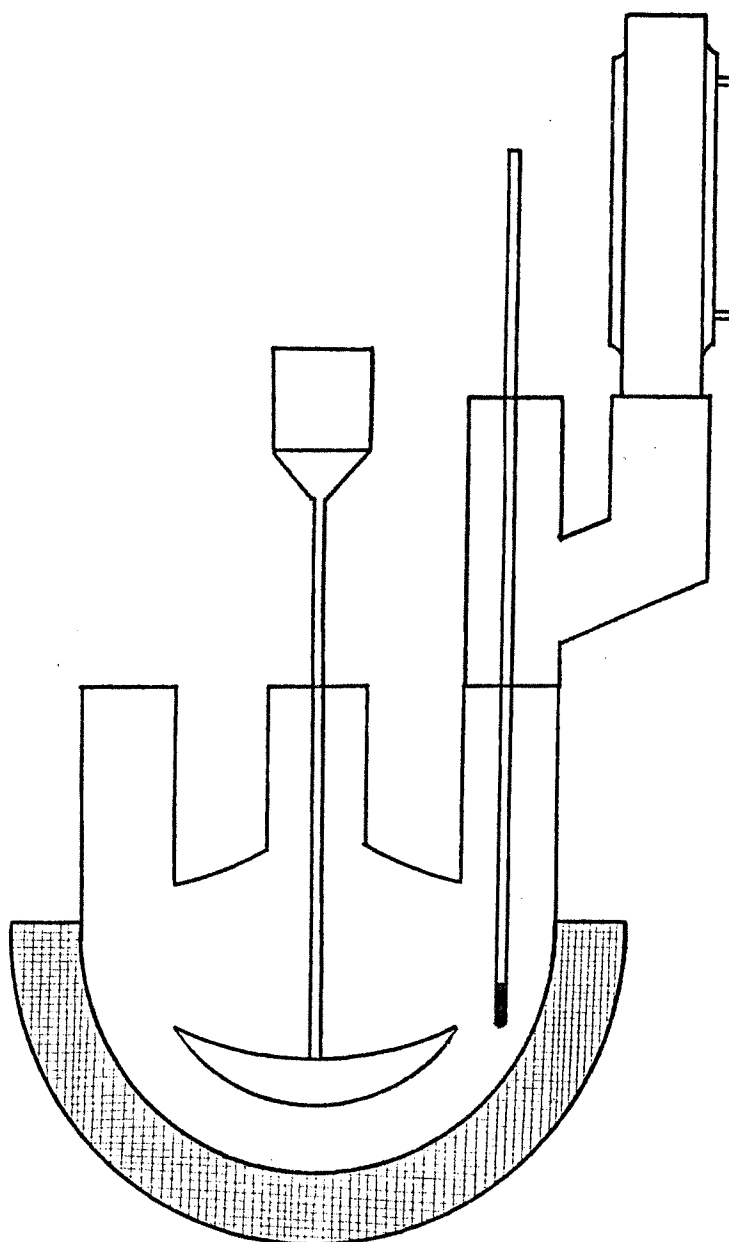
The essential difference between  $S_N1$  and  $S_N2$  displacements is seen to be principally in the formation of a carbonium ion intermediate in the  $S_N1$  reaction and the lack of formation of any free form of the alkyl group in the  $SN_2$  reaction.

### EXPERIMENTAL APPARATUS

A one liter, three neck, round bottom flask fitted with a stirrer, thermometer, reflux condensor, heating mantle and sample port was used in all experiments for this work. Figure 1 shows the assembly of this equipment.

When cooling was necessary the reaction flask was wrapped with rags which were soaked in an ice water bath. The ice water bath was also used to quench the reaction in the samples taken through out the experiments.

FIGURE 1  
EXPERIMENTAL APPARATUS



## EXPERIMENTAL PROCEDURE

### Chemical - Operating

To the flask as described in the experimental apparatus section was charged in order benzoic acid, toluene, and triethylamine in the quantities shown in Table 1 for each experiment. In each case the mixture was heated to approximately 10°C above the desired reaction temperature and allowed to attain steady state. When the temperature stabilized, the benzyl chloride was added to the solution in the quantities shown in Table 1 for each experiment, and the time noted. Since the reaction is exothermic, and under certain reaction conditions the temperature rose, it was necessary to cool down the reaction flask with rags soaked in ice water to maintain the desired temperature. This was especially true at the beginning of most experiments. No difficulty was encountered in controlling the reaction temperature  $\pm 0.5^\circ\text{C}$  by employing this method of cooling and an electric mantle for heating.

Samples were withdrawn from the sample port either 15 minutes or 30 minutes, depending on the anticipated results of each experiment, from the time of addition of the benzyl chloride, and every 15 or 30 minutes thereafter. a 10 ml pipette with a three way suction bulb proved to be quite a handy device for obtaining samples from the reaction flask. The reactions were continued for a three hour period or until a 90% or better conversion was

TABLE 1  
REAGENTS AND REACTION TEMPERATURE

<u>Exp. No.</u>	<u>Benzoic Acid</u>	<u>Xylene</u>	<u>Triethyl- Amine</u>	<u>Benzyl Chloride</u>	<u>Reaction Temp.</u>
	<u>gms</u>	<u>gms</u>	<u>gms</u>	<u>gms</u>	<u>°C</u>
A	146.8	264.0	121.5	151.8	80
B	146.8	264.0	121.5	227.7	80
C	146.8	264.0	121.5	151.8	80
D	146.8	264.0	121.5	151.8	79
E	146.8	264.0	121.5	151.8	96
F	146.8	264.0	121.5	151.8	105
G	146.8	264.0	121.5	151.8	99
H	146.8	264.0	121.5	151.8	70
I	109.8	264.0	90.9	227.8	80
J	61.0	232.0	50.5	316.4	80
K	36.6	264.0	30.3	379.7	80
L	73.3	264.0	60.7	76.0	80
M	146.5	264.0	121.4	76.0	80
N	109.8	264.0	90.9	113.9	80

obtained based on the limiting reagent.

In the case of experiment B the reaction was taken to 98% conversion at 80°C and allowed to agitate an additional 2 days. The triethylamine hydrochloride precipitate was then filtered from the xylene solution, washed three times each with 500 ml of fresh xylene and dried in a vacuum oven at 100°C and 28" Hg vacuum to a constant weight. The dried triethylamine hydrochloride was then weighed and 100% based on stoichiometry was recovered. This indicated that the reaction went to completion.

#### Data Procurement

Experiments were carried out in three major groups to study the effects of reactants, and to study the effects of initial concentration of reactants.

In each experiment samples of the reaction slurry were withdrawn either every 15 minutes or 30 minutes, depending on the anticipated reaction rate. Each sample was analyzed according to the potentiometric analytical procedure which is discussed in the analytical section, and the conversion determined from the respective calibration curve.

In each experiment, the reaction volume was noted both initially and at the end of reaction and found not

to change within 10% of the initial volume. Therefore the reaction volume was assumed constant. Since the total moles charged of each reactant is known and the volume of the reaction is known, the concentration of reactants and products at any given conversion can easily be calculated.

For example, Experiment A had a volume of 752 ml with an initial charge of 1.2 g-moles of triethylamine, benzoic acid, and benzyl chloride. This gives an initial concentration of 1.655 moles/liter for each reactant. As the reaction proceeds the concentrations will decrease at the rate of 0.01655 g-moles/liter/1% conversion. Table 7 of the Appendix gives the conversion factors used for each experiment to determine the concentration of each reactant.

#### Temperature Effects

Experiments were carried out at 70°C, 80°C, 96°C, 99°C and 105°C at a benzyl chloride to triethylamine mole ratio of 1.0 and initial concentrations of each reactant of 1.65 moles per liter. The concentration of triethylamine was recorded for each sample taken. The results are tabulated in Table 8 of the Appendix, and the concentration versus time plots are shown in Figures 8, 12, 13, 15 and 16 of the Appendix.

#### Reactant Mole Ratio Effects

Experiments were carried out at mole ratios of

benzyl chloride to triethylamine of 0.5, 1.0, 1.5, 2.0, 5.0 and 10.0. In each case the mole ratio of triethylamine to benzoic acid was 1.0. A constant temperature of 80°C was maintained during each experiment. The concentrations of triethylamine and benzyl chloride were recorded for each sample taken. The results are tabulated in Table 9 of the Appendix, and the concentration versus time plots are shown in Figures 8, 9, 16, 17, 18 and 20 of the Appendix.

#### Initial Reactant Concentration Effects

Experiments were carried out at a mole ratio of benzyl chloride to triethylamine of 1.0, at a temperature of 80°C and at initial reactant concentrations of 1.16 moles/liter, 1.45 moles/liter, and 1.65 moles/liter. The 1.65 moles/liter experiment was done in triplicate. The concentration of triethylamine was recorded for each sample taken. The results are tabulated in Table 10 of the Appendix and the concentration versus time plots are shown in Figures 8, 10, 11, 19 and 21 of the Appendix.

#### Analytical Procedure

To ensure accurate analysis of the samples obtained during each experiment, two analytical procedures were developed and checked against each other. Both procedures gave identical results and the potentiometric titration method, the less difficult of the two, was used for sample



analysis of the later runs.

#### Sample Preparation

Samples were prepared in the same fashion for both analytical procedures. Approximately 10 ml of sample were withdrawn from the reaction flask, placed in a 50 ml beaker and cooled in an ice water bath to quench the reaction. The cooled slurry was then filtered under vacuum and the filtrate collected and analyzed. This method ensures a representative sample since one of the products, triethylamine hydrochloride, is insoluble.

#### Gas Chromatograph Method

The first analytical method developed was based on the principles of Gas-Liquid Chromatography. In this method the various components of a sample are separated by means of their distribution between two phases. One of these phases is a stationary bed of large surface area which is a liquid spread as a thin film over an inert solid. The other phase is a continuous inert gas which percolates through the stationary bed. The solvent selectivity retards the sample components, according to their distribution coefficient, until they form separate bands in the carrier gas. These component bands leave the column in the gas stream and are recorded as a function of time by a detector.

In this particular case the stationary phase was a 6 ft x 1/4 in column containing 10% Octoil S [di-2 (ethylhexyl) sebacate] on 60/80 mesh Chromosorb W. The continuous phase was a stream of nitrogen gas flowing at a constant rate of 75 ml/min. A thermal conductivity detector was used connected to a strip chart recorder. A programmed temperature of 10°C/min over the range of 50-225°C was used along with a chart speed of 2 inches/minute. The Attenuator was set at 4 and a 1 microliter sample was used.

The first step of the method development was to inject samples of each pure component of the expected sample mixture into the gas chromatograph to determine their respective retention time and temperature. The following data were obtained: triethylamine 60°C, xylene 82°C, benzyl chloride 105°C, benzoic acid 142°C, and benzyl benzoate 203°C. Each component gave a sharp peak except for the benzoic acid. It was then decided to follow the reaction by taking the area fraction of benzyl benzoate to the total area of benzyl chloride plus benzyl benzoate. This eliminated any errors caused by the roundness of the benzoic acid peak and the accuracy of sample size.

The next step of the method development was the preparation of a calibration curve. Samples were

carefully prepared of the various components at different conversions and injected into the gas chromatograph. The height and width at half-height of the benzyl chloride and benzyl benzoate peaks were measured and areas for each peak were calculated. The area fraction of benzyl benzoate was also calculated and plotted as a fraction of conversion. Table 11 of the Appendix represents the results of this calibration. Figure 22 of the Appendix is the calibration curve for this system.

Samples from the experimental runs were injected into the gas chromatograph and the peak areas were calculated by the height times width at half-height method and the area fraction of benzyl benzoate was calculated. The conversion was obtained from Figure 22 of the Appendix.

#### Potentiometric Titration Method

The second analytical method developed was a potentiometric titration method. In this method the filtered sample was weighed on an analytical balance to the nearest 1/10 mg. The sample size was determined by the expected endpoint at 25 ml of titrant. The weighed sample was diluted with 50 ml of ethyl alcohol and titrated with 0.1 Normal hydrochloric acid to a pH of 3.5. The results were calculated to a milliequivalent per gram of sample number and the % conversion read from a

calibration curve. The calibration curves were calculated from theory based on stoichiometry. Tables 12 and 13 of the Appendix are examples of these calculations. Figures 23 through 31 of the Appendix represent the calibration curves used for all experiments.

The endpoint of  $\text{pH} = 3.5$  was determined from a plot of  $\text{pH}$  versus ml of 0.1 N hydrochloric acid. A total of four samples, representing different degrees of conversion, was used to draw the plot. Figure 32 of the Appendix represents this plot.

## DISCUSSION OF RESULTS

The experimental kinetic data was analyzed by means of the integral method of analysis. Because of the overall reaction equation, the test for an irreversible bimolecular-type second-order reaction was first attempted. Since in our first series of experiments the reactants were used in the stoichiometric ratio, a plot of  $1/CA$ , concentration of triethylamine, versus time was made. This plot did not yield a straight line. Since third order reactions are rare, the data was tested for an irreversible unimolecular-type first-order reaction. A plot of  $-\ln(CA/CA_0)$  versus time gave a straight line through the origin. The slope of this line is the reaction rate constant,  $k$ . The units of  $k$  are reciprocal hours. Since the overall reaction is first order, additional experiments were made to find the temperature dependency on the reaction rate constant and to find which reagent concentration determined the overall reaction rate.

### Temperature Dependency

The data from Experiments A, E, F, G and H were calculated to the form of  $-\ln(CA/CA_0)$  and compiled in Table 2. Plots of this form versus time were made and are shown in Figures 2 and 3. The values of the reaction

rate constant were calculated from the slopes of the plots and are summarized in Table 3. An arrhenius graph was made and gave a straight line as shown in Figure 4. The slope of this line is equal to  $-E/R$ , where  $E$  is activation energy and  $R$  is the universal gas constant and equal to 1.987 calories per gram mole per degree Kelvin. The activation energy calculates to 15,064 cal/g-mole from this plot.

#### Reactant Mole Ratio Dependency

Thus far the analysis shows that the overall reaction is first order and an Arrhenius type temperature dependency of the reaction. The next step of the analysis is to find which reactant concentration controls the reaction rate. Experiments were carried out at 80°C, a mole ratio of triethylamine to benzoic acid of 1.0 and mole ratios of benzyl chloride to triethylamine of 0.5, 1.0, 1.5, 2.0, 5.0 and 10.0. This analysis showed that the reaction rate was dependent on the benzyl chloride concentration. The data from these experiments was calculated to the form of  $-\ln(CA/CA_0)$  and compiled in Table 4. First order plots of these data were made and are shown in Figures 5 and 6.

Values of the reaction rate constant were calculated from the slopes of these figures and the results are tabulated in Table 5.

TABLE 2  
FIRST ORDER DATA  
STOICHIOMETRIC MOLE RATIO

TIME HRS.	Temperature				
	EXP. A 80°C	EXP. E 96°C	EXP. F 105°C	EXP. G 99°C	EXP. H 70°C
0.00	0.000	0.000	0.000	0.000	0.000
0.25	---	0.262	0.606	0.361	---
0.50	0.177	0.675	1.392	0.886	0.270
0.75	---	1.063	2.215	1.887	---
1.00	0.640	1.345	---	2.621	0.361
1.25	---	1.928	---	---	---
1.50	0.932	1.887	---	---	0.542
2.00	1.550	---	---	---	0.775
2.50	1.970	---	---	---	0.916
3.00	2.333	---	---	---	1.194

TABLE 3  
REACTION RATE CONSTANT SUMMARY  
TEMPERATURE DEPENDENCY

<u>TEMP.</u> <u>°C</u>	<u>k</u> <u>hr<sup>-1</sup></u>	<u>EXP.</u> <u>NO.</u>
70	0.38	H
80	0.77	A
96	1.36	E
99	2.41	G
105	2.92	F



FIGURE 2  
FIRST ORDER DATA  
RUNS A, E, F

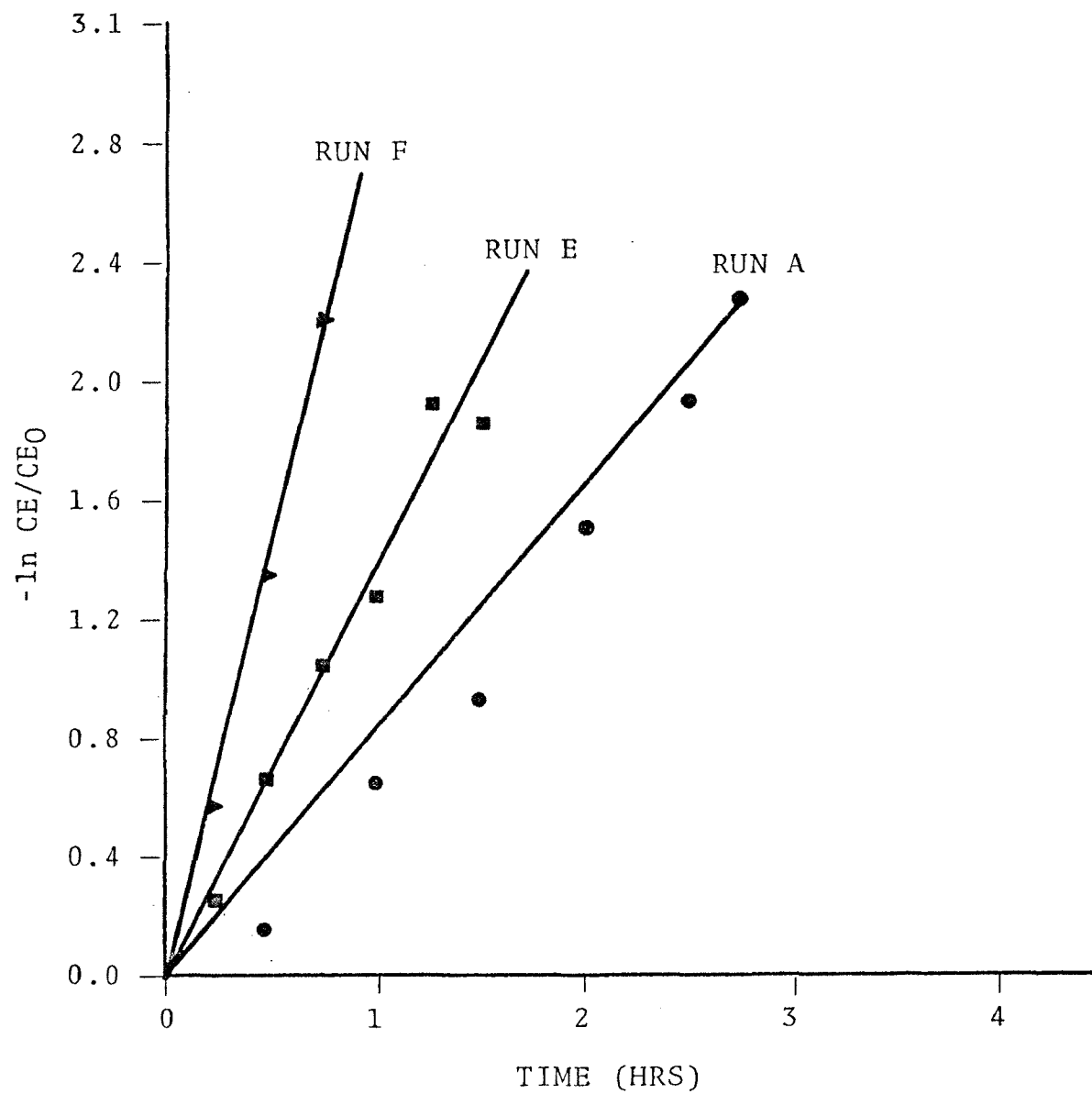


FIGURE 3  
FIRST ORDER DATA  
RUNS G, H

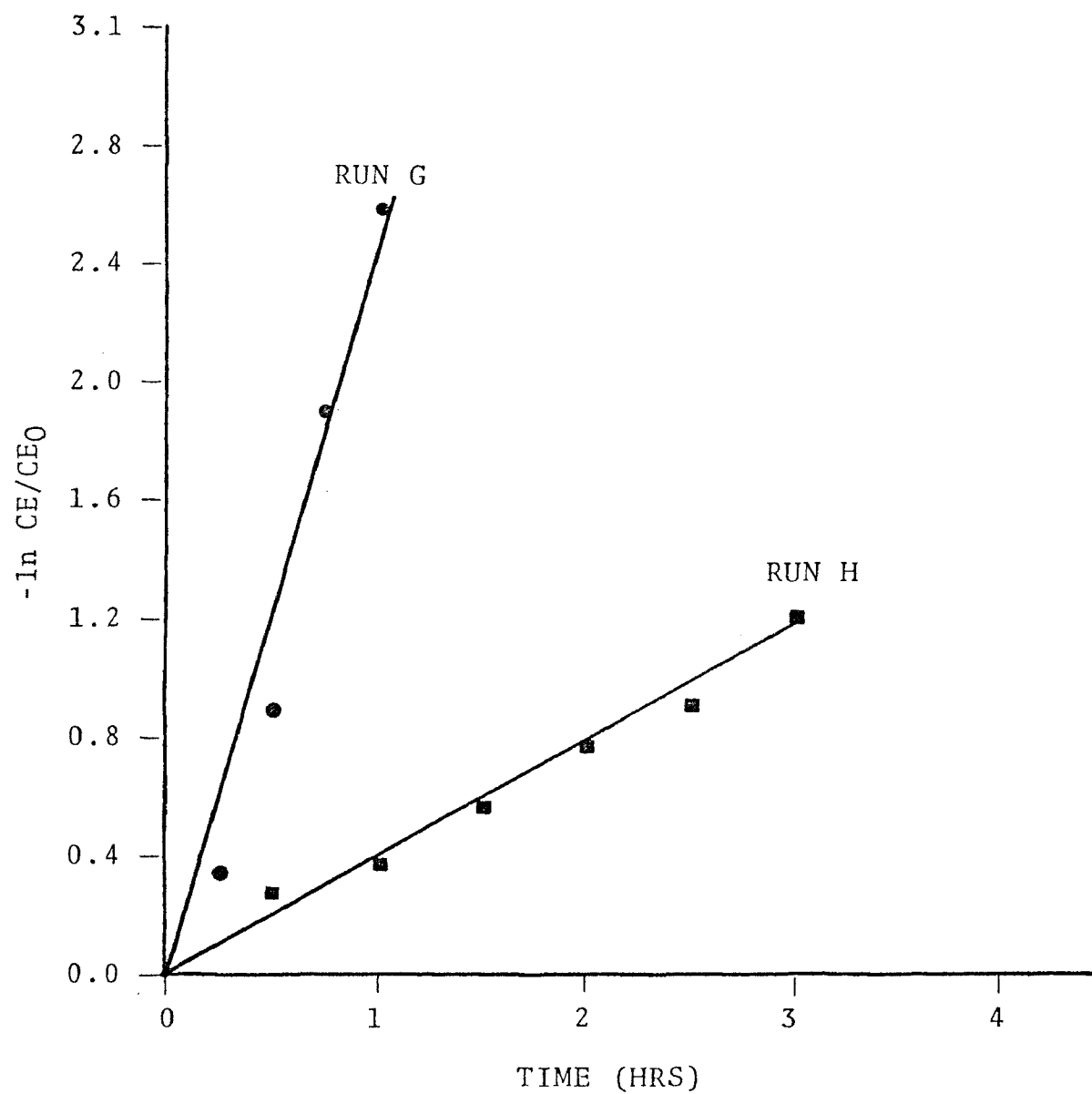


FIGURE 4  
ARRHENIUS PLOT

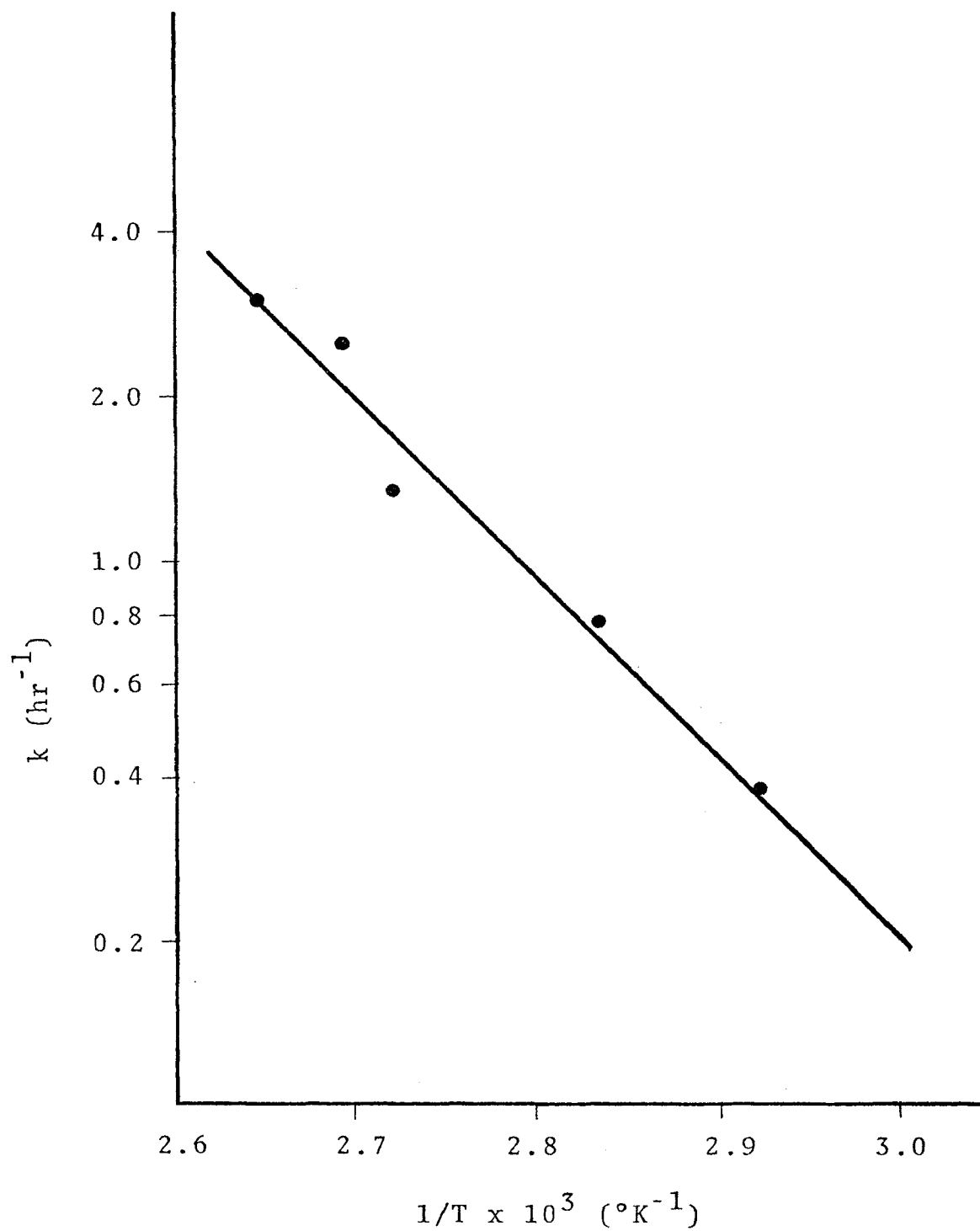


TABLE 4  
FIRST ORDER DATA  
REACTANT MOLE RATIO DEPENDENCY

TIME HRS.	Mole Ratio					
	EXP. A 1.0	EXP. B 1.5	EXP. I 2.0	EXP. J 5.0	EXP. K 10.0	EXP. M 0.5
0.00	0.000	0.000	0.000	0.000	0.000	0.000
0.25	---	---	0.080	0.050	0.024	---
0.50	0.177	0.214	0.152	0.095	0.039	0.496
0.75	---	---	0.266	0.153	0.062	---
1.00	0.640	0.601	0.395	0.194	0.082	0.784
1.25	---	---	0.530	0.211	0.096	---
1.50	0.932	0.975	0.616	---	---	1.303
2.00	1.550	1.035	---	---	---	1.957
2.50	1.970	---	---	---	---	2.912
3.00	2.333	---	---	---	---	---

FIGURE 5  
FIRST ORDER DATA  
RUNS B, I, J

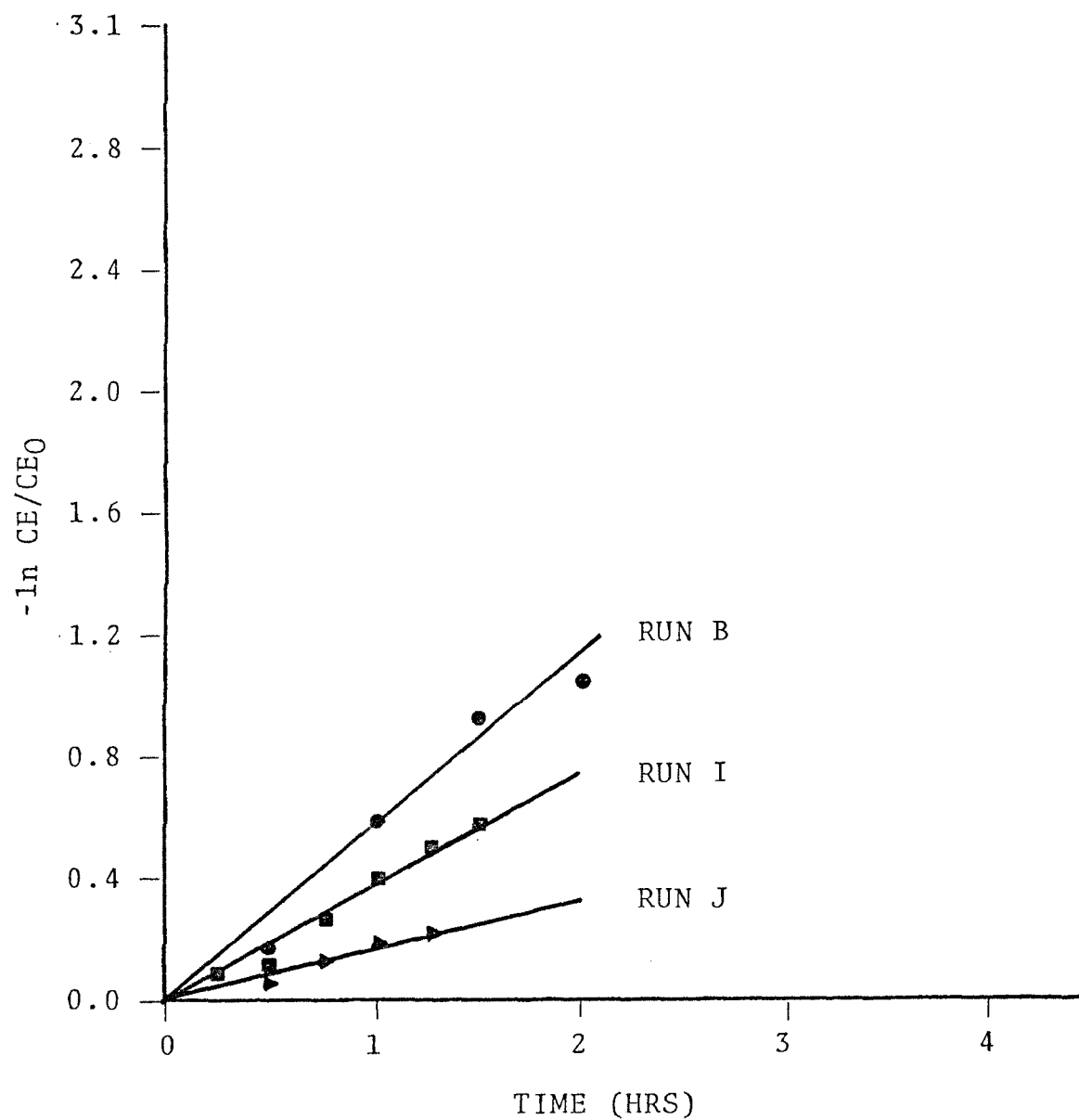
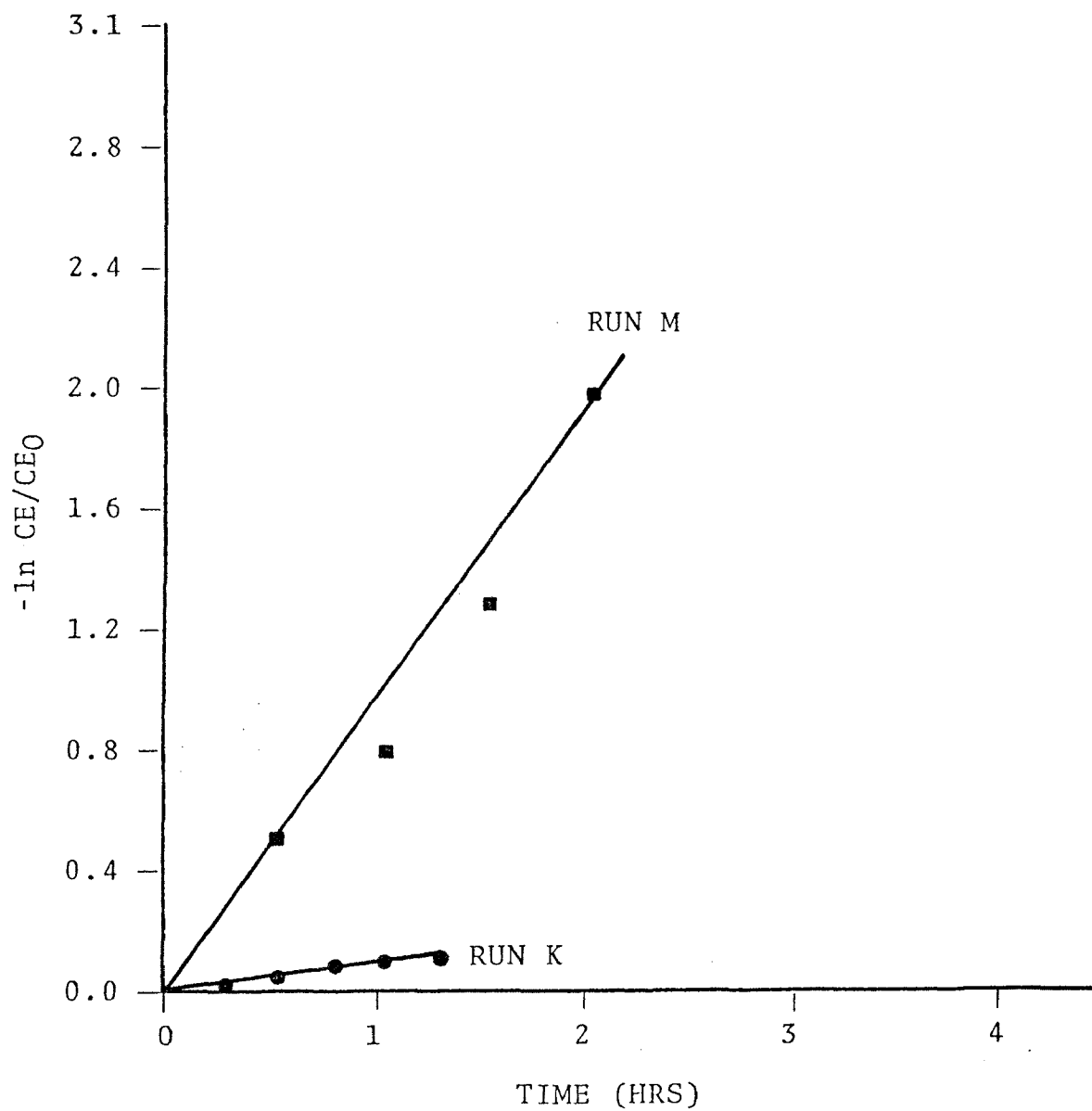


FIGURE 6  
FIRST ORDER DATA  
RUNS K, M



As can be seen from the data in Table 5, the reaction rate constants vary as a function of the initial mole ratio of benzyl chloride to triethylamine. Obviously this is not a simple first order reaction but a pseudo first order reaction with the observed reaction rate constant being a function of the initial mole ratio of benzyl chloride to triethylamine.

#### Empirical Solution

To determine the role of the initial mole ratio of benzyl chloride to triethylamine upon the observed reaction rate constant, an empirical equation was derived from a plot of the observed reaction rate constant ( $k_{\text{obs.}}$ ) versus the initial mole ratio of triethylamine to benzyl chloride. this plot is shown in Figure 7 and shows the relationship as an equation of the form.

$$k_{\text{obs.}} = 0.03 + 0.755 (M) \quad (7)$$

where  $M$  = the initial mole ratio of triethylamine to benzyl chloride. Substituting this value for the reaction rate constant into the reaction rate equation the following expression is derived.

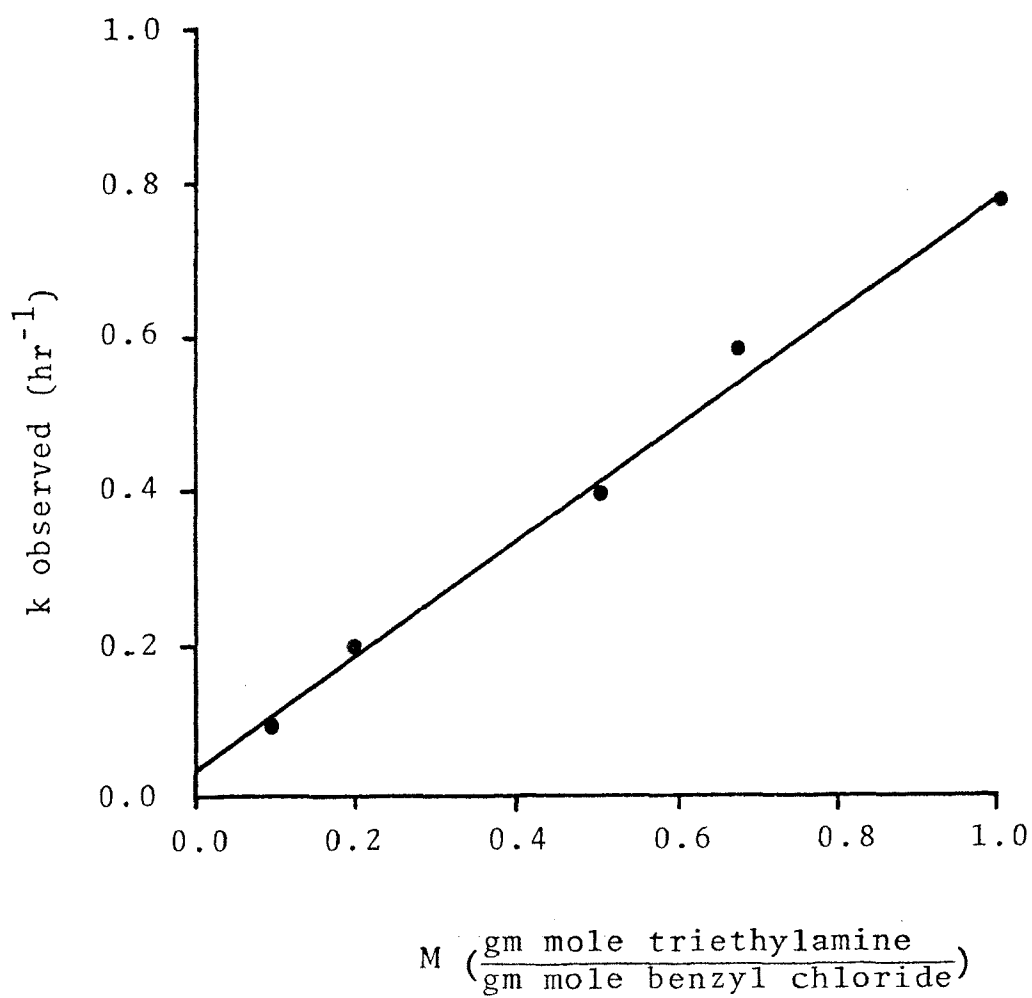
$$-r_A = (0.03 + 0.755M)[E] \text{ at } 80^\circ\text{C} \quad (8)$$

TABLE 5  
REACTION RATE CONSTANT SUMMARY  
REACTANT MOLE RATIO DEPENDENCY

<u>MOLE RATIO BENZYL CHLORIDE TRIETHYLAMINE</u>	<u>ARRHENIUS CONSTANT <math>k(\text{hr}^{-1})</math></u>	<u>EXP. NO.</u>
0.5	1.02	M
1.0	0.77	A
1.5	0.58	B
2.0	0.395	I
5.0	0.190	J
10.0	0.085	K



FIGURE 7  
EMPIRICAL SOLUTION AT 80°C



### CONCLUSIONS

The following conclusions can be made from this experimental thesis:

1. The reaction of benzyl chloride with the triethylamine salt of benzoic acid in toluene is a pseudo first order reaction solely dependent upon the concentration of benzyl chloride.
2. The energy of activation for this reaction is 15,064 calories per gram mole.
3. For a mole ratio of 1.0,  $k_0$  equals  $1.7 \times 10^9$  in the Arrhenius expression.
4. The observed first order reaction rate constant is a function of the initial mole ratio of triethylamine to benzyl chloride [ $k_{obs} = 0.03 + 0.755(M)$ ] at 80°C.
5. The degree to which the reaction occurs by the  $S_N1$  mechanism is approximately 4%, since 0.03 represents the reaction rate constant of the rate controlling step of the  $S_N1$  mechanism.

### RECOMMENDATIONS

Since the reaction kinetics studies performed for this reaction showed excellent conversions in a short period of time, the commercialization of this process should be explored. Particular attention should be paid to the recovery of triethylamine from the triethylamine hydrochloride by-product. Once a triethylamine recovery system has been developed, an economic evaluation of this process should be made and a direct comparison to existing processes also be made.

Analysis of the reaction mechanism indicates that the mole ratio of triethylamine to benzoic acid should have no effect on the observed reaction rate constant. This should be verified through experimentation.

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NOMENCLATURE

$CA, CB, CC, \text{ etc.}$	Concentration of A, B, C, etc.
$CA_0, CE_0$	Initial Concentration of A and E
E	Energy of Activation
$k_1, k_2, \text{ etc.}$	Specific Reaction Rate Constants
$k_0$	Arrhenius Constant
M	Initial Mole Ratio of Triethylamine to Benzyl Chloride
$r_A, r_B, r_C, \text{ etc.}$	Rate of Reaction of A, B, C, etc.
R	Universal Gas Constant
$(A), (B), (C), \text{ etc.}$	Concentration of A, B, C, etc.

## APPENDIX



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### REACTION MECHANISM

A reaction mechanism has been established which explains a pseudo first order reaction. The derivation of this mechanism follows. The following equations define the mechanism.

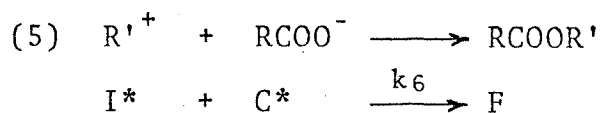
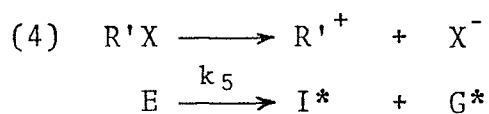
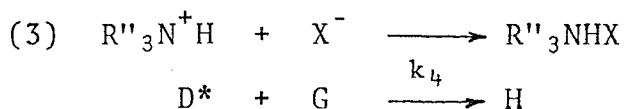
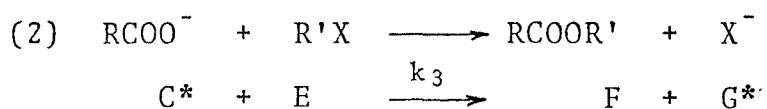
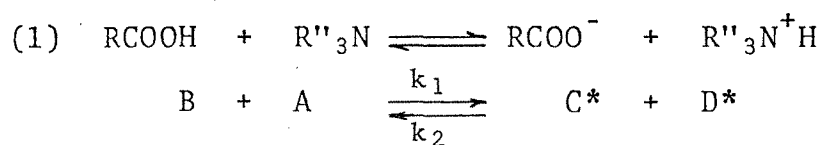


Table 13 lists the nomenclature used in this derivation. The following rate equations define the disappearance of reactants and appearance of products.

$$(6) \quad -r_A = k_1(A)(B) - k_2(C^*)(D^*)$$

$$(7) \quad -r_B = k_1(A)(B) - k_2(C^*)(D^*)$$

$$(8) \quad r_C = k_1(A)(B) - k_2(C^*)(D^*) - k_3(C^*)(E) - k_6(I^*)(C^*)$$

$$(9) \quad r_D^* = k_1(A)(B) - k_2(C^*)(D^*) - k_4(D^*)(G^*)$$

$$(10) \quad -r_E = k_3(C^*)(E) + k_5(E)$$

$$(11) \quad r_F = k_3(C^*)(E) + k_6(I^*)(C^*)$$

$$(12) \quad r_G^* = k_3(C^*)(E) - k_4(D^*)(G^*) + k_5(E)$$

$$(13) \quad r_H = k_4(D^*)(G^*)$$

$$(14) \quad r_I^* = k_5(E) - k_6(I^*)(C^*)$$

They form the basis for the derivation of the reaction mechanism.

#### Pseudo First Order Derivation

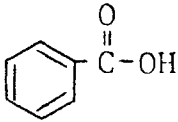
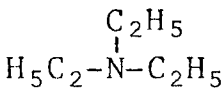
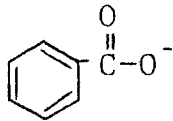
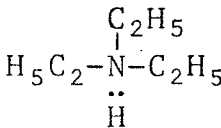
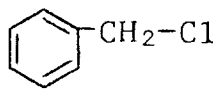
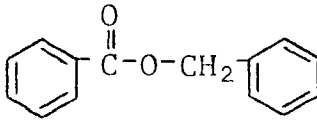
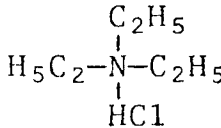
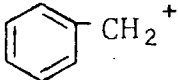
Since our analytical method measures the disappearance of triethylamine directly, we start our derivation with equation (6).

$$(6) \quad -r_A = k_1(A)(B) - k_2(C^*)(D^*)$$

$C^*$  and  $D^*$  are unstable reaction intermediates which cannot be measured. To eliminate them from equation (7) we solve equation (9) assuming the steady-state approximation which states that the rate of formation is equal to the rate of depletion. The net result is that the overall rate of formation is approximately equal to zero.

$$(9) \quad r_D^* = k_1(A)(B) - k_2(C^*)(D^*) - k_4(D^*)(G^*) = 0$$

TABLE 6  
DERIVATION NOMENCLATURE

A	RCOOH	Benzoic Acid	
B	R'' N	Triethylamine	
C*	RCOO <sup>-</sup>	Benzoate Ion	
D*	R''N <sup>+</sup> H	Triethylammonium Ion	
E	R'X	Benzyl Chloride	
F	RCOOR'	Benzyl Benzoate	
G*	X <sup>-</sup>	Chloride Ion	Cl <sup>-</sup>
H	R''NHX	Triethylamine Hydrochloride	
I*	R' <sup>+</sup>	Benzyl Ion	

Rearranging this equation to solve for  $-k (C^*)(D^*)$  we have:

$$(15) \quad -k_2(C^*)(D^*) = k_4(D^*)(G^*) - k_1(A)(B)$$

Substituting this value into equation (6) we have:

$$(16) \quad -r_A = k_1(A)(B) + k_2(D^*)(G^*) - k_4(A)(B)$$

The two  $k_1(A)(B)$  terms cancel out leaving:

$$(17) \quad -r_A = k_4(D^*)(G^*)$$

Next we solve equation (12) assuming the steady-state approximation again:

$$(12) \quad r_G^* = k_3(C^*)(E) - k_4(D^*)(G^*) + k_5(E) = 0$$

$$(18) \quad k_4(D^*)(G^*) = k_3(C^*)(E) + k_5(E)$$

Substituting the value for  $k_4(D^*)(G^*)$  into equation (17) we have equation (19):

$$(19) \quad -r_A = k_3(C^*)(E) + k_5(E)$$

If the steady-state approximation is true,  $r_C^* = 0$ , then the concentration of  $C^*$  must be constant for any given reaction condition, or

$$(20) \quad -r_A = [k_3(C^*) + k_5](E)$$

Equation (20) is a pseudo first order reaction equation with the observed rate constant being equal to  $[k_3(C^*) + k_5]$ .

EXPERIMENTAL DATA

TABLE 7

EXP. NO.	INITIAL CONCENTRATIONS		CONVERSION FACTOR MOLES/LITER/1%
	TRIETHYLAMINE MOLES/LITER	BENZYL CHLORIDE MOLES/LITER	
A	1.655	1.655	0.01655
B	1.519	2.278	0.01519
C	1.655	1.655	0.01655
D	1.655	1.655	0.01655
E	1.655	1.655	0.01655
F	1.655	1.655	0.01655
G	1.655	1.655	0.01655
H	1.655	1.655	0.01655
I	1.241	2.483	0.01241
J	0.704	3.521	0.00704
K	0.417	4.167	0.00417
L	1.165	1.165	0.01165
M	1.846	0.923	0.00923
N	1.460	1.460	0.01460

TABLE 8  
REACTANT CONCENTRATIONS  
TEMPERATURE EFFECTS

TIME HRS	Triethylamine Concentration (moles/liter)				
	EXP. A 80°C	EXP. E 96°C	EXP. F 105°C	EXP. G 99°C	EXP. H 70°C
0.00	1.65	1.65	1.65	1.65	1.65
0.25	---	1.27	0.90	1.15	---
0.50	1.38	0.84	0.41	0.68	1.26
0.75	---	0.57	0.18	0.25	---
1.00	0.87	0.43	---	0.12	1.15
1.25	---	0.24	---	---	---
1.50	0.65	0.25	---	---	0.96
1.75	---	---	---	---	---
2.00	0.35	---	---	---	0.76
2.50	0.23	---	---	---	0.66
3.00	0.16	---	---	---	0.50

TABLE 9  
 REACTANT CONCENTRATIONS - REACTANT MOLE RATIO EFFECTS

		Concentration (moles/liter)											
		0.5		1.0		1.5		2.0		5.0		10.0	
E/A	TIME HRS.	EXP. M		EXP. A		EXP. B		EXP. I		EXP. J		EXP. K	
		[A]	[E]	[A]	[E]	[A]	[E]	[A]	[E]	[A]	[E]	[A]	[E]
0.00	1.85	0.92	1.65	1.65	1.65	1.52	2.28	1.24	2.48	0.70	3.52	0.42	4.17
0.25	---	---	---	---	---	---	---	1.05	2.29	0.53	3.35	0.32	4.07
0.50	1.49	0.56	1.38	1.38	1.38	1.08	1.84	0.89	2.13	0.38	3.20	0.26	4.01
0.75	---	---	---	---	000	---	---	0.66	1.90	0.20	3.02	0.17	3.92
1.00	1.34	0.42	0.87	0.87	0.87	0.49	1.25	0.43	1.67	0.08	2.90	0.09	3.84
1.25	---	---	---	---	---	---	---	0.22	1.46	0.03	2.85	0.04	3.79
1.50	1.17	0.24	0.65	0.65	0.65	0.10	0.86	0.10	1.34	---	---	---	---
2.0	1.05	0.13	0.35	0.35	0.35	0.65	0.81	---	---	---	---	---	---
2.5	0.97	0.04	0.23	0.23	0.23	---	---	---	---	---	---	---	---
3.0	0.92	0.00	0.16	0.16	0.16	---	---	---	---	---	---	---	---

E = Benzyl Chloride  
 A = Triethylamine



TABLE 10

REACTANT CONCENTRATIONSINITIAL REACTANT CONCENTRATION EFFECTS

<u>TIME HRS.</u>	<u>Triethylamine Concentration (moles/liter)</u>				
	<u>EXP. A</u>	<u>EXP. C</u>	<u>EXP. D</u>	<u>EXP. L</u>	<u>EXP. N</u>
0.0	1.65	1.65	1.65	1.16	1.46
0.5	1.38	1.30	1.30	1.02	1.18
1.0	0.87	0.94	0.84	0.90	0.92
1.5	0.65	0.66	0.58	0.82	0.67
2.0	0.35	0.29	0.31	0.61	0.42
2.5	0.23	0.13	---	0.43	0.23
3.0	0.16	---	---	0.40	0.13
3.5	---	---	---	---	0.09

FIGURE 8  
REACTANT & PRODUCT CONCENTRATIONS  
RUN A

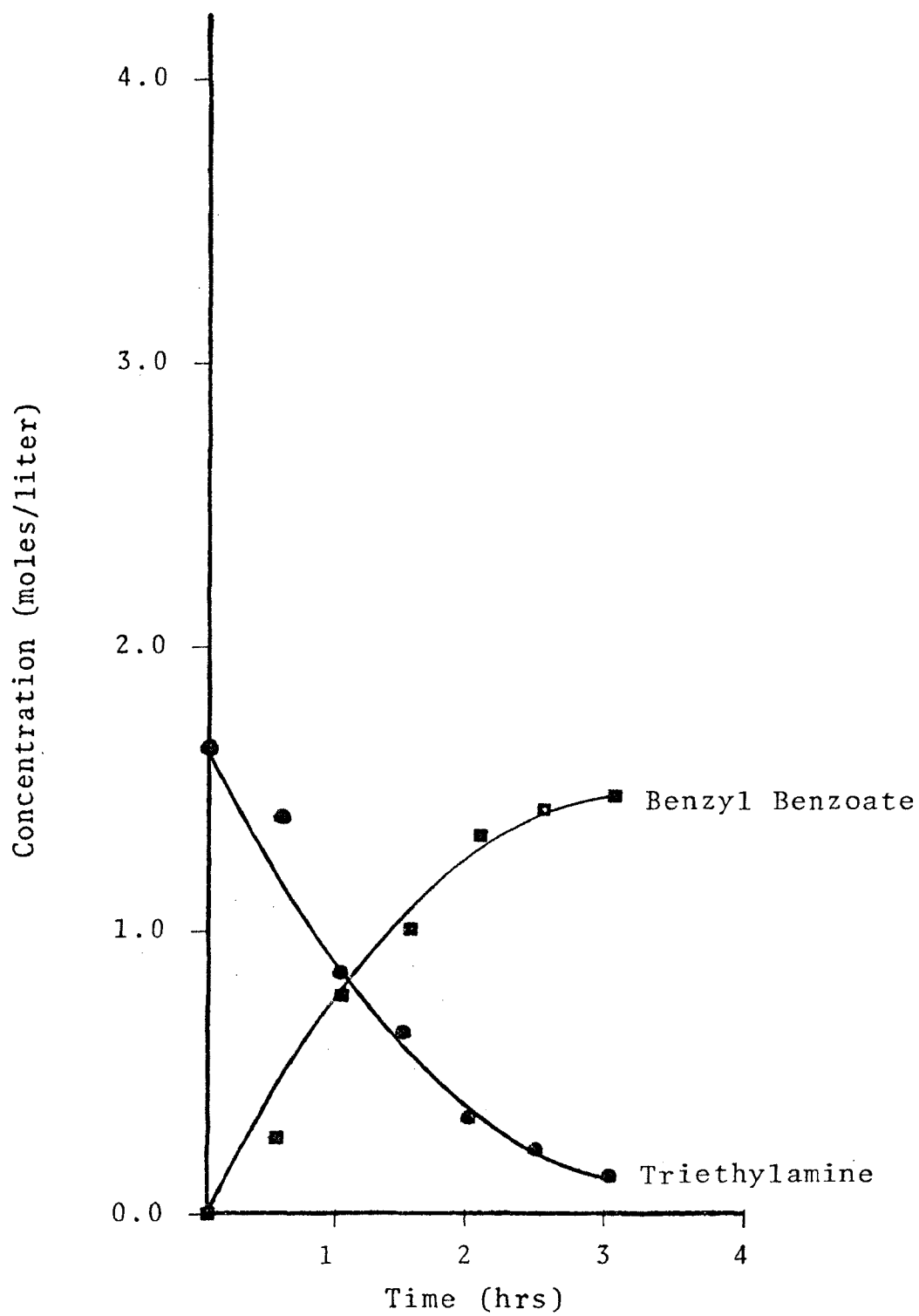


FIGURE 9  
REACTANT & PRODUCT CONCENTRATIONS  
RUN B

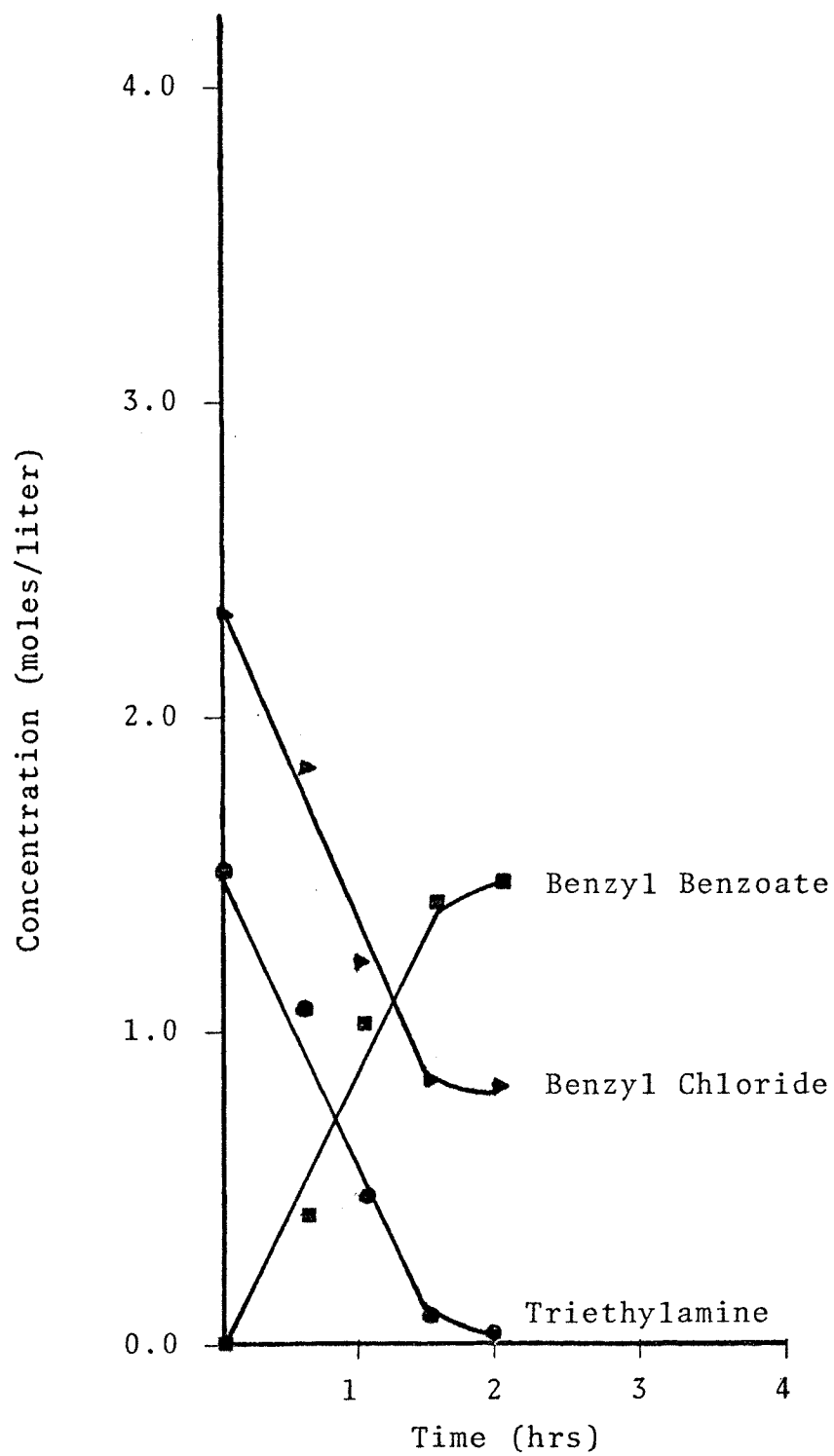


FIGURE 10  
REACTANT & PRODUCT CONCENTRATIONS  
RUN C

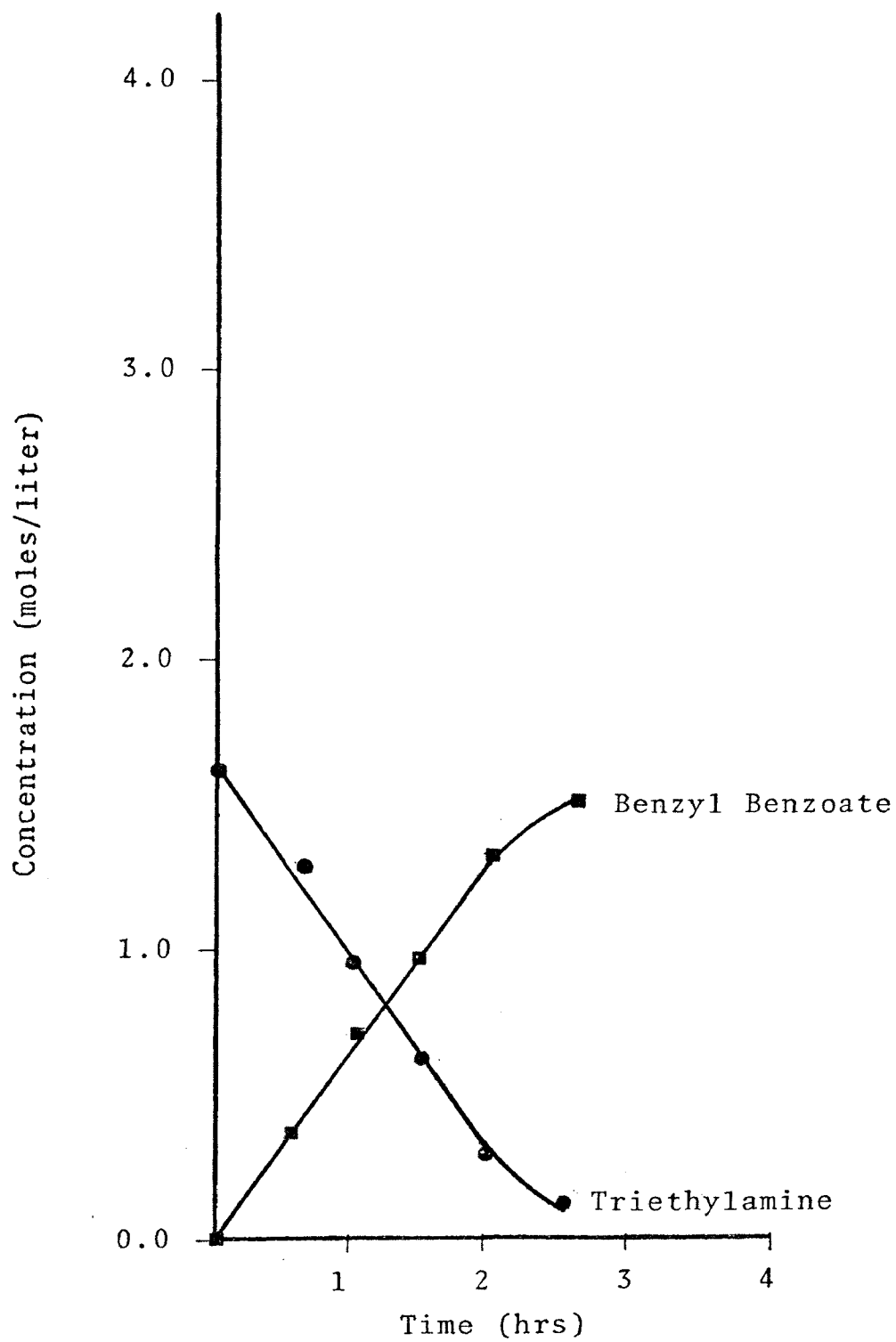


FIGURE 11  
REACTANT & PRODUCT CONCENTRATIONS  
RUN D

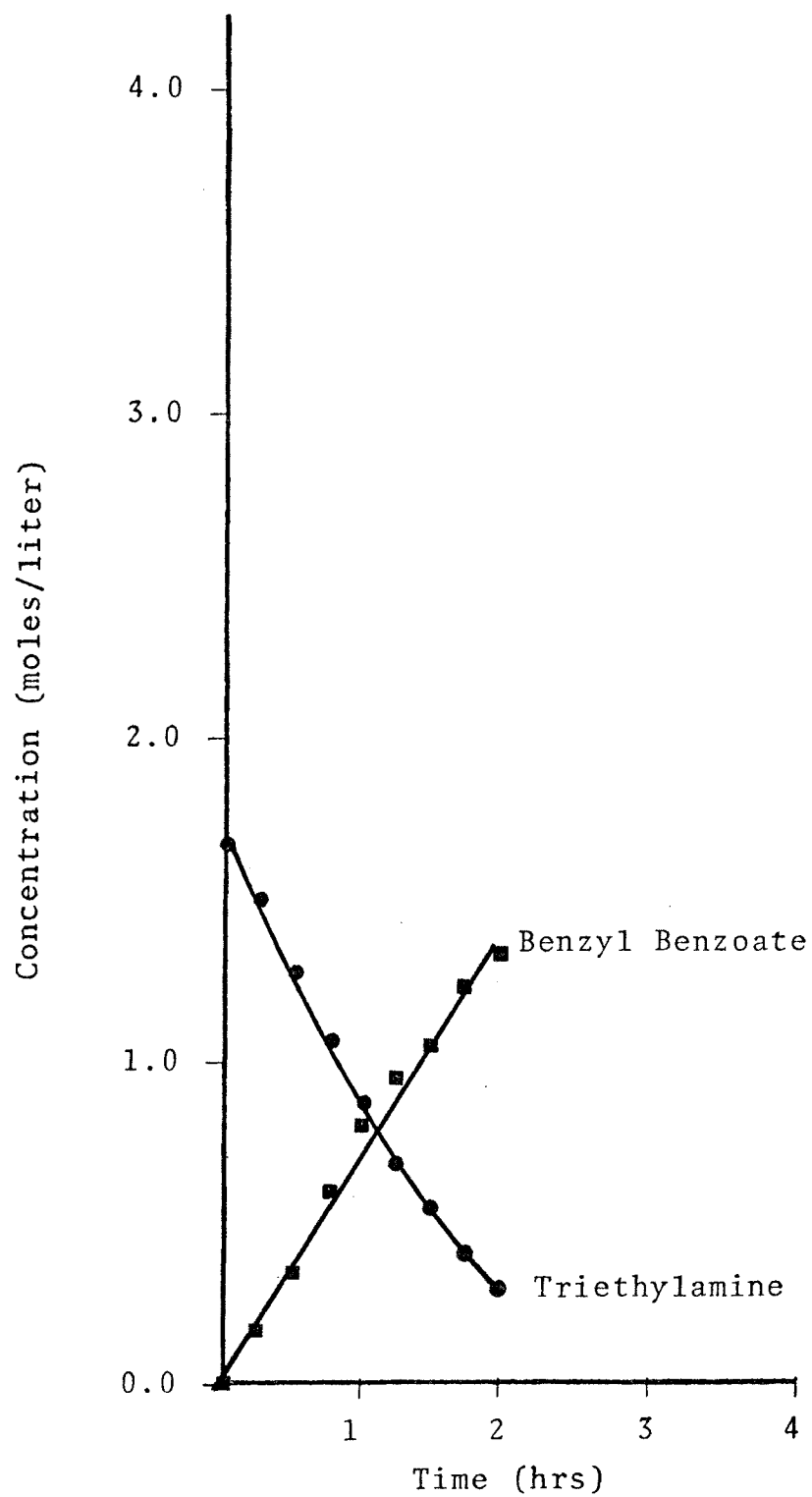


FIGURE 12  
REACTANT & PRODUCT CONCENTRATIONS  
RUN E

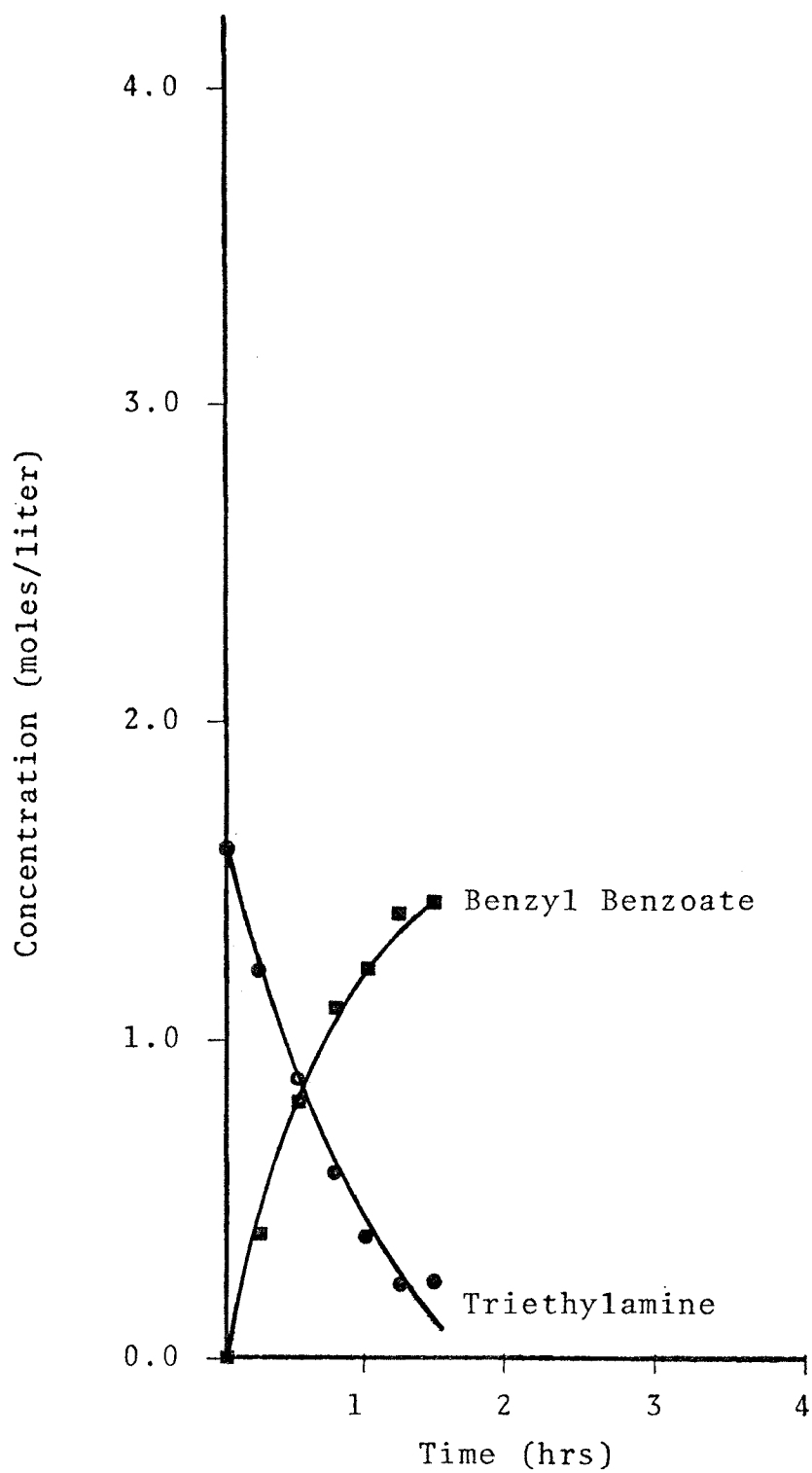


FIGURE 13  
REACTANT & PRODUCT CONCENTRATIONS  
RUN F

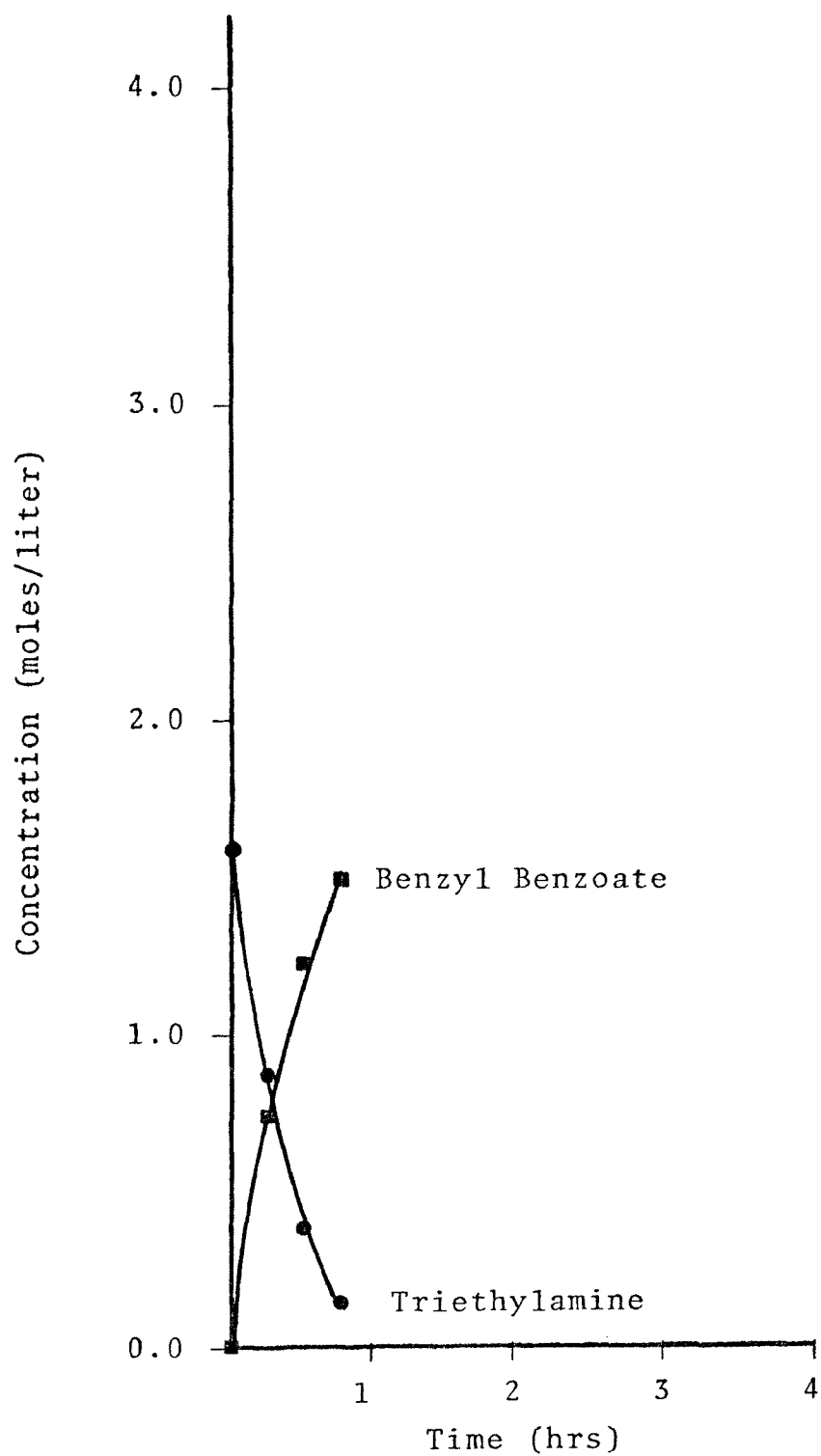


FIGURE 14  
REACTANT & PRODUCT CONCENTRATIONS  
RUN G

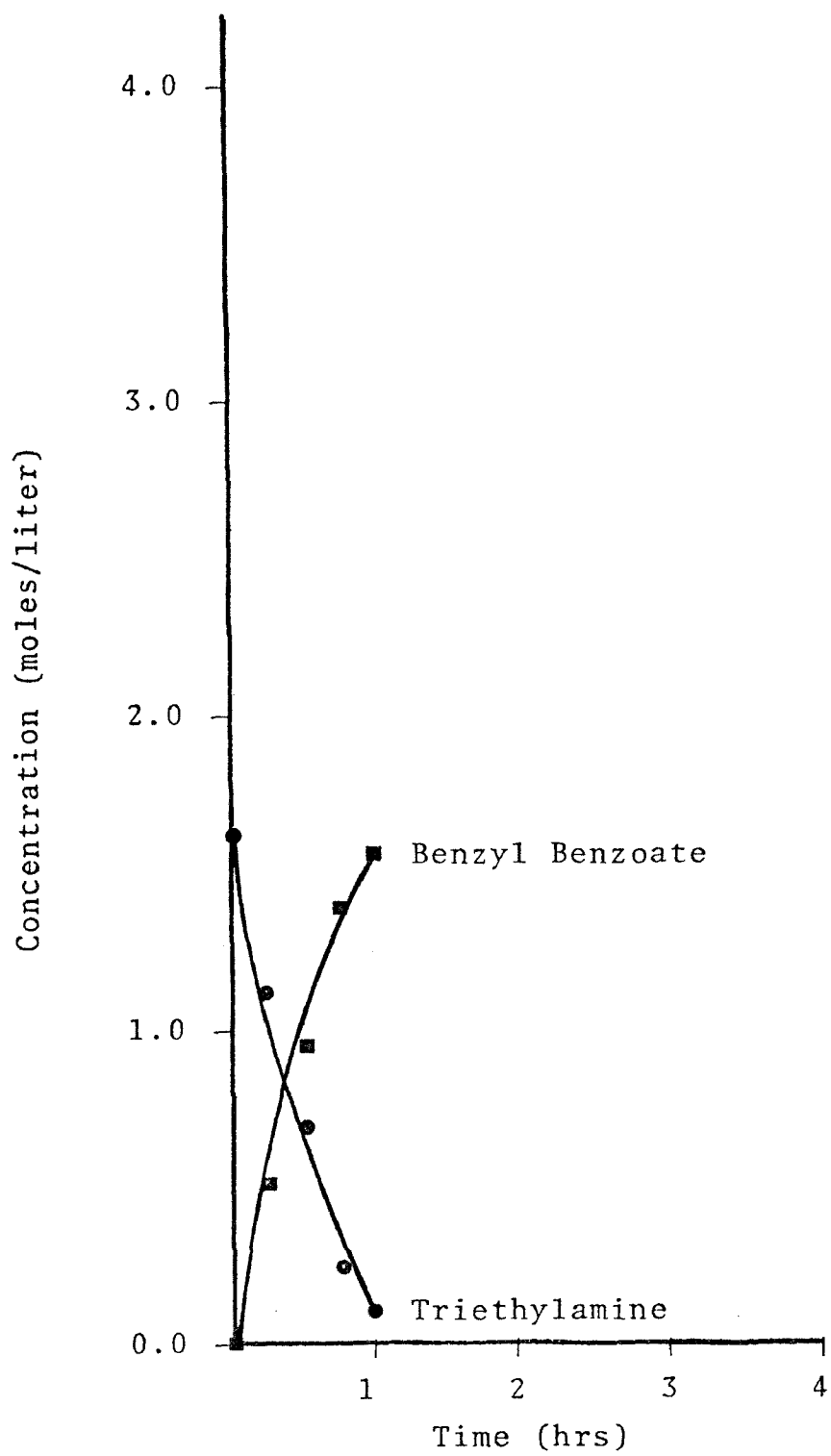




FIGURE 15  
REACTANT & PRODUCT CONCENTRATIONS  
RUN H

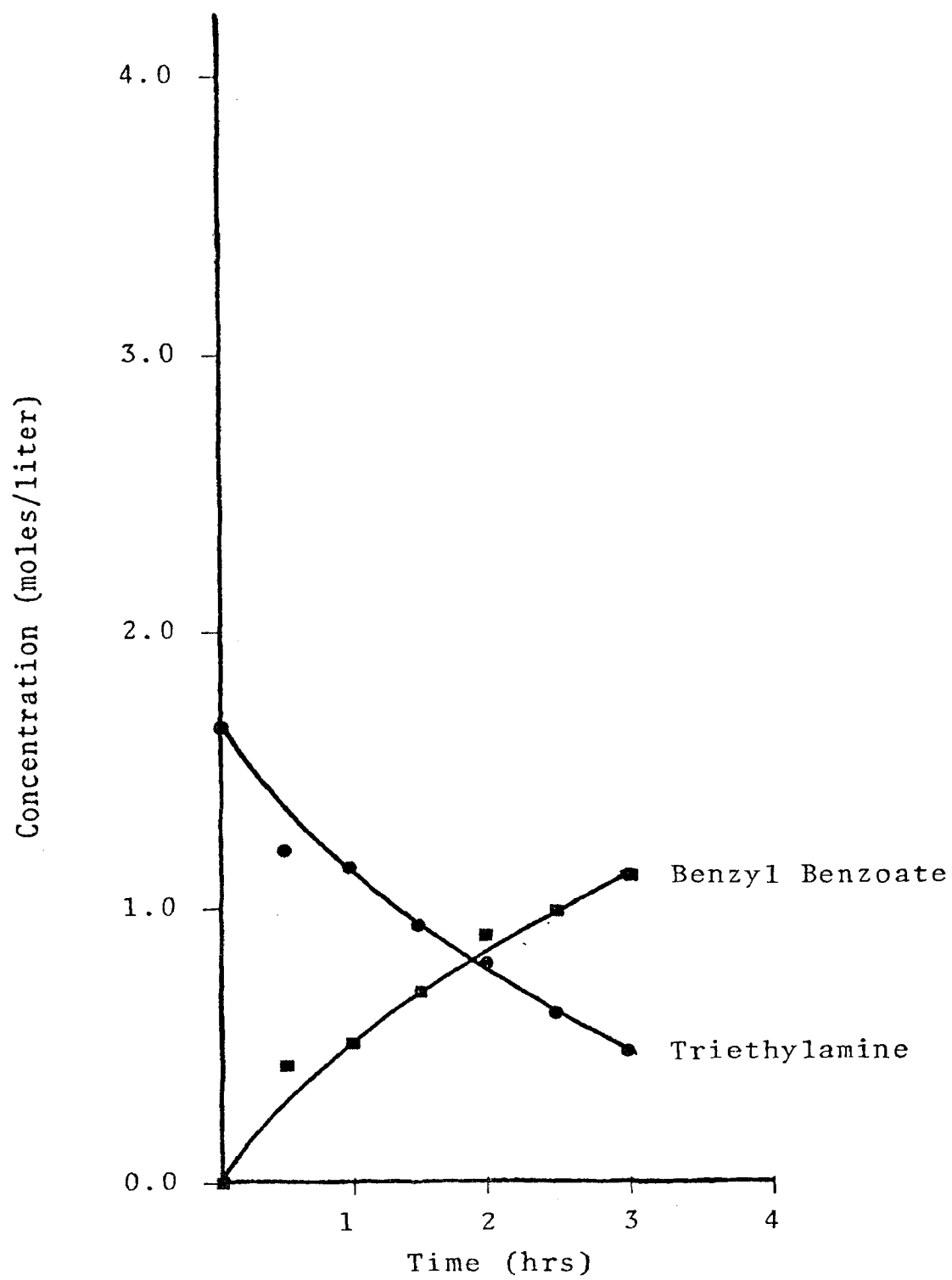


FIGURE 16  
REACTANT & PRODUCT CONCENTRATIONS  
RUN I

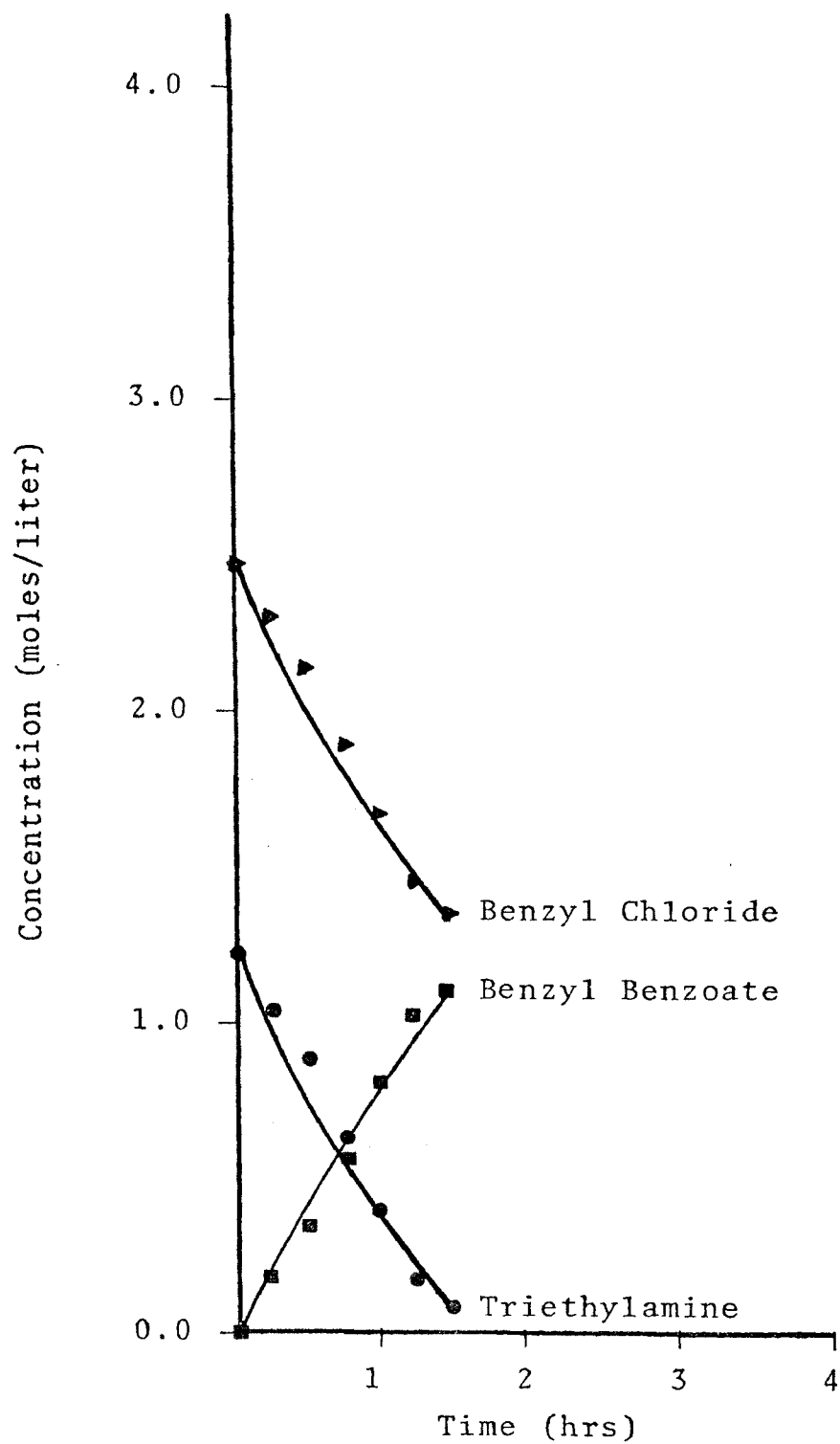


FIGURE 17  
REACTANT & PRODUCT CONCENTRATIONS  
RUN J

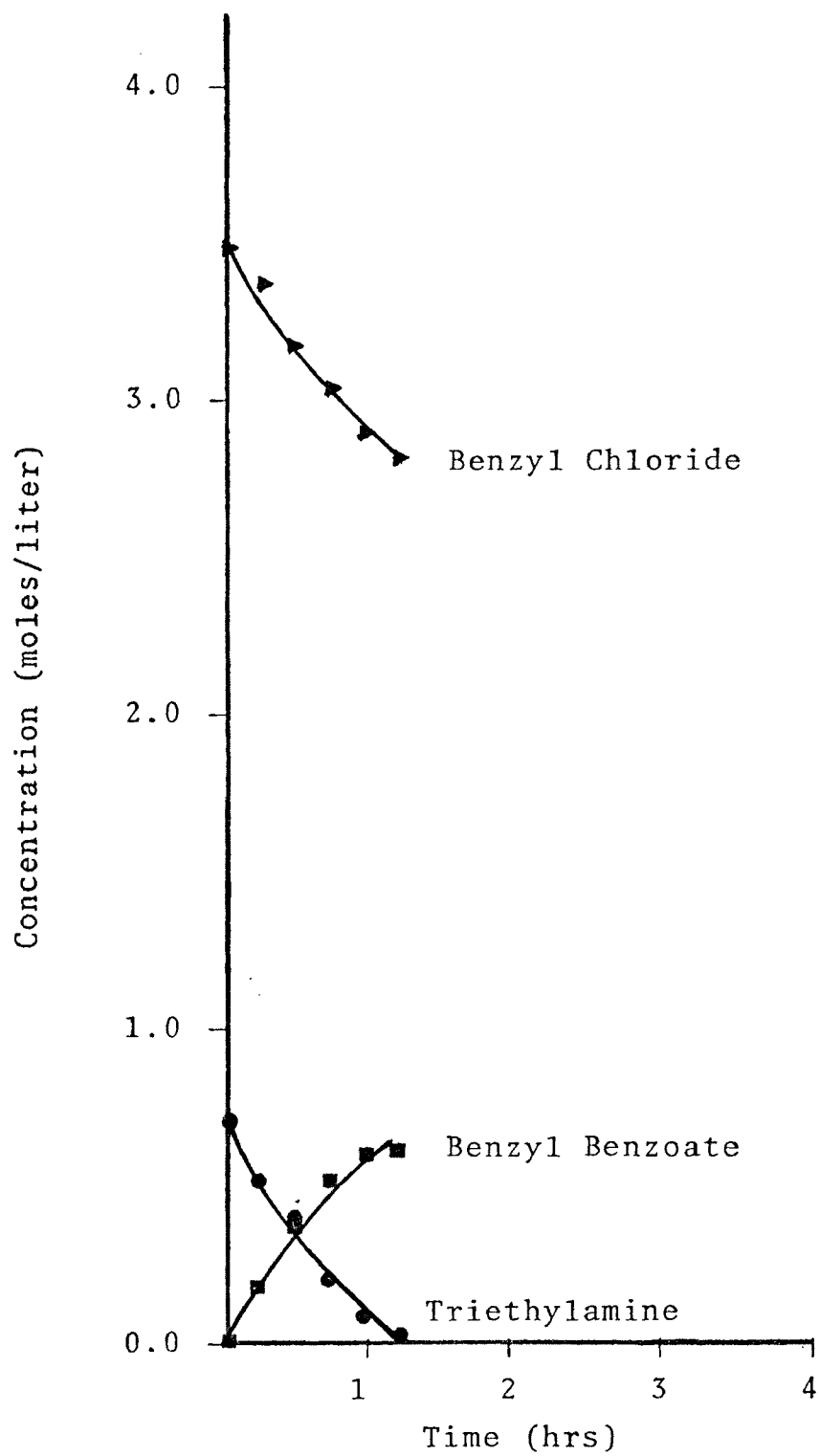


FIGURE 18  
REACTANT & PRODUCT CONCENTRATIONS  
RUN K

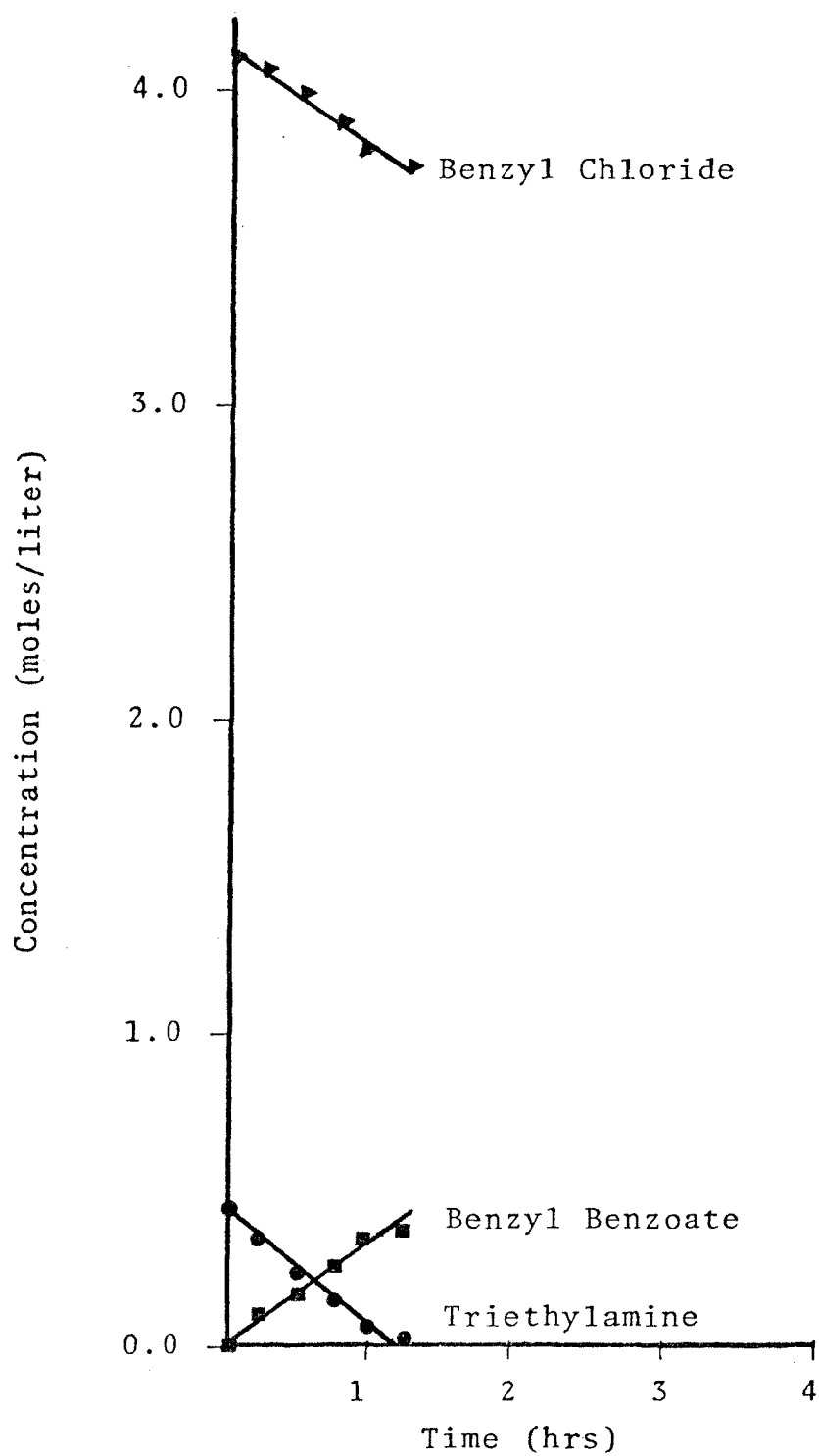


FIGURE 19  
REACTANT & PRODUCT CONCENTRATIONS  
RUN L

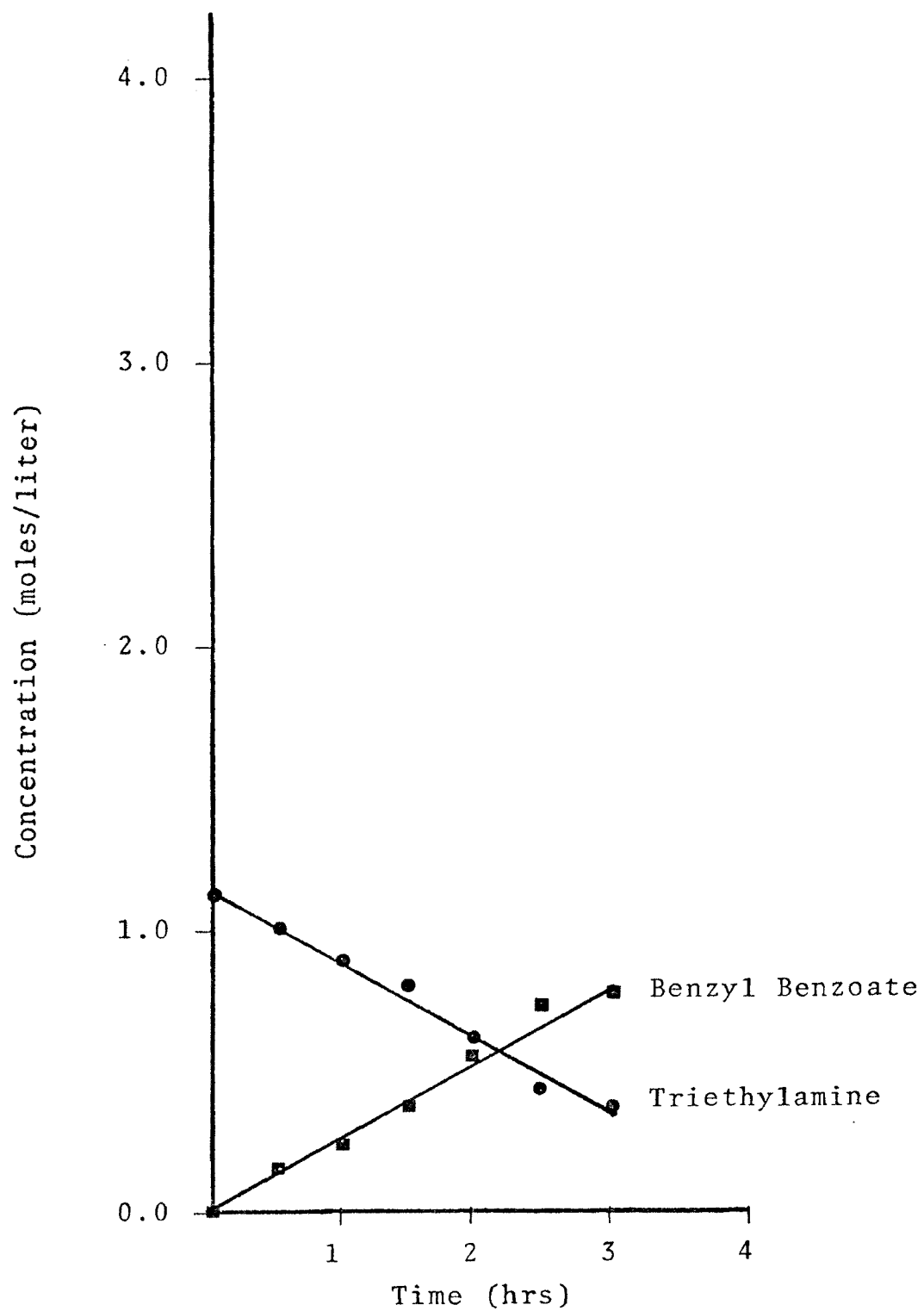


FIGURE 20

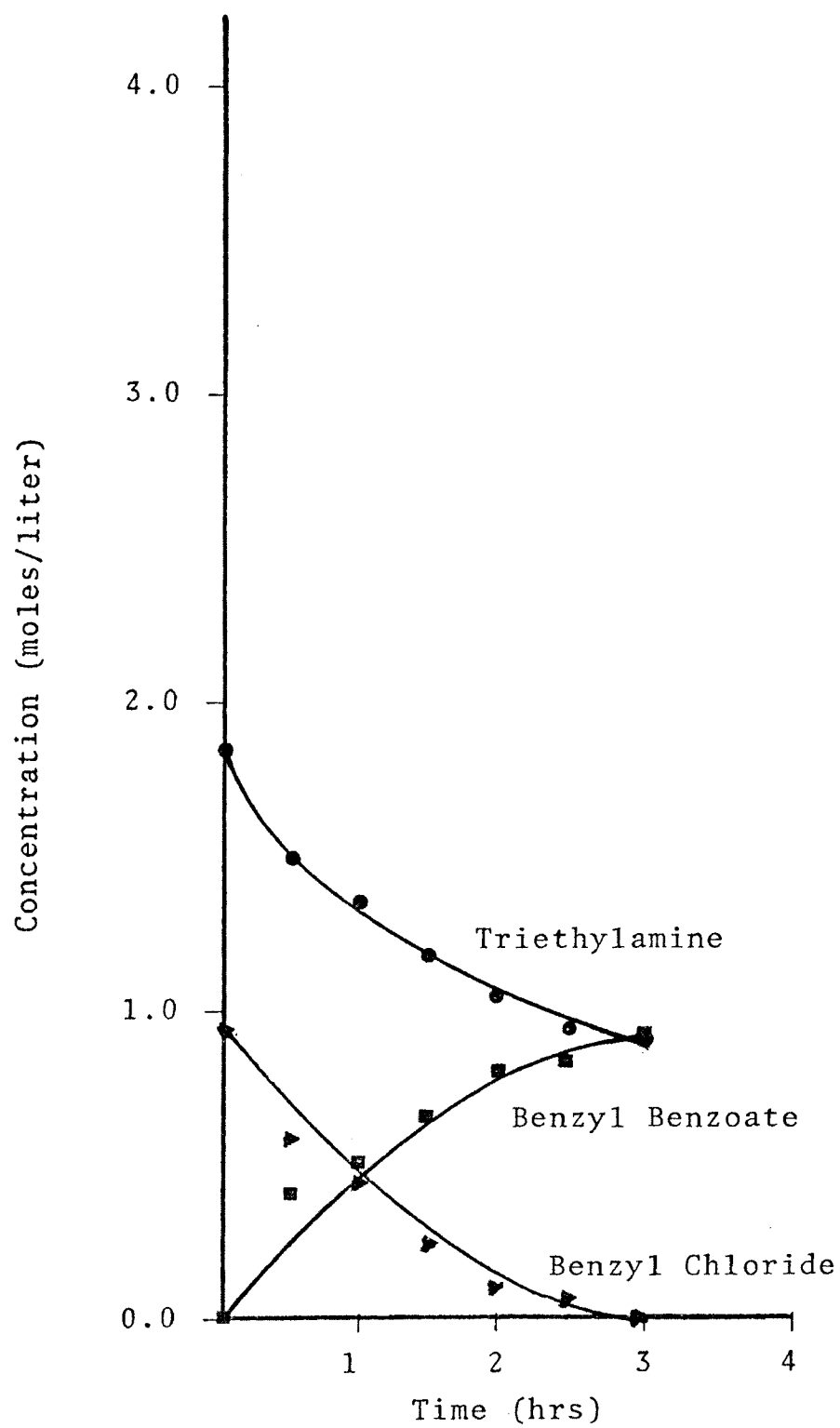
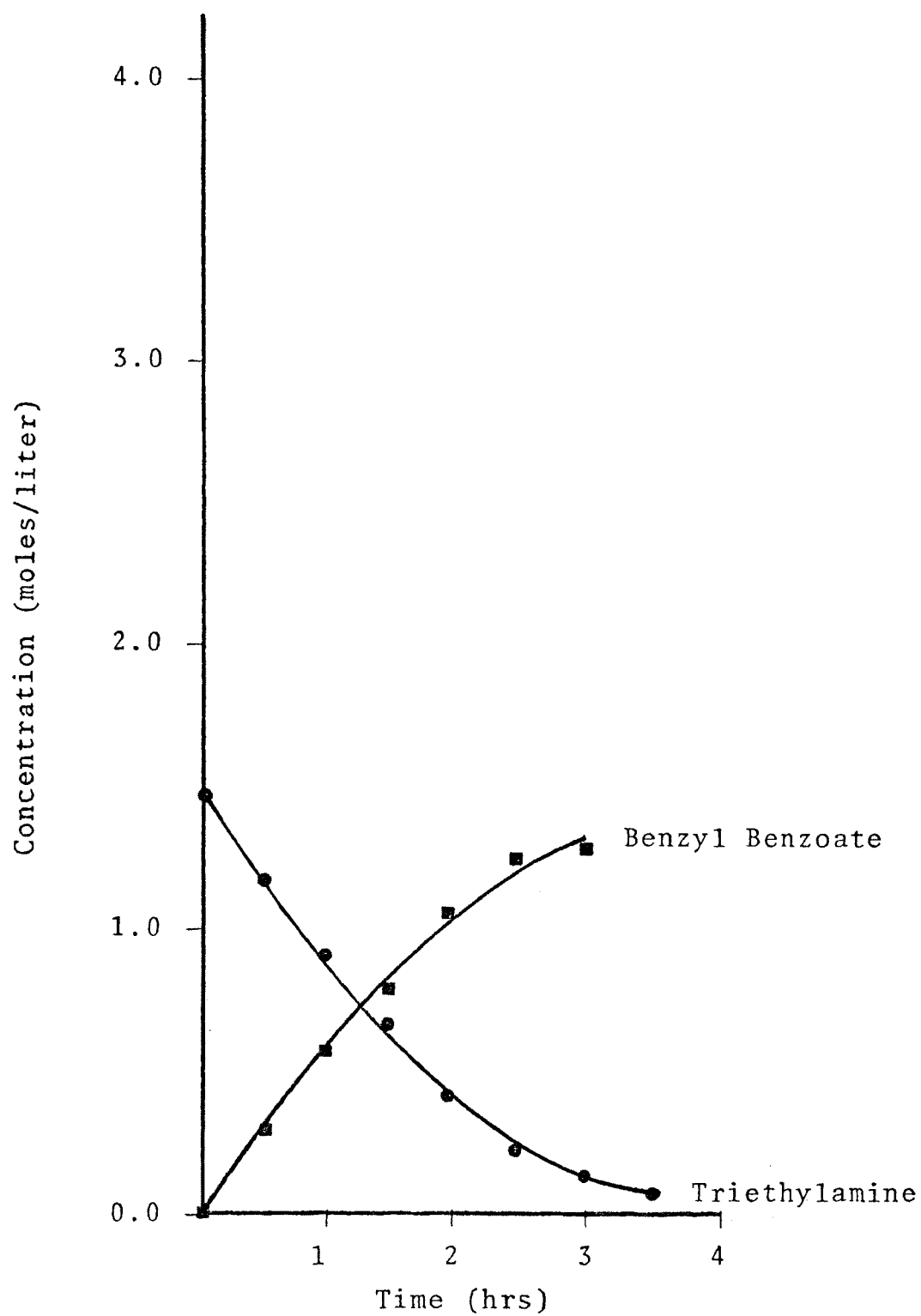
REACTANT & PRODUCT CONCENTRATIONSRUN M

FIGURE 21  
REACTANT & PRODUCT CONCENTRATIONS  
RUN N



ANALYTICAL



TABLE 11  
GAS CHROMATOGRAPH CALIBRATION

<u>Conversion</u>	<u>Benzyl Chloride</u>			<u>Benzyl Benzoate</u>			<u>Area Frac. Benz. Benz.</u>
	<u>Height</u>	<u>Width @ <math>\frac{1}{2}h</math></u>	<u>Area</u>	<u>Height</u>	<u>Width @ <math>\frac{1}{2}h</math></u>	<u>Area</u>	
20	42.2	5.7	240.5	11.4	7.2	82.1	0.254
40	31.1	5.7	188.7	28.1	6.5	182.6	0.492
60	21.0	5.7	119.7	45.9	6.3	289.2	0.707
80	11.1	6.2	68.8	68.1	6.5	442.6	0.865

TABLE 12  
REACTION STOICHIOMETRY  
EXPERIMENTS A, C, D, E, F, G, H

% Conv.	<u>Grams Present</u>				<u>Total Soln.</u>
	<u>Benzyl Chloride</u>	<u>TEA Benzoate</u>	<u>Benzyl Benzoate</u>	<u>Xylene</u>	
0	151.8	268.3	0.0	264.0	684.1
10	136.7	240.8	25.5	264.0	667.0
20	121.5	214.1	50.9	264.0	650.5
30	106.3	187.3	76.4	264.0	634.1
40	91.1	160.6	101.9	264.0	617.6
50	75.9	133.8	127.4	264.0	601.1
60	60.8	107.0	152.8	264.0	584.6
70	45.6	80.3	178.3	264.0	568.1
80	30.4	53.5	203.8	264.0	551.7
90	15.2	26.8	229.2	264.0	535.1
95	7.6	13.4	242.0	264.0	527.1

TABLE 13  
CALLIBRATION CURVE CALCULATIONS  
EXPERIMENTS A, C, D, E, F, G, H

<u>% Conv.</u>	<u>Total Wt. Sol'n</u>	<u>G-Moles TEA</u>	<u>MEQ TEA GM. Sol'n</u>
0	684.1	1.20	1.754
10	667.0	1.08	1.619
20	650.5	0.96	1.476
30	634.1	0.84	1.325
40	617.6	0.72	1.166
50	601.1	0.60	0.998
60	584.6	0.48	0.821
70	568.1	0.36	0.634
80	551.7	0.24	0.435
90	535.1	0.12	0.224
95	527.1	0.06	0.114

FIGURE 22  
GAS CHROMATOGRAPH CALIBRATION CURVE

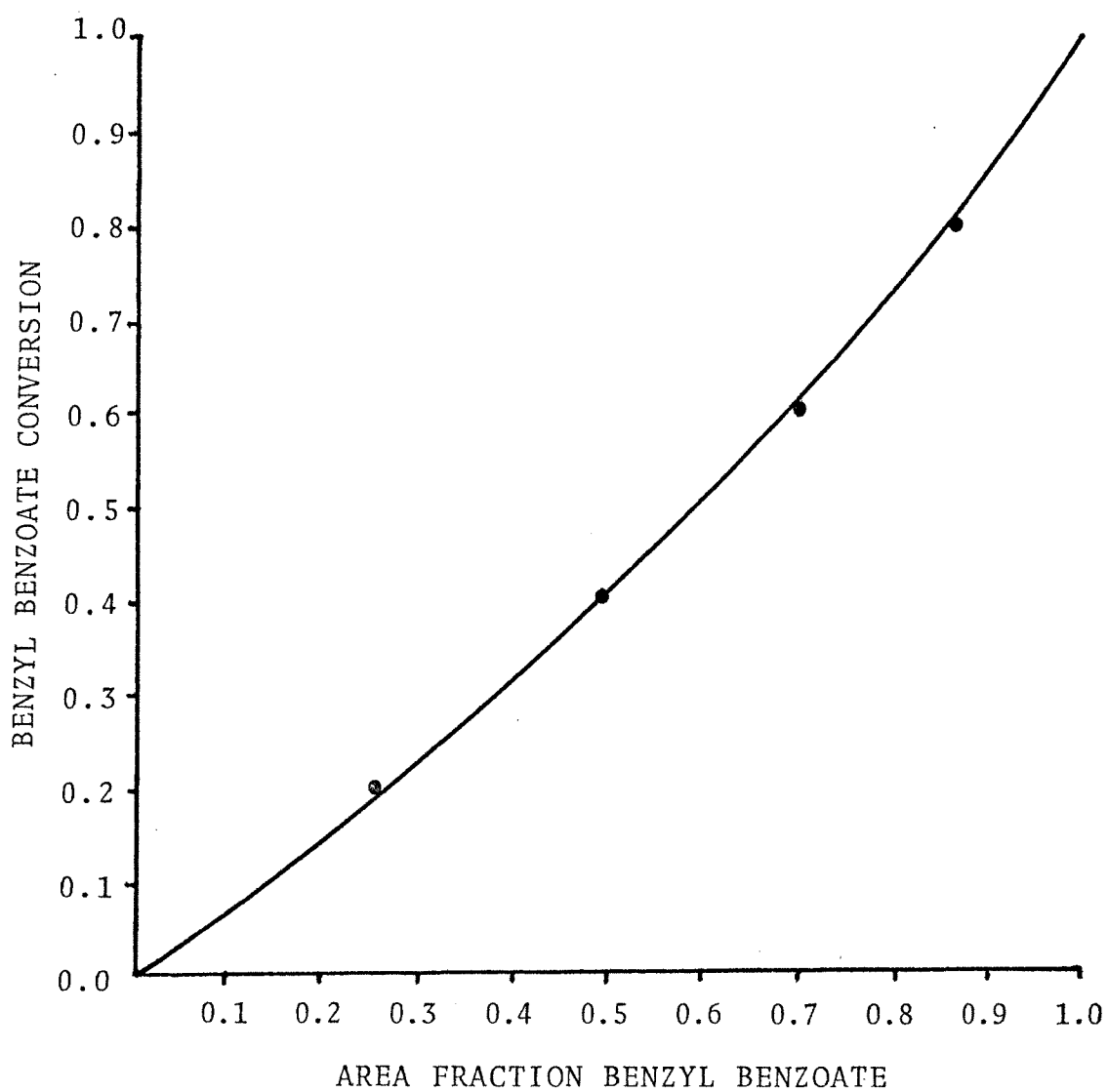


FIGURE 23  
CALIBRATION CURVE  
EXPERIMENTS A, C, D, E, F, G, H

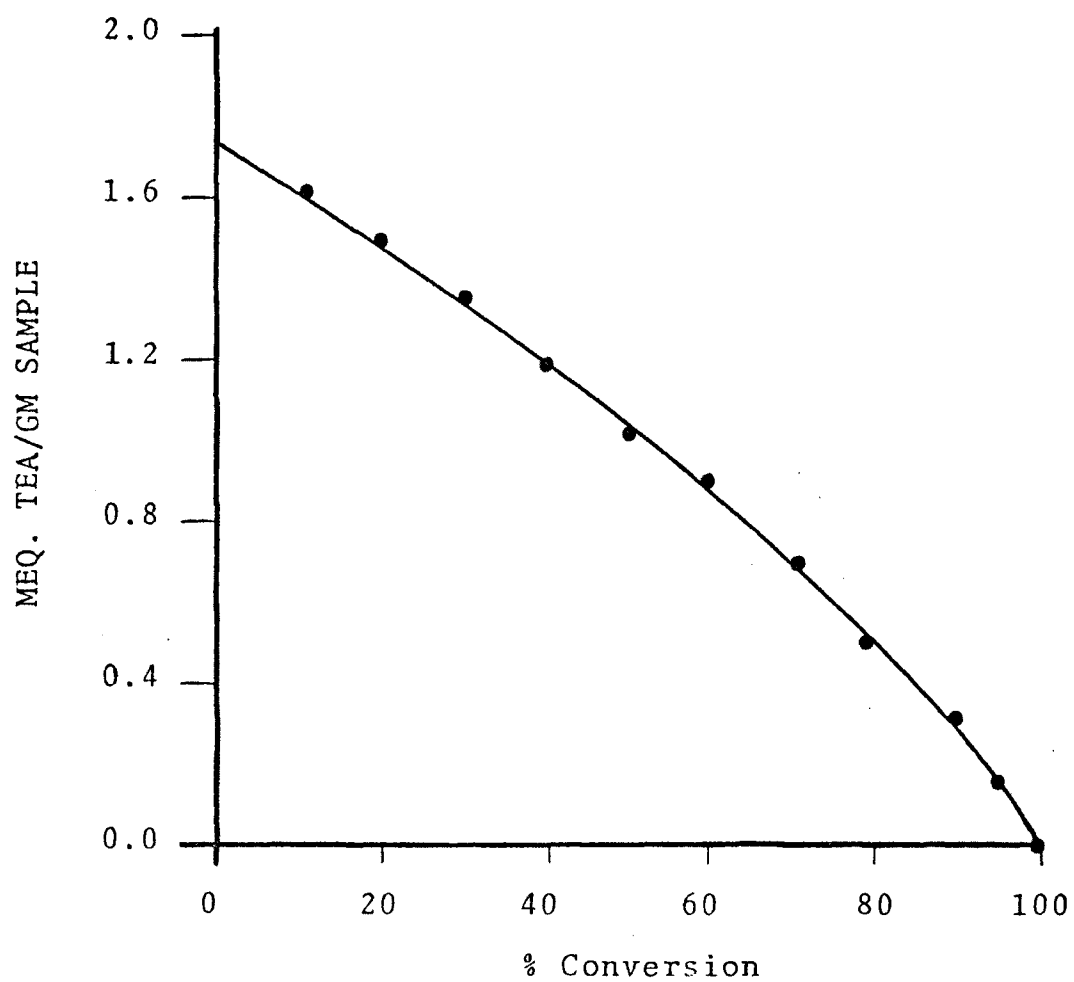


FIGURE 24  
CALIBRATION CURVE  
EXPERIMENT B

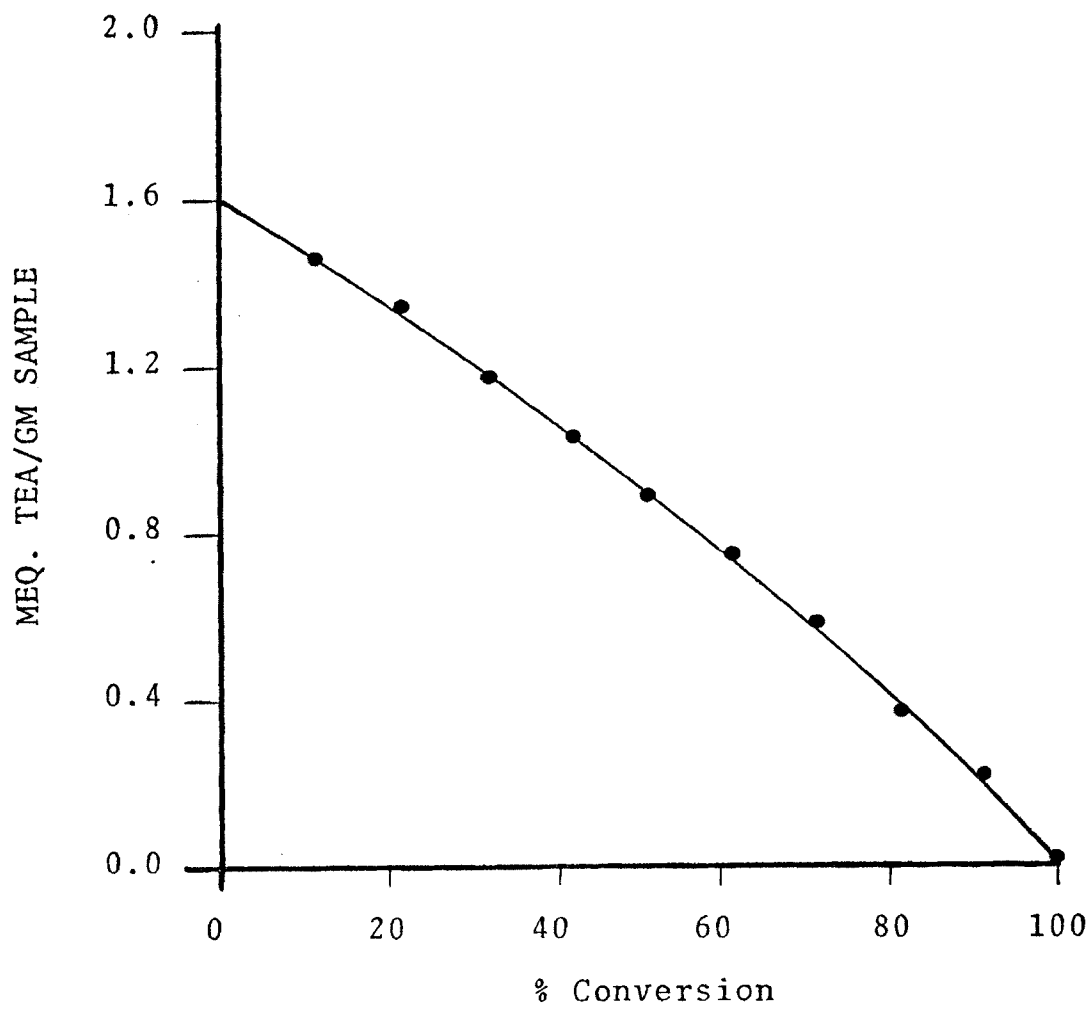


FIGURE 25  
CALIBRATION CURVE  
EXPERIMENT I

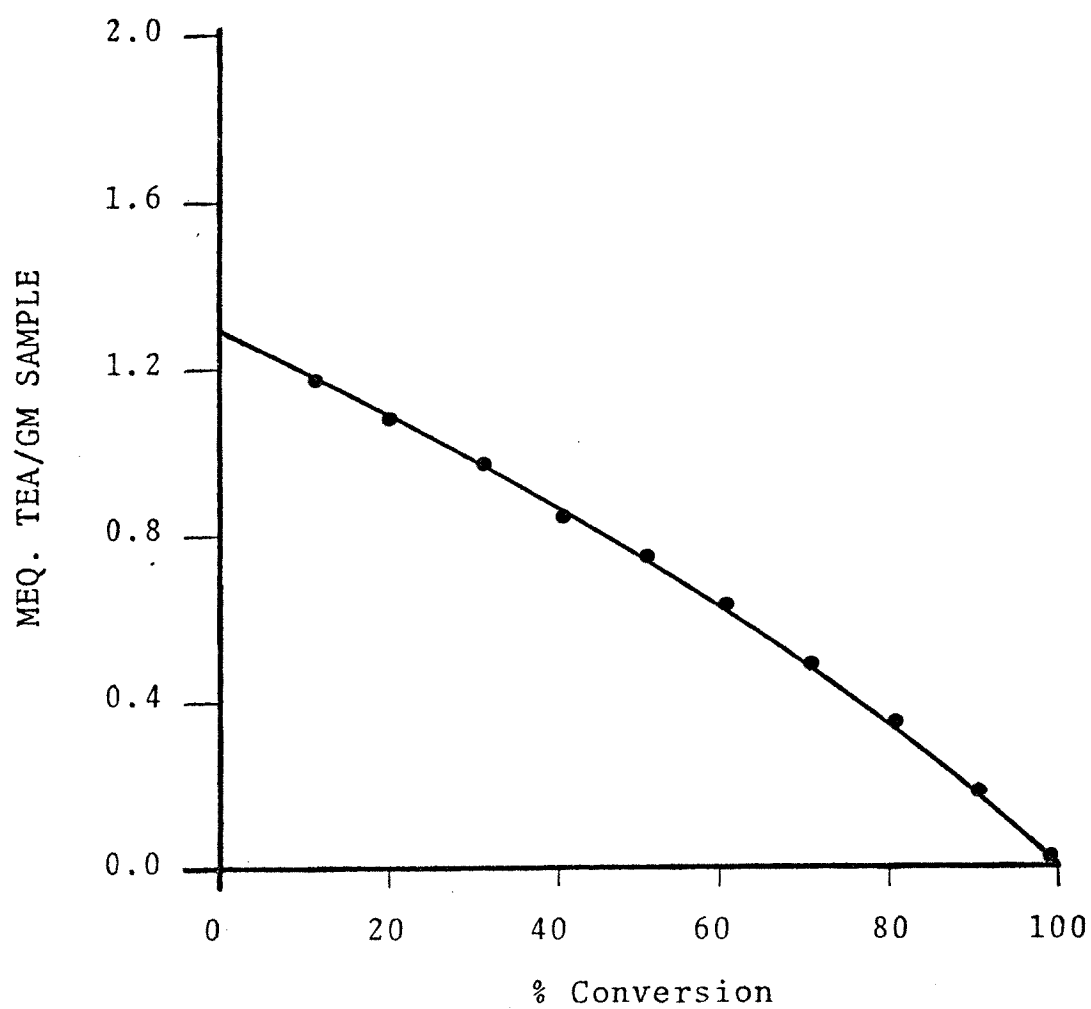


FIGURE 26  
CALIBRATION CURVE  
EXPERIMENT J

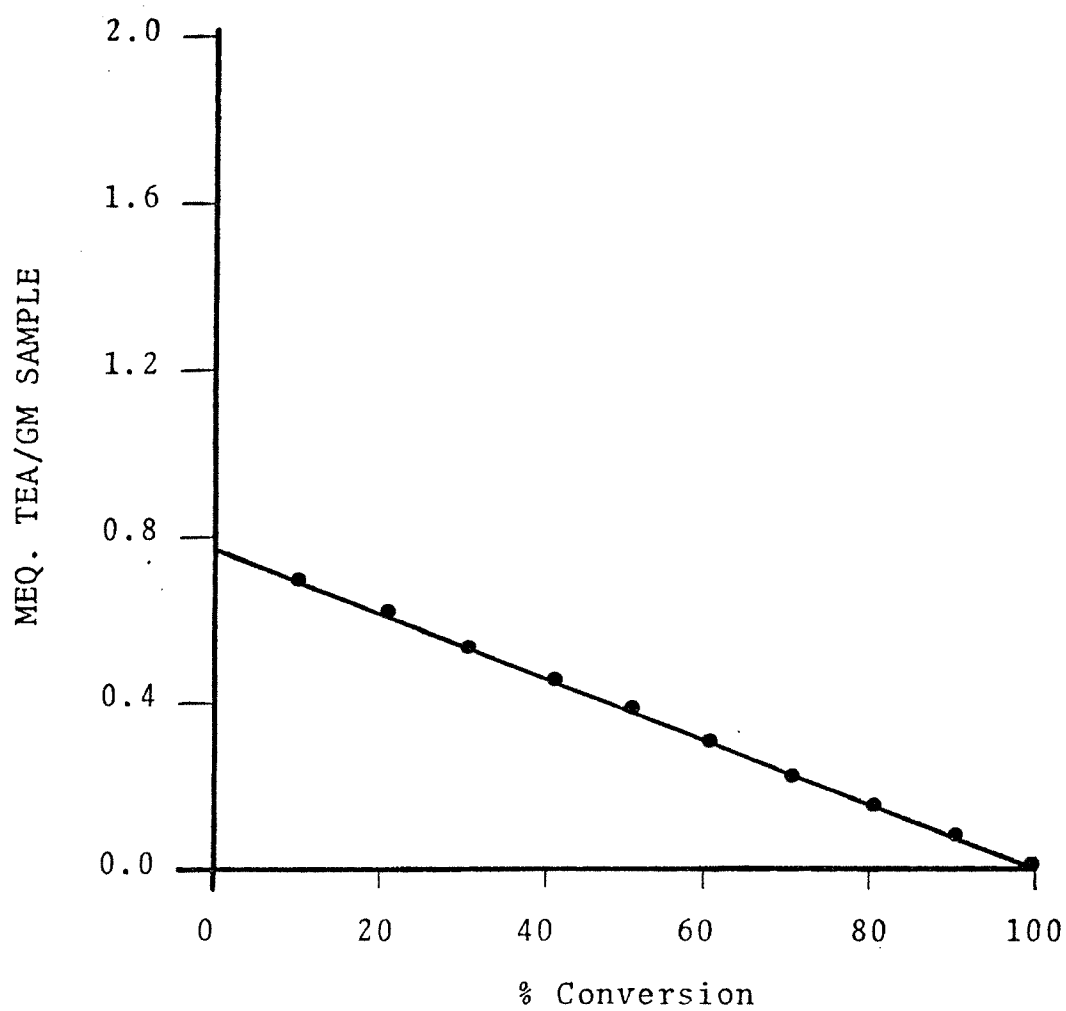




FIGURE 27  
CALIBRATION CURVE  
EXPERIMENT K

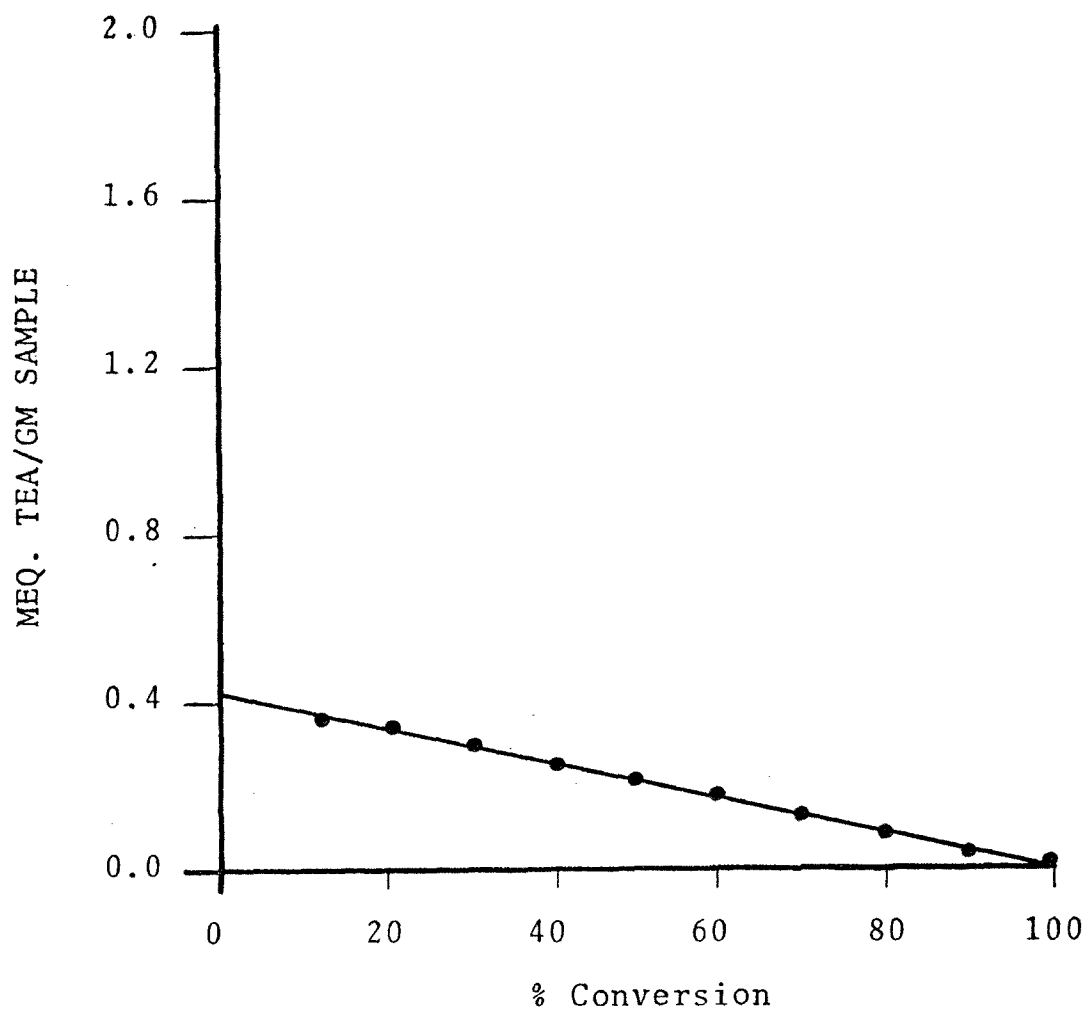


FIGURE 28  
CALIBRATION CURVE  
EXPERIMENT L

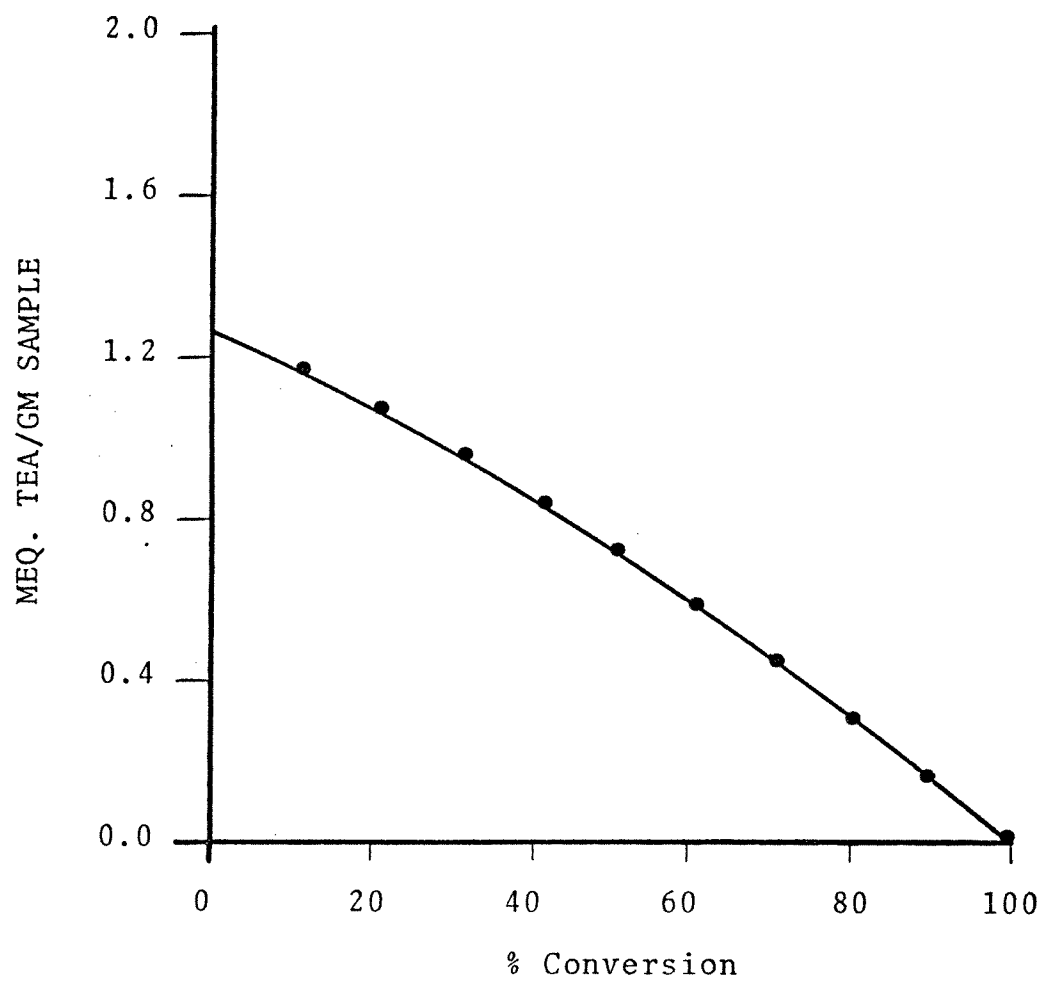


FIGURE 29  
CALIBRATION CURVE  
EXPERIMENT M

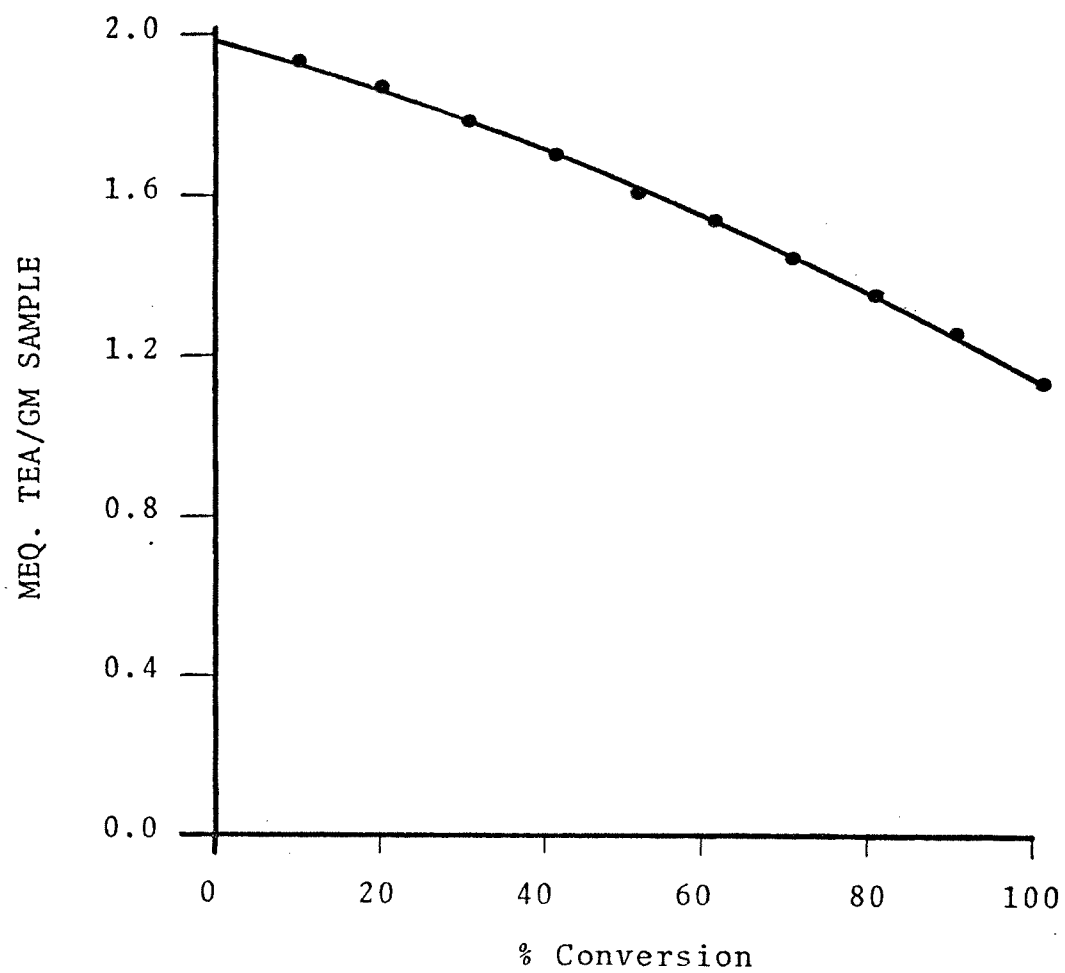


FIGURE 30  
CALIBRATION CURVE  
EXPERIMENT N

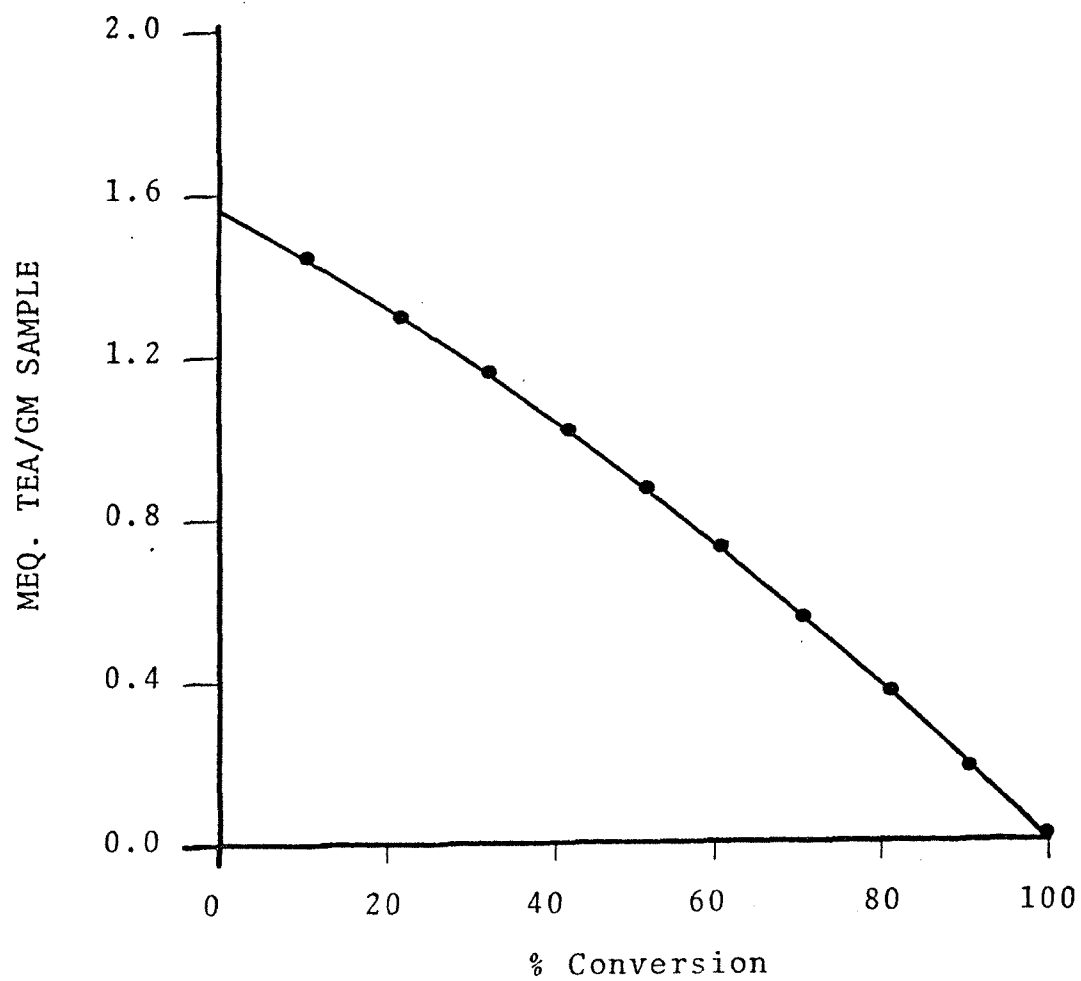


FIGURE 31  
CALIBRATION CURVE  
EXPERIMENT O

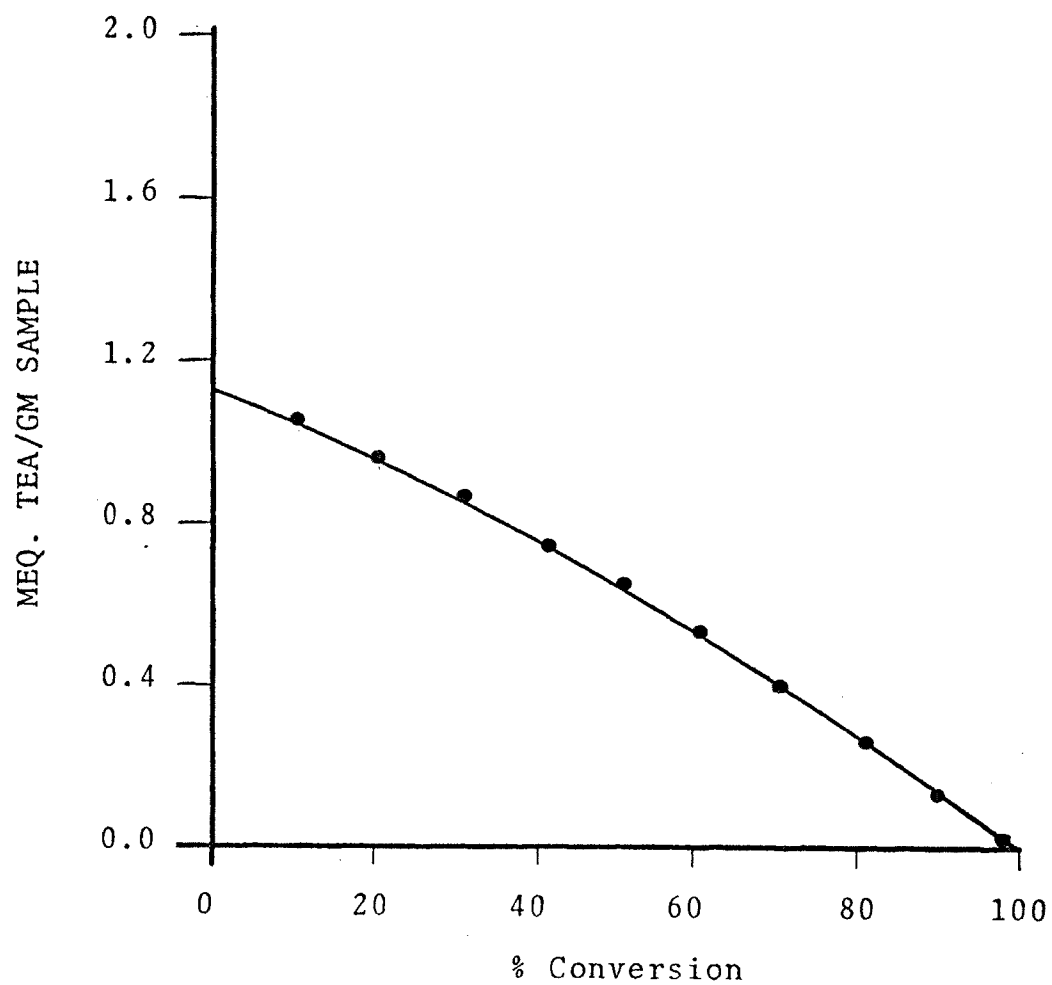


FIGURE 32  
POTENTIOMETRIC TITRATION CURVE

