THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

KINETICS OF THE LIQUID-PHASE ADDITION REACTIONS INITIATED BY PROPYLENE OXIDE AND METHANOL AND CATALYZED BY SODIUM HYDROXIDE

Manchiu D. S. Lay

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
1958

February 1959

IP-353

Doctoral Committee:

Professor Julius T. Banchero, Chairman
Professor Leigh Anderson
Professor Stuart W. Churchill
Professor Joseph J. Martin
Professor Robert R. White

ACKNOWLEDGMENT

The author wishes to take this opportunity to thank the following persons who contributed in one way or another to the completion of this work:

Professor J. T. Banchero, for his understanding, advice and the many helpful suggestions during this investigation.

The other members of the Doctoral Committee for their continued interest: Professors L. Anderson, S. W. Churchill, J. J. Martin and R. R. White.

Mr. H. Maget for many fruitful discussions on this subject and otherwise.

The Dow Chemical Company for the propylene oxide and Dowanols used in this work.

Miss Bertha Hugh for typing the manuscript and the Industry Program of the College of Engineering for printing this work.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

LIST OF TABLES

Table Page

LIST OF TABLES (CONT'D)

LIST OF TABLES (CONT'D)

LIST OF FIGURES

LIST OF FIGURES (CONT'D)

NOMENCLATURE

A,	Moles of component A.
[A],	Alcohol, moles per 100 grams.
A,	Pre-exponential factor in the Arrhenius Equation.
AB_n	Moles of alcohol-ethers at any time t.
B,	Moles of propylene oxide at any time t.
[B],	Propylene oxide, moles per 100 grams.
C_{A^-},	Concentration of the anion of alcohol, moles per liter.
C_A ,	Concentration of methanol at any time t, moles per liter.
C_{A_o},	Initial concentration of methanol, moles per liter.
$C_{\underline{A}_o}$,	Pure methanol, moles per liter.
C_{AB_n},	Concentration of alcohol-ethers at anytime t, moles per liter.
C_B,	Concentration of propylene oxide, moles per liter.
C_n,	Constants used in the equation for rate constants.
D,	Dielectric constant.
D_o,	Dielectric constant of the pure alcohol.
E,	The measured Arrhenius activation energy, calories per gram-mole.
E_β,	The activation energy obtained by extrapolating to $1/D = 0$.
G_A,	$k_1C_A + k_2C_{AB}$.
K,	Boltzmann constant.
$K_{eq.}$	Equilibrium constant.
M,	Reciprocal of the molal volume of methanol at the temperature of the reaction.
N,	Avogadro's number.
RO^-,	Anion of the alcohol.

NOMENCLATURE (CONT'D)

R,	The gas constant, 1.987 calories per gram-mole per degrees Kelvin.
T,	Absolute temperature, °K.
V,	Volume, liters.
Z,	Charge.
a_i,	Distance of closest approach of another ion to the ith ion.
c_i,	Concentration of the ith ion, moles per liter.
c_n, c_j,	Distribution constant, k_n/k_1, k_j/k_1. $j,n > 1$.
c',	Catalyst concentration, moles per liter.
e,	Electronic charge.
$f(C_A)$,	A function of methanol concentration.
h,	Planck's constant.
k,	Rate constant.
k',	Rate constant at infinite dilution.
k_c,	Catalyzed second order rate constant, $\text{moles}^{-2}\text{liter}^{2}\text{min.}^{-1}$.
k_m,	Rate constant as function of the reacting medium.
$\underline{k_n}$,	Catalyzed second order rate constants corresponding to an excess of alcohol in the reacting medium at unit molar catalyst concentration, $\text{moles}^{-2}\text{liter}^{2}\text{ min.}^{-1}$
k_n,	Second order rate constant at unit molar catalyst concentration, $\text{moles}^{-2}\text{liter}^{2}\text{min.}^{-2}$
k_u,	Uncatalyzed second order rate constants, $\text{moles}^{-2}\text{liter}^{2}\text{min.}^{-1}$
k_o,	Rate constant referred to the gas phase.
n_t,	Total number of moles per 100 grams of initial charge.
n_D^{25},	Refractive index at 25°C.
r_a,	Radius of molecule a.
$r^{\neq}$	Radius of the activated complex.

NOMENCLATURE (CONT'D)

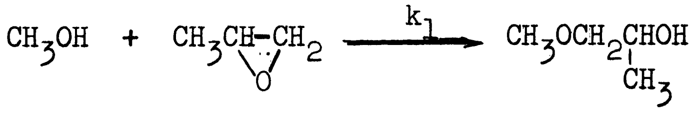
t,	Time in minutes.
v,	Ratio of moles of oxide consumed to moles of initial alcohol.
α,	Activity coefficient.
$\gamma_{a,b}$,	Activity coefficient of the reactants.
γ_i,	Activity coefficient of the ith ion.
$\gamma^{\neq}$,	Activity coefficient of the activated complex.
$\Delta S^{\neq}$,	Entropy of activation.
$\Delta H^{\neq}$,	Heat of activation.
μ,	Ionic strength = $1/2 \overset{i}{\Sigma} c_i Z_i$

INTRODUCTION

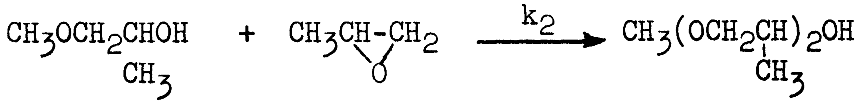
The interest in reactions between epoxides and alcohols goes back as far as 1894 when Roithner(64) observed the reaction of ethylene oxide and propylene oxide with phenol. Industrial applications for the reaction products were proposed even then. However, it was not until about thirty years later that these reactions received widespread attention when I. G. Farbenindustrie(20) patented the process for condensing short chain alcohols with ethylene oxide in the presence of acidic or basic catalysts. Since then, the reaction products obtained from the condensation of epoxides with alcohols have been extensively used as solvents, lubricants, wetting, emulsifying and drying agents, and as chemical intermediates.

Considerable information is found in the patent and technical literature about these reactions, most of which however, are concerned with the applications of the products. Rate studies of these reactions have received scant attention until recently.

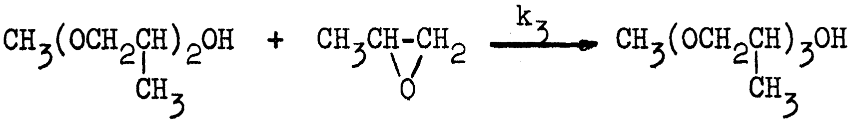
Pecorini(57), in this laboratory, has initiated the investigation of the liquid-phase kinetics of the reaction between propylene oxide and methanol, catalyzed by sodium hydroxide. The reaction gives rise to a system of consecutive addition steps represented as follows:



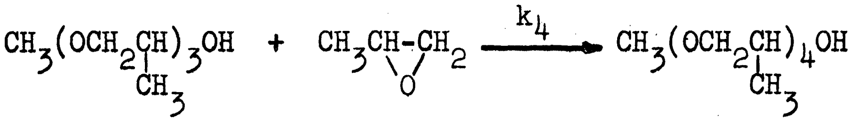
$$CH_3OH + CH_3CH\text{-}CH_2 \ (O) \xrightarrow{k_1} CH_3OCH_2CH(CH_3)OH \qquad (1)$$



$$CH_3OCH_2CH(CH_3)OH + CH_3CH\text{-}CH_2 \ (O) \xrightarrow{k_2} CH_3(OCH_2CH(CH_3))_2OH \qquad (2)$$

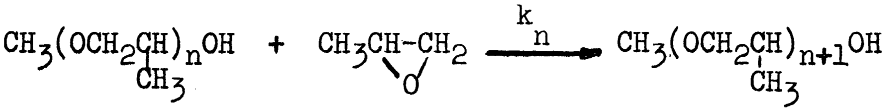


$$\mathrm{CH_3(OCH_2\underset{CH_3}{CH})_2OH + CH_3\underset{\backslash O /}{CH\text{-}CH_2} \xrightarrow{k_3} CH_3(OCH_2\underset{CH_3}{CH})_3OH} \qquad (3)$$



$$\mathrm{CH_3(OCH_2\underset{CH_3}{CH})_3OH + CH_3\underset{\backslash O /}{CH\text{-}CH_2} \xrightarrow{k_4} CH_3(OCH_2\underset{CH_3}{CH})_4OH} \qquad (4)$$

or in general,



$$\mathrm{CH_3(OCH_2\underset{CH_3}{CH})_nOH + CH_3\underset{\backslash O /}{CH\text{-}CH_2} \xrightarrow{k_n} CH_3(OCH_2\underset{CH_3}{CH})_{n+1}OH} \qquad (5)$$

where $n = 1, 2, 3, \ldots$

Although different isomeric products are possible for the reactions, it was shown that for the first reaction the product is exclusively a secondary alcohol(57). In the present work, the glycol ethers used and the products formed from the succeeding reactions were assumed to consist of only one isomer.

The work of Pecorini was limited to the study of the individual rates of reactions 1 and 2 and of the rates when the two reactions occurred consecutively. Semi-empirical rate equations were derived so that the rate data for reactions (1) and (2) when occurring consecutively could be predicted from the rate constants obtained for the individual reactions. However, most of the work on individual reactions was limited to an alcohol to oxide mole ratio of 5 to 1 and the data obtained from the study of the consecutive reactions are mainly based on a starting mole ratio of alcohol to oxide of 1 to 1. The effect of composition change on the rate constants was therefore investigated only over a limited range.

In a consecutive and competitive reaction system, as the one described above, the nature of the distribution of the products is of major importance. Theoretically, if the reaction velocity of each of the individual steps is known, the product distribution of the system can be readily calculated.

A frequently observed phenomenon concerning reaction systems similar to the one mentioned above is the inability of the individually-determined rate of reaction to describe the product distribution of the system.(46,54,55,57,76) Although no satisfactory explanation has yet been advanced to explain this behavior, it is generally believed that factors such as solvent effects, ionization equilibria and the different acidities of the reactants may be involved.

The present investigation was therefore initiated to extend Pecorini's work as well as to try to gain an insight in to the factors that may influence the reaction velocity of the system under varied conditions and to derive a set of consistent rate equations that can describe the kinetics of the system under all the conditions studied.

LITERATURE REVIEW

Most of the fundamental work reported in the literature on the reactions of low molecular weight epoxides with alcohols are mechanism studies. To our knowledge, only the following papers reported rate investigations on the reactions of ethylene or propylene oxide with short chain aliphatic alcohols.(55,57,58,76) On the other hand, extensive, work on the reaction of epoxides with water has been reported.(6,9,13, 41,46,48,65)

Kinetic and Product Distribution Studies

Natta(55) reported kinetic and product distribution studies of the uncatalyzed reaction of ethylene oxide with methanol and with their products of reaction. From product distribution data, the ratios of rate constants (distribution constants) at constant temperatures were derived and it was shown that the individual second order rate constants can be calculated by a simple substitution if the time, amount of initial reactants and the distribution constants were known. Specific second order rate constants, obtained in this manner, were presented for the uncatalyzed reactions between ethylene oxide and methanol; ethylene oxide and ethylene glycol monomethyl ether. It was observed, however, that the specific rate constants calculated for the reactions ethylene oxide-ethylene glycol monomethyl ether and ethylene oxide-diethylene glycol monomethyl ether from product distribution data initiated by the reaction of ethylene oxide with methanol have values quite different from the rate constants evaluated from product distribution data initiated by the reactions themselves.

Weibull and Nycander(76) investigated the product distributions initiated by the reaction of ethylene oxide with ethanol and ethylene oxide with ethylene glycol monoethyl ether using sodium as a catalyst. The ratio of rate constants (distribution constants) from the product distribution studies were compared with ratios of individually determined rate constants using dilute solutions of ethylene oxide in the respective alcohols. The data presented were limited and the distribution data were obtained at 65°C while the individual rate constants reported were at a temperature of 25°C. Nevertheless, the discrepancies between the distribution constants and the ratio of the rate constants were too large to be attributed to temperature effects alone.

Pecorini and Banchero(58) studied the liquid-phase sodium hydroxide catalyzed reactions of propylene oxide with methanol and propylene oxide with propylene glycol monomethyl ether. The individual rate constants were obtained using a starting mole ratio of alcohol to propylene oxide of 5/1. The data obtained covered the temperature range 35-100°C and catalyst concentrations from 0-1.5 weight percent. It was found that normal second order reaction rate constants calculated from data obtained from single reaction experiments do not agree with rate constants derived from time-composition data wherein several additional products were formed. As a result, a semi-empirical rate equation was developed which was shown to correlate all the experimental data.

Recently, Satkowski and Hsu(66) reported kinetic data on the addition reaction of ethylene oxide with tridecyl alcohol in the presence of various basic catalysts in a constant pressure reactor. They found that at elevated temperatures (190°-200°C) the rate of addition of ethylene oxide is constant indicating that the rate constants of each succeeding reaction are equal.

The reactions of ethylene oxide and propylene oxide with phenols in alkaline solutions have been investigated by Boyd and Marle(7) and second order velocity constants were obtained for the reactions at one temperature.

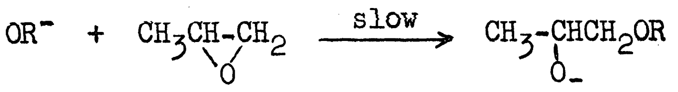
Miller, Bann, and Thrower(49), and Patat, Cremer, and Bobleter(56) reported product distributions for the base-catalyzed reactions initiated by ethylene oxide and phenol. Their data indicated that the rate of reaction of ethylene oxide with phenol to form ethylene glycol monophenyl ether is very much faster than the reactions of ethylene oxide with the succeeding products formed.

More extensive work on the kinetics of the reactions of ethylene oxide and propylene oxide with water, uncatalyzed(13,41,46,65) and catalized by acids(6,9,48,65) or bases (13,41,46), has been reported. The similarity of the structures of alcohols and water suggests the usefulness of the hydration data in understanding the alcoholysis of epoxides.

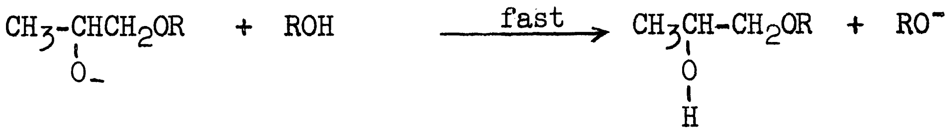
Reaction Mechanisms

The alcoholysis and hydrolysis of epoxides proceed in three kinetically distinct reactions. Namely, the base-catalyzed reaction, the pH independent reaction, and the acid-catalyzed reaction. Ingold(32) has summarized the probable mechanisms involved in these reactions.

The formulated mechanism for the base-catalyzed reaction is an S_N2 (substitution, nucleophilic, bimolecular) mechanism as follows:



$$OR^- + CH_3CH\text{-}CH_2(O) \xrightarrow{slow} CH_3\text{-}\underset{O^-}{CH}CH_2OR \qquad (6)$$



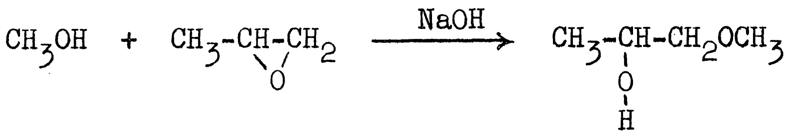
$$CH_3\text{-}\underset{O^-}{CH}CH_2OR + ROH \xrightarrow{fast} CH_3\underset{OH}{CH}\text{-}CH_2OR + RO^- \qquad (7)$$

where the rate may be represented as rate = k (epoxide)(RO^-). This has been deduced and corroborated by mechanism studies in the hydration of epoxides(9,41,42,62,65) and from extensive work on the mechanism of the reaction of epoxides with alcohols(3,11,33,69,72).

Specific support for the S_N2 mechanism has come from the following sources:

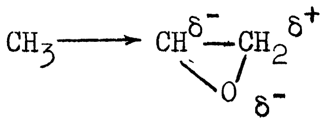
1. Structural isomers formed from the reaction

It is well known that the base-catalyzed reaction between unsymmetrical epoxides and alcohols gives two isomeric products(2,11,33, 63,72) although the preferential attack of the anion on the primary carbon atom usually yields a high percentage or near exclusive amount of the secondary alcohol-ethers. For example, the reaction of propylene oxide with methanol, catalyzed by sodium hydroxide, yields exclusively:



$$CH_3OH + CH_3\text{-}CH\text{-}CH_2(O) \xrightarrow{NaOH} CH_3\text{-}\underset{OH}{CH}\text{-}CH_2OCH_3 \qquad (8)$$

the secondary alcohol-ether(63). This has been interpreted as a bimolecular nucleophilic (S_N2) attack of the alkoxy ion selectively at the primary carbon atom because of its lower electron density as shown by the configuration denoting the relative charge in the various atoms of the propylene oxide molecule



$$CH_3 \longrightarrow CH^{\delta^-}\text{—}CH_2^{\delta^+}(O^{\delta^-})$$

The charge distribution of the propylene oxide molecule as represented is a consequence of the electron-repelling nature of the methyl group and the electronegativity of the oxygen atom. One would therefore expect a nucleophilic attack of the alkoxy ion predominantly on the primary carbon atom of the epoxide ring. This has been shown to be the case experimentally(11,69).

Furthermore, for other unsymmetrical epoxides the ratio of the isomeric products obtained was observed to be constant as the base strength was increased, indicating that the cleavage of both C-O bonds proceed under the same mechanism(3). The type of attacking alkoxy ion was found to have no effect on the direction of ring openings, although the rates of reaction were affected(11). The type of epoxide, however, has a marked effect on the ratio of isomeric products formed. This can be readily clarified by the charge distribution of the molecule and the possibility of steric hindrances(32).

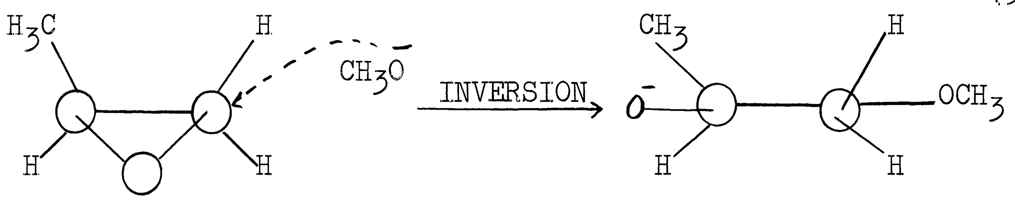
2. Base-catalyzed reactions

Most base-catalyzed homogeneous organic reactions are characterized by two distinct steps (1) The protolytic step in which the acid transfers a proton to the base and, (2) the subsequent reaction of the product of protolysis to form the end product. Both steps are bimolecular processes.

3. Stereochemical considerations

The mechanism of bimolecular nucleophilic (S_N2) displacement involves backside attack on the carbon atom -- this position of approach, which requires the least amount of energy, would result in the inversion of configuration(28). Hammett(30) has pointed out that total inversion is a consequence of a bimolecular nucleophilic substitution. Such an inversion for the case of an S_N2 attack of the propylene oxide molecule by an anion may be represented as follows:

(9)



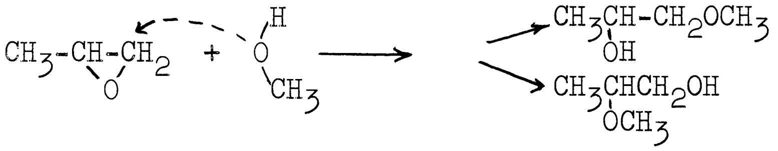
Backside attack of the propylene oxide
molecule by methoxy ion

4. Isotopic tracer studies

More recent work using isotopic oxygen (O^{18}) and chlorine (Cl^{38}) further reinforced the bimolecular nucleophilic mechanisms of the base-catalyzed reactions of epoxides with alcohols(42).

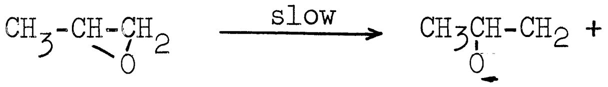
For the uncatalyzed reactions, the proposed mechanism were not as specific. Ingold(32) listed three possible mechanisms for the spontaneous reaction. They are, in the order of acceptance, as follows:

1. The S_N2 substitution of the epoxide base with the alcohol molecule as a substituting agent.

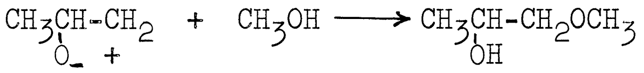


$$CH_3\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} + O\begin{matrix}H\\ CH_3\end{matrix} \longrightarrow \begin{matrix} CH_3\underset{OH}{CH}\text{-}CH_2OCH_3 \\ CH_3\underset{OCH_3}{CH}CH_2OH \end{matrix} \qquad (10)$$

2. The S_N1 substitution of the epoxide base.

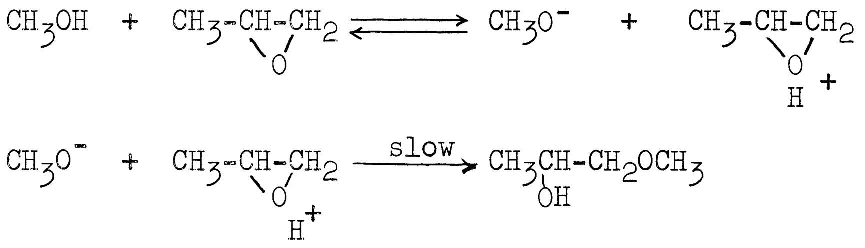


$$CH_3\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \xrightarrow{\text{slow}} CH_3\underset{O_-}{CH}\text{-}CH_2\ + \qquad (11)$$



$$CH_3\underset{O_-}{CH}\text{-}\underset{+}{CH_2} + CH_3OH \longrightarrow CH_3\underset{OH}{CH}\text{-}CH_2OCH_3 \qquad (12)$$

3. S_N2 substitution by the alkoxy ion in the conjugate acid of the epoxide.

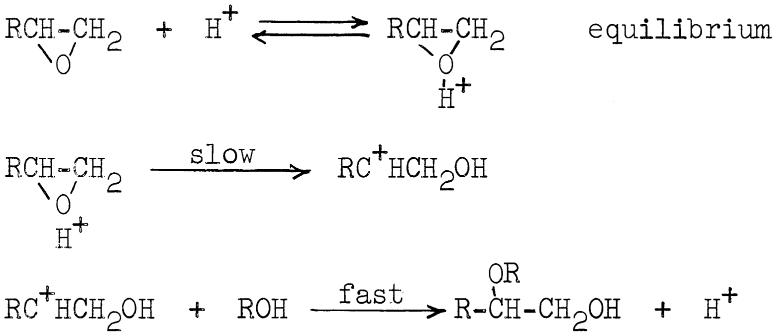


$$CH_3OH + CH_3\text{-}\underset{O}{CH\text{-}CH_2} \rightleftharpoons CH_3O^- + CH_3\text{-}\underset{\underset{H^+}{O}}{CH\text{-}CH_2} \qquad (13)$$

$$CH_3O^- + CH_3\text{-}\underset{\underset{H^+}{O}}{CH\text{-}CH_2} \xrightarrow{slow} CH_3\underset{OH}{CH}\text{-}CH_2OCH_3 \qquad (14)$$

The slow rate of reaction for the uncatalyzed alcoholysis of epoxides is one of the reasons for not having a better understanding of the mechanism of the reaction.

In the acid-catalyzed alcoholysis of epoxides, the favored mechanism is an S_N1 substitution of the conjugated acid(32,42) where a carbonium ion is an intermediate.



$$\underset{O}{RCH\text{-}CH_2} + H^+ \rightleftharpoons \underset{\underset{H^+}{O}}{RCH\text{-}CH_2} \quad \text{equilibrium} \qquad (15)$$

$$\underset{\underset{H^+}{O}}{RCH\text{-}CH_2} \xrightarrow{slow} RC^+HCH_2OH \qquad (16)$$

$$RC^+HCH_2OH + ROH \xrightarrow{fast} R\text{-}\overset{OR}{CH}\text{-}CH_2OH + H^+ \qquad (17)$$

Examples in support of this mechanism are the reversla of orientation in the ethyl alcoholysis of propylene oxide on changing from alkaline to acidic condition(11) and also from the work by Long and Pritchard(42)

It is quite possible to have several mechanisms operating concurrently. There is actually no sharp dividing line between the S_N1 and S_N2 mechanism(32). Cases have been known wherein the mechanism for a series of homologous reactions changed from an S_N1 mechanism to an

S_N2 mechanism as was the case with the alkaline hydrolysis of alkyl halides(32).

Equations Describing Product Distributions

For a system of consecutive additional reactions such as those shown on page 2, the product distribution is proportional to the reaction probabilities of each individual reaction. The general case of the distribution of products in a series of bimolecular competitive reactions at constant temperature, with different rates for each step, in terms of the remaining concentration of the starting material has been derived by Natta and Mantica(54). Less comprehensive treatments have also been considered previously by Abel(1), Fuoss(26), and Martin and Fuchs(47).

Several simplified forms of the general case have also been derived. Flory(23) considered the case where all the reaction probabilities are equal and showed that the Poisson distribution describes the products obtained. Weibull and Nycander(76), going a step further, considered the case where only the rate of the first step is different from the rates of all the succeeding steps, the rates of the succeeding steps being all equal.

Solvent Effects on the Rates of Reaction and Product Distribution

No results are available in the literature on the effects of solvents and changing compositions on the rates of reaction or product distributions on epoxide-alcohol reactions although speculations have been made(54,55). Maget(46) studied these effects on the sodium hydroxide catalyzed propylene oxide-water reaction and has shown that these effects may be predicted in terms of the starting concentrations of the reactants or the dielectric constants of the reacting medium.

EXPERIMENTAL METHODS AND APPARATUS

The scope of the experimental work may be conveniently divided into three distinct parts:

In the first part, the effects of temperature and catalyst concentration upon the rate constants for the homogeneous reaction of propylene oxide with dipropylene glycol monomethyl ether, and the reaction of propylene oxide with tripropylene glycol methyl ether, using sodium hydroxide as catalyst were investigated. Additional rate data on the reaction of propylene oxide with methanol were also obtained at several temperatures.

The second part of the experimental work consisted of obtaining product distribution data initiated by the reaction of propylene oxide with methanol and by the reaction of propylene oxide with monoglycol methyl ether.

While the first part of the work was primarily performed to obtain reaction rate constants of the individual reactions, the second part was run to test the applicability of these rate constants under conditions where several consecutive reactions were occurring at the same time.

Finally, the remaining part consisted of experimental work done in an attempt to explain the results obtained in the first two parts. They comprised several runs in which the sodium hydroxide catalyzed reaction of propylene oxide with methanol in dioxane as solvent and the catalyzed reaction of propylene oxide with methanol and monoglycol monomethyl ether were studied.

TABLE I

SUMMARY OF EXPERIMENTAL WORK

Reactions	Temp. °C	Cat. conc. mols./lit.	Starting alcohol to oxide mole ratio	Table No.
<u>Single Reactions</u>				
methanol-propylene oxide	35-55	0.139 - 0.252	38.4 - 48.8	XXVI
dipropylene glycol methyl ether - propylene oxide	35-87	0.0556 - 0.3469	5 - 10	XXVII
tripropylene glycol methyl ether - propylene oxide	45-100	0.05683 - 0.3495	7 - 10.25	XXVIII
<u>Product Distribution (Initiating Reaction)</u>				
methanol-propylene oxide	45	.152 - .305	0.645 - 10	VII
propylene glycol methyl ether - propylene oxide	60	.215 - .305	0.667 - 3	VIII
<u>Mixed Reactions</u>				
methanol - propylene oxide in dioxane	45	0.1839 - 0.234	12.51 - 37.20 0.575 - 6.90 (dioxane conc. mol./lit.)	XXIX
methanol and propylene glycol methyl ether - propylene oxide	45	0.1625 - 0.266	6.67 - 35.20(methanol/oxide) 4.06 - 13.50(glycol/oxide)	XXX

All experimental data were obtained in batch reactors described in page 17 . A tabulated summary of all the experimental work is presented in Table I.

Materials

The propylene oxide, propylene glycol ether, dipropylene glycol ether and tripropylene glycol ether were Dow Chemical Company commercial grade products and were used without further purification.

The methyl alcohol used was reagent grade material.

The dioxane used in the solvent experiments was a technical grade product that had been refluxed with sodium hydroxide for two hours and then distilled.

A summary of the physical properties and purity of the reactants is tabulated in Table II. More detailed physical properties of the reactants and products including their infrared spectra are presented in Appendix I.

Experimental Apparatus

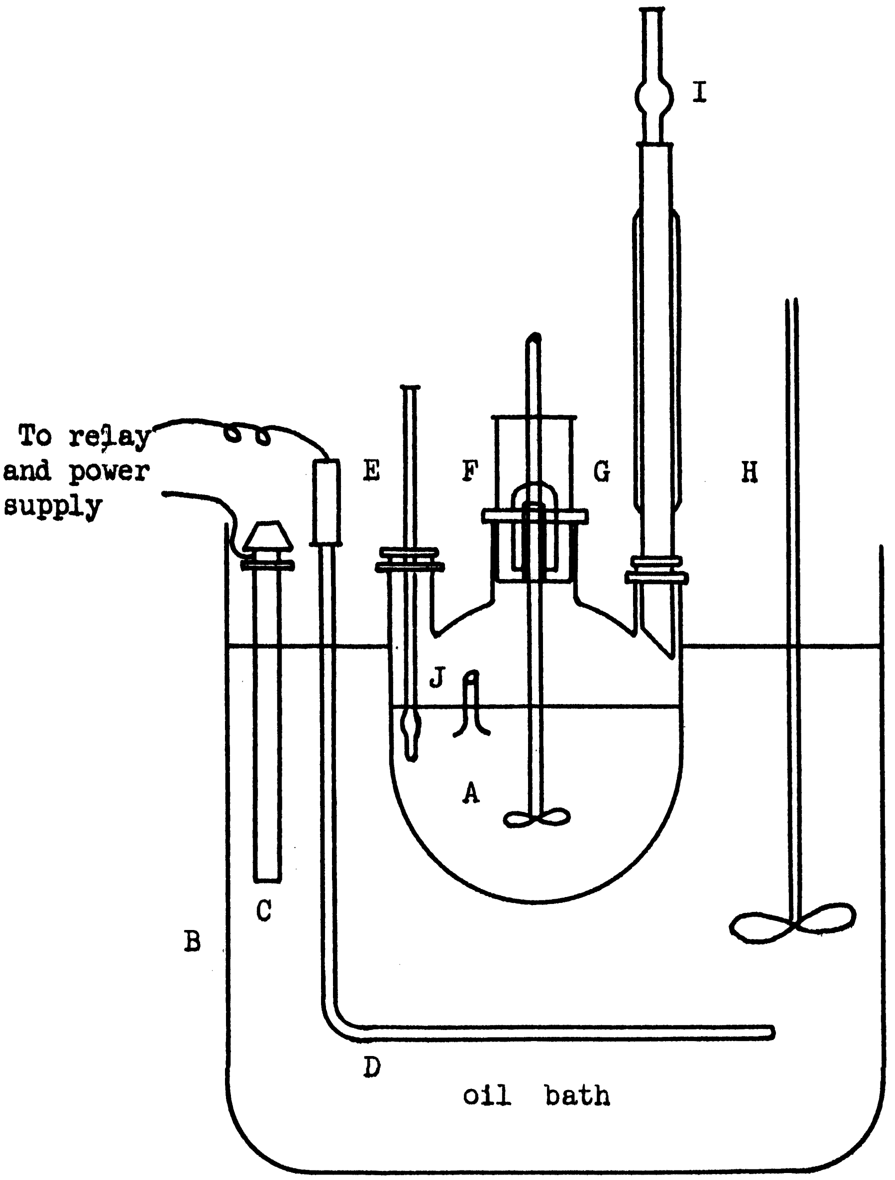
All of the experiments, except for the uncatalyzed runs, were performed in a 500 ml. glass reactor kept at a constant temperature by an oil bath as shown in Figure 1. Heat was supplied to the bath by a 200-watt copper resistance coil heater and controlled through a relay by a Fenwal contact type thermoregulator. The thermoregulator was sen sitive to a temperature change of ± 0.1°C in the range of temperatures of the experiments. An air-driven bath stirrer kept the bath temperature uniform. The temperature inside the reactor generally does not vary by

TABLE II

PHYSICAL PROPERTIES OF REACTANTS AND PRODUCTS

Materials	Molecular Weight	Density 25°C	Boiling Point °C 760 mm Hg.	Refractive Index n_D^{25}	Water Content wt. %	Ref.
Propylene oxide	58.08	0.824	33.9	1.363	0.1	(10)
Methanol	32.04	0.787	64.7	1.3275	0.1	(57)
Propylene glycol monomethyl ether	90.12	0.918	120.0	1.402*	-	(16)
Dipropylene glycol monomethyl ether	148.20	0.947	190.0	1.419*	0.15*	(16)
Tripropylene glycol monomethyl ether	206.28	0.965	242.8	1.428*	0.15*	(16)
Tetrapropylene glycol monomethyl ether	264.36	0.9738*		1.432*		(16)
Dioxane	88.10	1.041	101.3	1.42		(10)

* Values experimentally determined by the author.



A - 500 ml. round bottom flask
B - 5 gal. battery jar
C - Fenwal Thermoregulator
D - Copper heating coil
E - Thermometer
F - Mercury-seal stirrer
G - Water condenser
H - Motor driven stirrer
I - Soda-Lime drying tube
J - Sample withdrawal tube

Figure 1. Glass Reactor Set-Up.

more than 0.20°C. A temperature history of a typical run is shown in Appendix VI. Although the propylene oxide-alcohol reaction is an exothermic one(57), the addition of about 4 mass percent propylene oxide to start the reaction produces negligible temperature change of the reacting mixture.

The glass reactor was a modified 3-neck 500 ml. round bottom flask with a fourth opening added in the form of an 8 mm. Pyrex glass tubing as shown in Figure 1. A water condenser and a calibrated thermometer were inserted in the two side necks while an air-driven, mercury seal, stirrer passed through the center neck. The glass tubing opening was sealed with a serum cap and samples were withdrawn through this cap by means of a hypodermic needle and calibrated syringe.

The uncatalyzed runs were performed at 200°C in an autoclave previously described by Pecorini(57). This was a Monel pressure vessel with a capacity of 2.7 liters and equipped with a magnetically operated agitator. Lines were provided for the introduction of reactants as well as removal of products at any time during the run.

Analysis of the products obtained in the product distribution runs was made by distillation using fractionating columns and auxiliary equipment which have been described in the literature(74). Two columns were used, one was a twelve mm.I.D. column packed with 89 cm. of 3/16 single-turn glass helices corresponding to about thirty theoretical plates and having a hold-up of about 5 c.c. The other column was a 4 mm.I.D. column with a continuous Monel wire spiral and corresponding to about ten theoretical plates. The hold-up of this second column is negligible. The second column was primarily used to separate the higher molecular fractions. The fractionation column had two heating jackets to compensate for any heat losses from the column to the surroundings. A magnetic reflux splitter actuated by a controlled timer relay system regulated the reflux and provided for regular take-off of distilled products.

Experimental Procedures

In the determination of the rate constants of each of the consecutive reactions (see page 1), the time-composition history of propylene oxide was obtained at predetermined temperatures and catalyst concentrations. An excess of the starting alcohol reactant was necessary to insure that no higher products are formed and also to keep the medium change during the reaction negligible. The degree of dilution of the propylene oxide was dictated only by the limitations of the analytical methods. A starting concentration of about 4 mass percent propylene oxide was used for all runs in the determination of the individual rate constants. This corresponds to alcohol to oxide mole ratios for reactions (3) and (4) of 10 and 7 respectively. An analysis of the reaction products of reactions (3) and (4) using these starting alcohol to oxide mole ratios has shown no detectable amount of higher products formed other than the first additional product.

Approximately the same mass concentration of propylene oxide was used for the reaction of propylene oxide with methanol in dioxane and the reaction of propylene oxide with a starting mixture of methanol and propylene glycol ether.

In the product distribution studies, various amounts of propylene oxide were reacted to completion with the alcohol and the final mixture was analyzed.

The procedure used in conducting the runs in the glass reactor was essentially as follows: A predetermined amount of the alcohol with a corresponding amount of dissolved sodium hydroxide catalyst was weighed into the glass reactor. The thermometer, water condenser and mercury seal stirrer were then put in place and the whole reactor placed into the oil bath set at the desired temperature. Propylene oxide was then introduced into the reactor through the capped glass tubing by means of a calibrated syringe and hypodermic needle. The concentration of propylene oxide with respect to time during the reaction was then obtained by analysis of samples taken from the reacting mixture through the capped tubing at frequent intervals.

In the case of a product distribution run, no samples were taken. The reactions were run to their conclusion by letting the reaction flask stay in the temperature bath for a prolonged period. An analysis for propylene oxide was made at the end of the run to insure that all the propylene oxide was reacted. The resulting mixture was then distilled and the fractions analyzed to determine the concentrations of the various products.

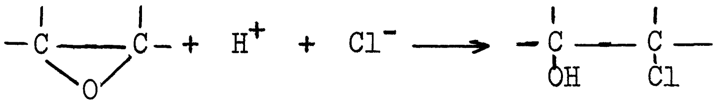
For the uncatalyzed runs the pressurized batch reactor, described previously, was used. The same procedure used by Pecorini(57) was followed.

Analytical Methods

1. Analysis of Propylene Oxide

Several methods were evaluated for the analysis of propylene oxide in the presence of the reactants and products. Two were chosen as the most desirable for our work.

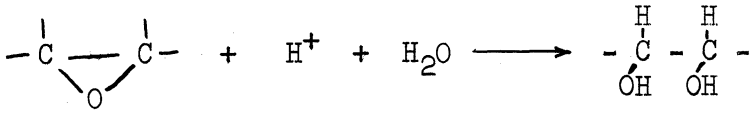
(1) The hydrochloric acid-calcium chloride method(50). This method is essentially based on the fact that hydrogen chloride adds to the alpha epoxide group to form a chlorohydrin according to the following equation



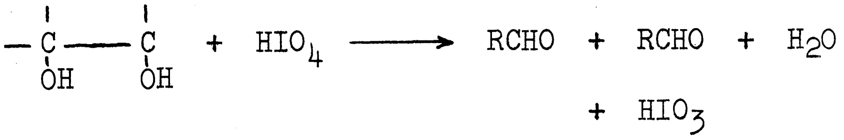
(18)

The difference between the amount of acid added and the amount unconsumed, allowing for the presence of catalyst is the measure of the epoxide.

(2) The periodic-perchloric acid method(17). The essential feature of this method is the hydration of the alpha epoxide group and the subsequent oxidization of the alpha glycol formed. The periodic acid is the specific oxidizing agent. The reactions proceed according to the following equations:



(19)



$$-\underset{OH}{C}-\underset{OH}{C} + HIO_4 \longrightarrow RCHO + RCHO + H_2O + HIO_3 \qquad (20)$$

The free iodine liberated from the excess HIO_4 by the addition of an aqueous solution of 10 percent potassium iodide is titrated with standard sodium thiosulfate. The difference of the amount of thiosulfate used between a blank and the sample is the measure of the epoxide content of the sample.

Both of the methods gave satisfactory results although prior calibration of the methods were necessary. A detailed summary of the work performed in reviewing and calibrating various methods are presented in Appendix II.

2. Product Distribution Analyses

Physical as well as chemical methods were used to obtain a complete product distribution analysis.

A charge of about 100 grams of the reaction mixture from a product distribution run was first separated into binary fractions using the distillation columns previously described. By controlling the distillate temperature and operating the column under vacuum, each cut of the distillate from the column was taken such that only one or two components are present in any particular cut. The various fractions were then analyzed for the relative amount of the two components by refractive index measurements. Binary refractive index calibration curves of the reactants and products were prepared for this purpose. The calibration curves are shown in Appendix I.

The residue left in the distillation flask which was of the order of ten grams was not amenable to the refractive index analysis. However, by assuming the residue is a binary mixture, an analysis of the hydroxyl group in the residue together with a material balance for the hydroxyl group results in a complete description of the concentrations of the products. It may be noted that the hydroxyl concentration is invariant throughout the reaction.

The method of acetylation with acetic anhydride in pyridine(50) was used for the analysis of the hydroxyl group. The method was found to be satisfactory and in general gave quantitative results. Details of this method are found in Appendix II.

EXPERIMENTAL DATA AND RESULTS

The experimentally determined data consisting of propylene oxide concentration versus time are tabulated in Appendix V.

In Tables XXVI-XXVIII the concentration-time data of propylene oxide for the single reactions of propylene oxide with methanol, propylene oxide with dipropylene glycol methyl ether, and propylene oxide with tripopylene glycol methyl ether are collected. Table XXIX tabulates the experimental data for the propylene oxide-methanol reaction in dioxane while Table XXX presents the data for the experiments where propylene oxide was reacted with methanol and propylene glycol methyl ether simultaneously.

In Figures 2 and 3 typical concentration curves for the reaction of propylene oxide with dipropylene glycol methyl ether and with tripropylene glycol methyl ether are shown.

The product distribution data for the initial reaction of propylene oxide with methanol at 45°C and the initial reaction of propylene oxide with propylene glycol methyl ether are tabulated in Tables VII and VIII on page 40.

Considerations In the Formulation of the Rate Equations

According to all available evidence, the most logical mechanism for the sodium hydroxide catalyzed liquid-phase reactions initiated by propylene oxide and methanol can be represented by the following simple steps:

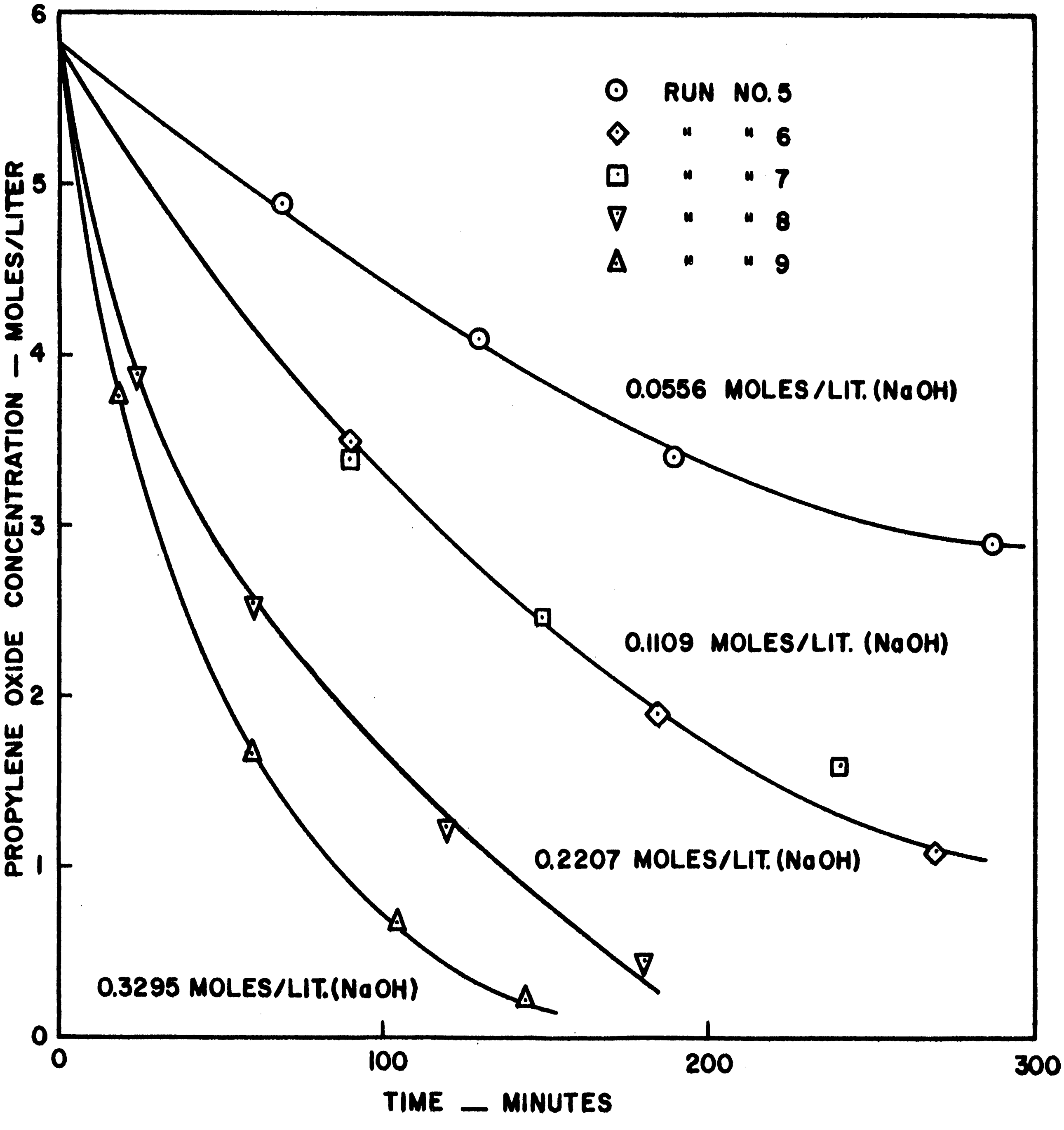


Figure 2. Concentration-Time Curves of Propylene Oxide in the Reaction of Propylene Oxide with Dipropylene Glycol Methyl Ether at 85°C.

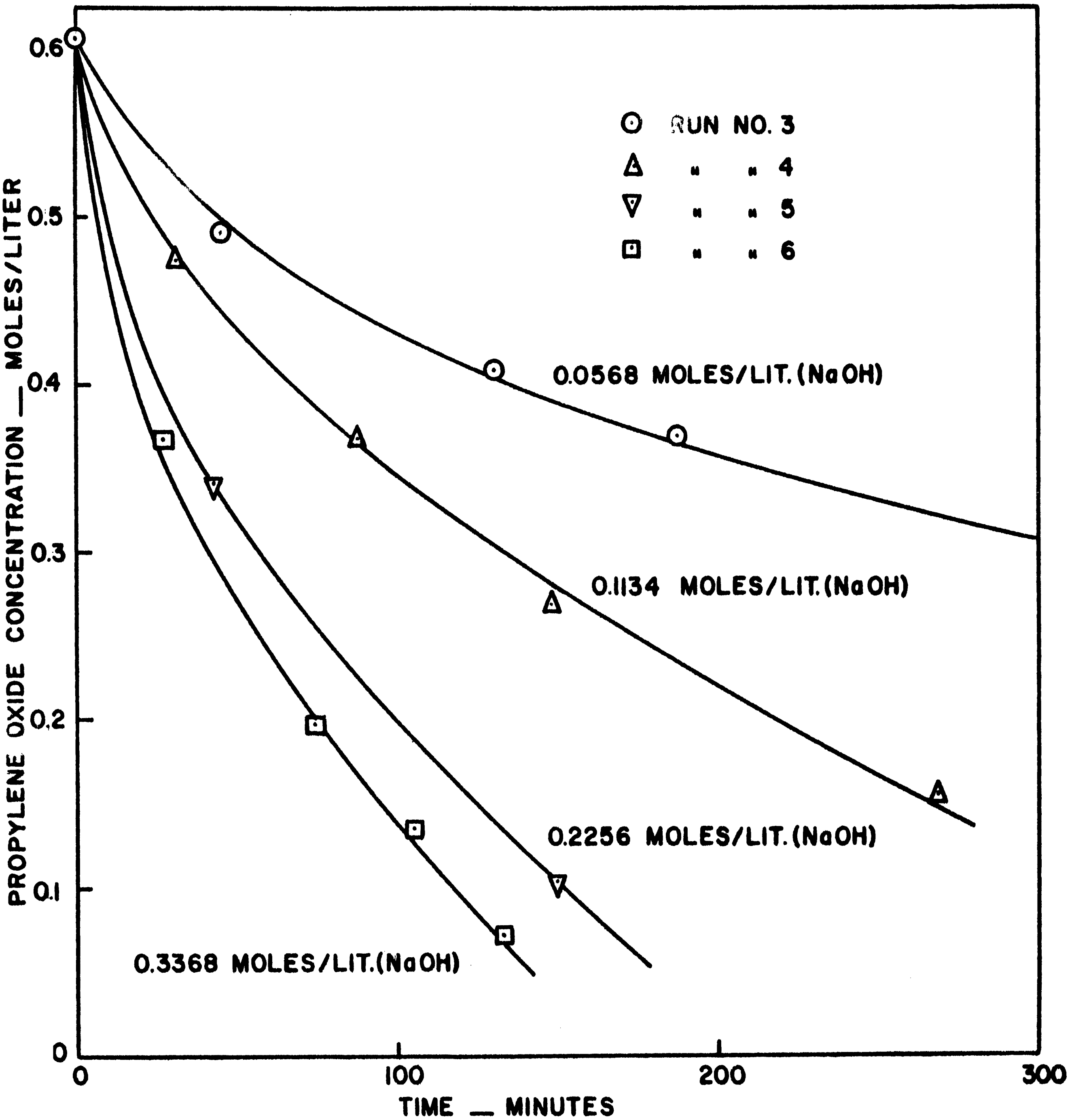
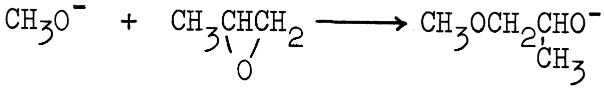


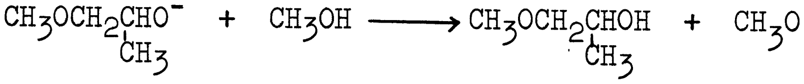
Figure 3. Concentration-Time Curves of Propylene Oxide in the Reaction of Propylene Oxide with Tripropylene Glycol Methyl Ether at 85°C.

$$NaOH \rightleftharpoons Na^+ + OH^- \qquad (21)$$

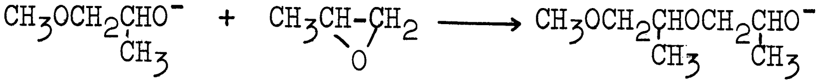
$$CH_3OH + OH^- \overset{K_{eq.}}{\rightleftharpoons} CH_3O^- + H_2O \qquad (22)$$



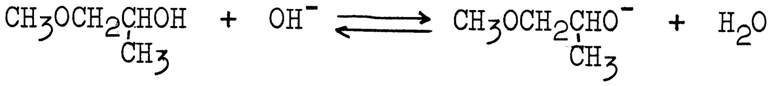
$$CH_3O^- + \underset{\diagdown O \diagup}{CH_3CHCH_2} \longrightarrow CH_3OCH_2\underset{CH_3}{C}HO^- \qquad (23)$$



$$CH_3OCH_2\underset{CH_3}{C}HO^- + CH_3OH \longrightarrow CH_3OCH_2\underset{CH_3}{C}HOH + CH_3O \qquad (24)$$

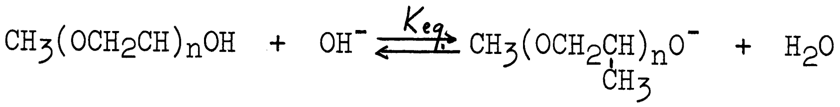


$$CH_3OCH_2\underset{CH_3}{C}HO^- + \underset{\diagdown O \diagup}{CH_3CH\text{-}CH_2} \longrightarrow CH_3OCH_2\underset{CH_3}{C}HOCH_2\underset{CH_3}{C}HO^- \qquad (25)$$

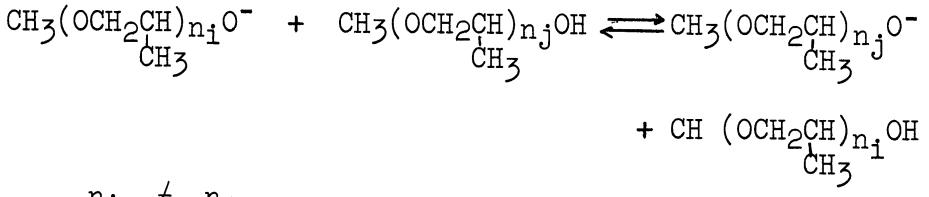


$$CH_3OCH_2\underset{CH_3}{C}HOH + OH^- \rightleftharpoons CH_3OCH_2\underset{CH_3}{C}HO^- + H_2O \qquad (26)$$

or in general



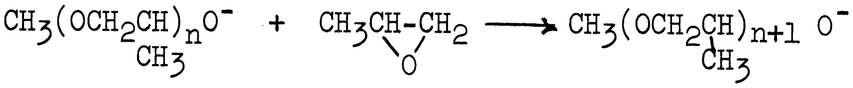
$$CH_3(OCH_2CH)_nOH + OH^- \overset{K_{eq.}}{\rightleftharpoons} CH_3(OCH_2\underset{CH_3}{C}H)_nO^- + H_2O \qquad (27)$$



$$CH_3(OCH_2\underset{CH_3}{C}H)_{n_i}O^- + CH_3(OCH_2\underset{CH_3}{C}H)_{n_j}OH \rightleftharpoons CH_3(OCH_2\underset{CH_3}{C}H)_{n_j}O^-$$

$$+ CH\ (OCH_2\underset{CH_3}{C}H)_{n_i}OH \qquad (28)$$

$$n_i \neq n_j$$



$$CH_3(OCH_2\underset{CH_3}{C}H)_nO^- + \underset{\diagdown O \diagup}{CH_3CH\text{-}CH_2} \longrightarrow CH_3(OCH_2\underset{CH_3}{C}H)_{n+1}\ O^- \qquad (29)$$

and $n = 0,1,2,3,\ldots n$.

the rate-controlling step is denoted by Equation (29). Pecorini$^{(57)}$ has shown that the protolytic step is not the rate-determining step in these series of reactions.

In essence, the rate equation for each of the individual reactions of propylene oxide with the alcohol or alcohol-ethers may be represented as:

rate = k (Propylene oxide)(RO^-)

where k = constant for constant temperature

RO^- = anion of the alcohol

such a rate equation is valid only however under restricted conditions wherein intermolecular forces between reactants are kept at a minimum, e.g. in gas-phase reactions at moderate pressures and in dilute solutions in the condensed phase. In liquid-phase reactions where the compositions of reactants and products vary over a wide range of concentrations, the influence of the changing environment usually has to be taken into account.

For a bimolecular reaction

$$A + B \rightleftarrows \underset{\substack{\text{activated}\\ \text{complex}}}{X^{\neq}} \longrightarrow \text{Products} \tag{30}$$

the general rate expression is given by

$$\text{rate} = k' C_A C_B \frac{\gamma_a \gamma_b}{\gamma^{\neq}} \tag{31}$$

where the specific rate constant

$$k = k' \frac{\gamma_a \gamma_b}{\gamma^{\neq}} \tag{32}$$

and

k' = the rate constant at infinite dilution

$\gamma_{a,b}$ = activity coefficient of the reactants

$\gamma^{\neq}$ = activity coefficient of the activated complex

Equation (32) may be written in the equivalent logarithmic form as

$$\ln k = \ln k' + \ln \frac{\gamma_a \gamma_b}{\gamma^{\neq}} \tag{33}$$

The whole problem therefore reduces to the evaluation of the activity coefficients which are functions of temperature, pressure, and compositions. The actual experimental evaluation of these activity coefficients, however, is not only impractical but often times impossible. For example, $\gamma^{\neq}$ cannot be evaluated experimentally. Theoretical or empirical calculation of these activity coefficient are possible for some cases but their reliability is not expected to be very good.

Appendix III presents some of the theoretical and empirical treatments of reaction rates in solution which are pertinent to this investigation.

Method of Correlation of Single Reactions

According to the mechanism postulated on page 26, the general form of the rate equation for the base-catalyzed reaction of propylene oxide with an alcohol or an alcohol-ether maybe represented as:

$$\frac{dC_B}{dt} = -k_m C_{A^-} C_B \tag{34}$$

where

k_m = specific rate constant, liter mols.$^{-1}$ min.$^{-1}$ The subscript m is used to indicate that it is a function of the reacting medium.

C_{A^-} = anion of the alcohol, moles per liter.

C_B = propylene oxide, moles per liter.

The concentration of A^- in the case where the reactions are confined individually by the use of high alcohol to oxide mole ratio is wholly dependent on the hydroxyl ion concentration.

Depending on the equilibrium constant of Equation (22), the observed kinetics maybe second-order, first order in C_{A^-}, and first order in C_B in the case when $K_{eq.}$ for Equation (22) is large or for the more usual case when $K_{eq.}$ is small the observed kinetics will be third order, first order in C_{OH^-}, C_A, and C_B. Since C_{OH^-} is constant, being regenerated by the reaction shown in Equations (22) and (27) the kinetics maybe pseudo-second order or pseudo first order depending on the concentrations of C_A.

In the case where A is in great excess

$$C_A + C_{OH^-} \xrightleftharpoons{K_{eq.}} C_{A^-} + C_{H_2O} \tag{35}$$

and $K_{eq.}$ small, C_A is essentially constant and the observed kinetics is a pseudo-first order one.

By the use of Equations (21) and (22), Equation (34) may be rewritten as:

$$\frac{dC_B}{dt} = -k_m' C_A C_B (NaOH) \tag{36}$$

and since (NaOH) is constant in any one reaction, then

$$\frac{dC_B}{dt} = -k_m'' C_A C_B \tag{37}$$

where k_m'' is also dependent on the catalyst concentration.

For any experimental run the condition of the medium can be kept practically constant through out the duration of the run by using a great excess of one of the reactants -- in our case, the alcohol.

Integration of Equation (37) gives

$$k_m'' (t) = \frac{1}{C_{Ao} - C_{Bo}} \ln \frac{C_{Bo} C_A}{C_{Ao} C_B} \tag{38}$$

where t = time in minutes

C_{A_0} = initial concentration of alcohol, moles per liter

C_{B_0} = initial concentration of propylene oxide, moles per liter

C_A = concentration of alcohol at time t, moles per liter

C_B = concentration of propylene oxide at time t, moles per liter

Concentration units of moles per liter and a time unit of minutes were used throughout the correlations for the rate equations and rate constants. The use of average density values for the reacting mixtures is not expected to introduce significant error with the dilute solutions used in the single reaction experiments. The errors involved are discussed on page 69 .

The specific rate constant k''_m can therefore be evaluated from experimental concentration-time data of propylene oxide obtained in the individual reaction experiments. We must however keep in mind that these rate constants are dependent on the catalyst concentration and possibly on the composition of the reacting medium.

Representative results of rate constants calculated from data obtained in the single reactions experiment using Equation (38) are given in Table III.

The Individual Reactions

In Tables IV-VI, the values of the rate constants are tabulated for the reactions of propylene oxide with methanol; propylene oxide with dipropylene glycol methyl ether and propylene oxide with tripropylene glycol methyl ether. The values were obtained using Equation (38).

TABLE III

REPRESENTATIVE RESULTS OF CALCULATED RATE CONSTANTS

Run No. 1

Methanol-Propylene Oxide Reaction (temp. = 55°C, catalyst conc. = 0.252 mols./lit.) Initial Mole Ratio, Methanol to Oxide = 48.1

Time mins.	Propylene Oxide Conc. Mols./Lit.	k moles^{-1} lit. min.$^{-1}$
0	0.465	--
11	0.380	0.0000806
30	0.254	0.0000894
55	0.157	0.0000878
85	0.086	0.0000885
131	0.045	0.0000796

Run No. 6

Dipropylene Glycol Methyl Ether-Propylene Oxide Reaction (temp. = 85°C, catalyst conc. = 0.1109 mole/lit.) Initial Mole Ratio, Diglycol Ether to Oxide = 10

Time mins.	Propylene Oxide Conc. Mols./Lit.	k moles^{-1} lit. min.$^{-1}$
0	0.576	--
90	0.341	0.00111
185	0.192	0.00107
270	0.109	0.00113
360	0.057	0.00118

Run No. 1

Tripropylene Glycol Methyl Ether-Propylene Oxide Reaction (temp. = 100°C, catalyst conc. = 0.1895 moles/liter) Initial Mole Ratio, Triglycol Ether to Oxide = 9.25

Time mins.	Propylene Oxide Conc. Mols./Lit.	k moles^{-1} lit. min.$^{-1}$
0	0.457	--
14.5	0.307	0.00662
26.0	0.271	0.00487
39.0	0.171	0.00566
57.0	0.114	0.00625
69.0	0.078	0.00644

The experimental data from which the rate constants were calculated are given in Appendix V.

The linear dependence of the rate on the catalyst concentration is well known for many reactions involving acid-base catalysis. In the case of the system of reactions now under study, Pecorini(57) has shown that this is so for the NaOH-catalyzed reactions of propylene oxide with methanol, and propylene oxide with propylene glycol methyl ether. In Figures 4 and 5, the dependence of the rate constants on the concentration of NaOH is again shown to be linear for the reaction of propylene oxide with dipropylene glycol methyl ether and the reaction of propylene oxide with tripropylene glycol methyl ether.

The temperature dependence of the rate constants presented in Tables IV-VI may be conveniently represented by the Arrhenius Equation

$$k = A e^{-\frac{E}{RT}} \tag{39}$$

where k = specific rate constant

A = the pre-exponential factor

E = activation energy, calories/gm. mole

R = Boltzmann constant, calories/gm mole °K

T = temperature, °K.

To do so, the values of the rate constants in Table IV-VI must all be reduced to one reference catalyst concentration such that the resultant rate constants would be independent of the catalyst concentration. In this case, the reference catalyst concentration is unit molar catalyst per liter.

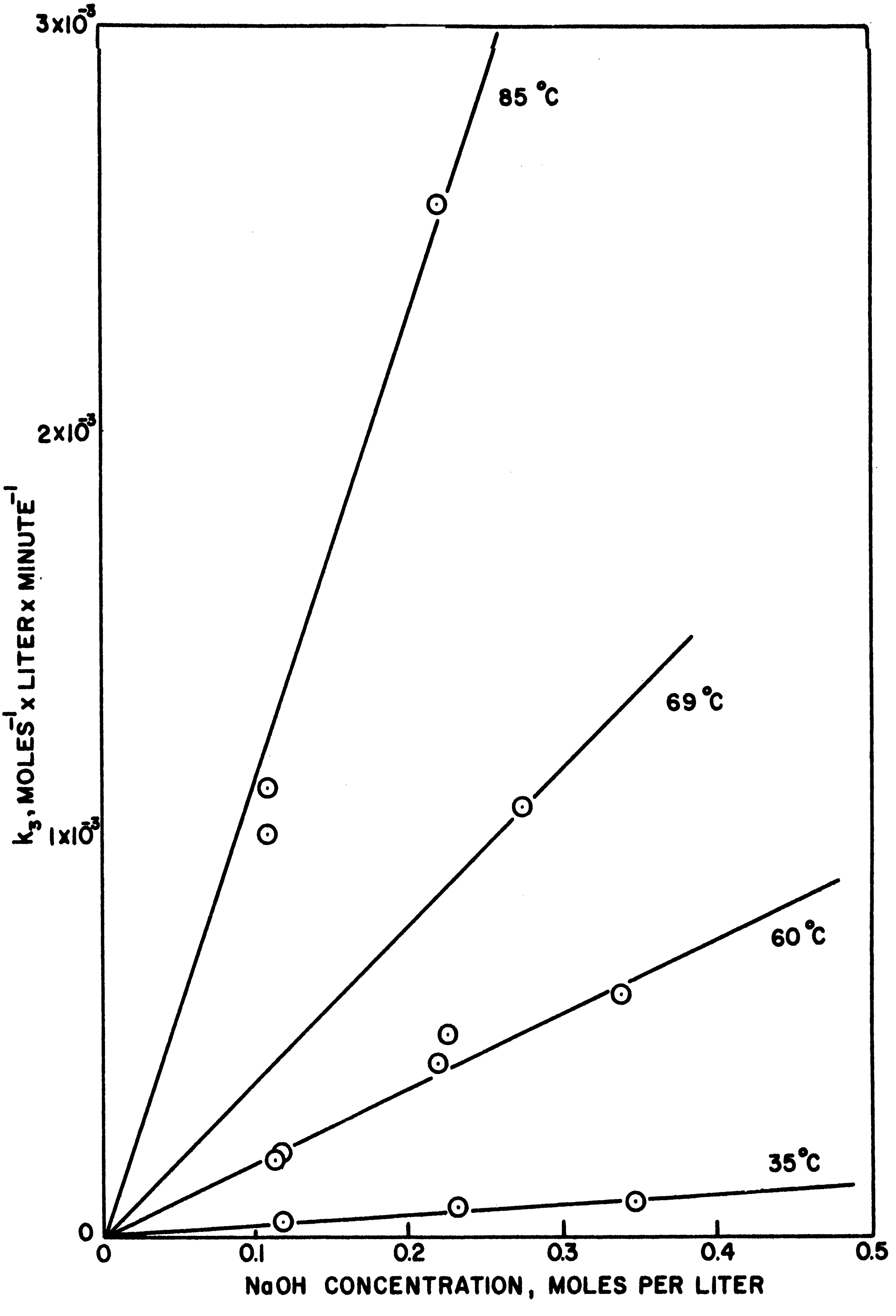


Figure 4. Effect of Catalyst Concentration on the Reaction Velocity Constants of the Propylene Oxide-Dipropylene Glycol Methyl Ether Reaction.

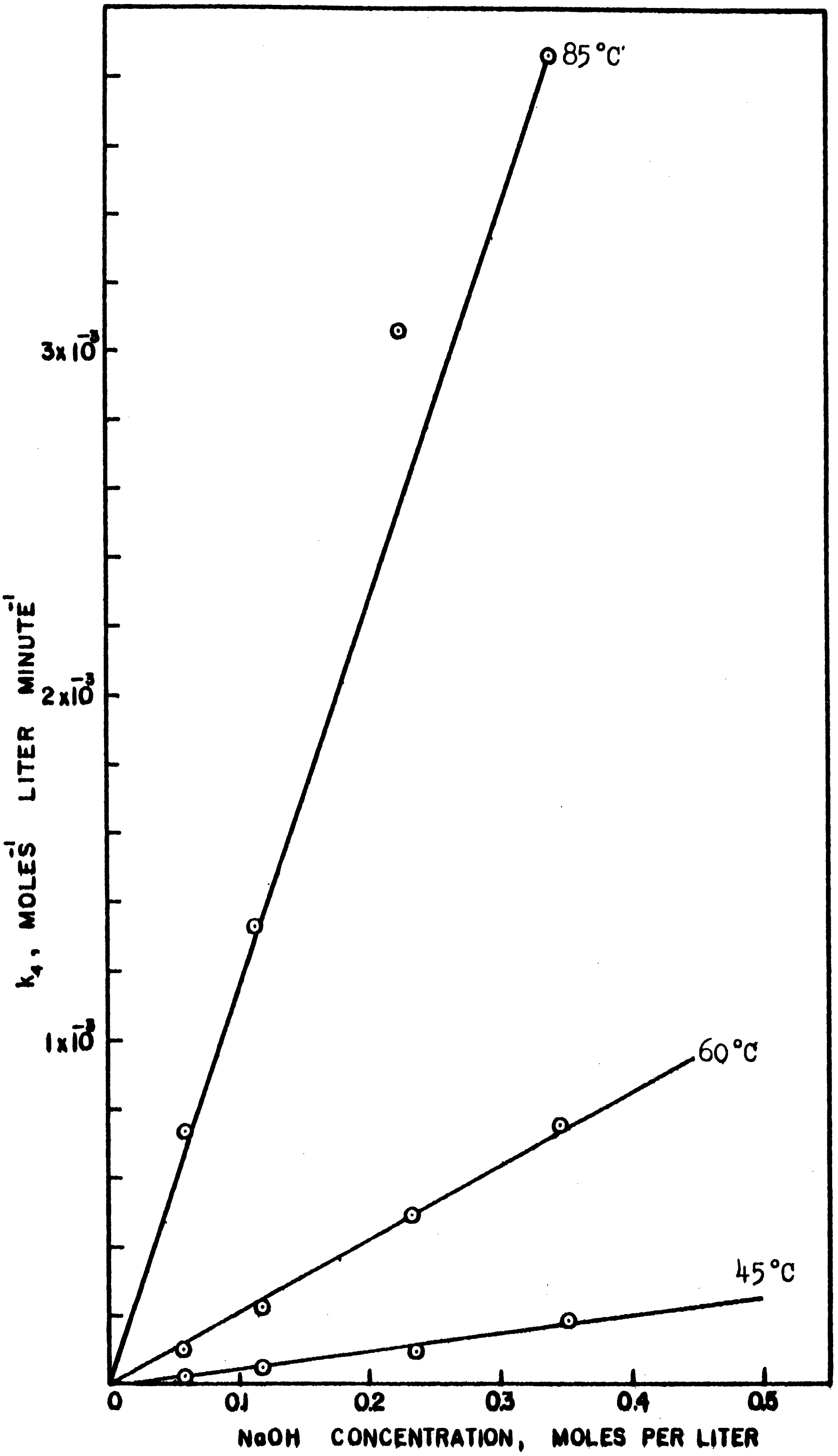


Figure 5. Effect of Catalyst Concentration on the Reaction Velocity Constants of the Propylene Oxide - Tripropylene Glycol Methyl Ether Reaction.

TABLE IV

RATE CONSTANTS FOR THE REACTION BETWEEN METHANOL AND PROPYLENE OXIDE

Run Number	Temp. °C	Mole Ratio Alcohol/Oxide	Cat. Conc. Mols./Lit.	k $\frac{\text{lit.}}{\text{mols.mins.}}$
1	35	48.1	0.139	0.0000884
2	45	38.4	0.172	0.000292
3	55	48.8	0.252	0.000852

TABLE V

RATE CONSTANTS FOR THE REACTION BETWEEN DIPROPYLENE GLYCOL METHYL ETHER AND PROPYLENE OXIDE

Run Number	Temp. °C	Mole Ratio Alcohol/Oxide	Cat. Conc. Mols./Lit.	k $\frac{\text{lit.}}{\text{mols.mins.}}$
1	87	10	0.1764	0.00179
2	87	10	0.1764	0.001924
3	87	10	0.1764	0.001941
4	87	5	0.1764	0.002265
5	85	10	0.0556	0.000445
6	85	10	0.1109	0.001121
7	85	10	0.1109	0.000987
8	85	10	0.2207	0.002250
9	85	10	0.3295	0.003790
10	69	10.1	0.2746	0.001060
11	60	10	0.1138	0.000194
12	60	10	0.1195	0.000224
13	60	10	0.2227	0.000425
14	60	10	0.2264	0.000503
15	60	10	0.3380	0.000602
16	35	10	0.1168	0.0000315
17	35	10	0.2323	0.000723
18	35	10	0.3469	0.000908

TABLE VI

RATE CONSTANTS FOR THE REACTION BETWEEN TRIPROPYLENE GLYCOL METHYL ETHER AND PROPYLENE OXIDE

Run Number	Temp °C	Mole Ratio Alcohol/Oxide	Cat. Conc. Mols./Lit.	k $\frac{\text{lit.}}{\text{mols. mins.}}$
1	100	9.25	0.1895	0.00597
2	100	10.25	0.1900	0.00612
3	85	7	0.05683	0.00742
4	85	7	0.1134	0.00133
5	85	7	0.2256	0.00306
6	85	7	0.3368	0.00386
7	60	7	0.05683	0.000106
8	60	7	0.1162	0.000224
9	60	7	0.2311	0.000502
10	60	7	0.345	0.00076
11	45	7	0.05897	0.0000276
12	45	7	0.1177	0.0000536
13	45	7	0.2341	0.000106
14	45	7	0.3495	0.000205

The constants in the Arrhenius Equation were then evaluated for each reaction by the least squares method (see Appendix IV). The rate constants $\underline{k_1}$, $\underline{k_2}$, $\underline{k_3}$ and $\underline{k_4}$ were calculated from experimental runs using an initial alcohol to oxide mole ratio of 40:1, 5:1, 10:1, and 7:1 respectively. The Arrhenius Equation for $\underline{k_2}$ was evaluated from data reported by Pecorini(57). It is being included here for the sake of completeness. The subscripts on each rate constant refers to the equations on page 1. For example $\underline{k_1}$ refers to the propylene oxide-methanol reaction, etc.,

$$\underline{k_1} = 1.02\ (10^9)\ e^{-\frac{17,200}{RT}}\ \text{moles}^{-2}\ \text{lit.}^2\ \text{min.}^{-1} \qquad (40)$$

$$\underline{k_2} = 0.97\ (10^5)\ e^{-\frac{11,700}{RT}}\ \text{moles}^{-2}\ \text{lit.}^2\ \text{min.}^{-1} \qquad (41)$$

$$\underline{k_3} = 4.75\ (10^7)\ e^{-\frac{15,800}{RT}}\ \text{moles}^{-2}\ \text{lit.}^2\ \text{min.}^{-1} \qquad (42)$$

$$\underline{k_4} = 2.25\ (10^9)\ e^{-\frac{18,500}{RT}}\ \text{moles}^{-2}\ \text{lit.}^2\ \text{min.}^{-1} \qquad (43)$$

In Figure 6 the four rate constants were plotted versus the reciprocal of the absolute temperature. The significance of these curves is discussed in page 57.

Product Distributions

The general applicability of the rate constants as represented by Equations (40-43) may be evaluated by the ability of these rate constants to reproduce experimental product distribution data. With this in mind, two sets of product distribution data were obtained experimentally. The first experimental product distribution was obtained by reacting methanol with various amounts of propylene oxide to completion at 45°C. The data are tabulated in Table VII.

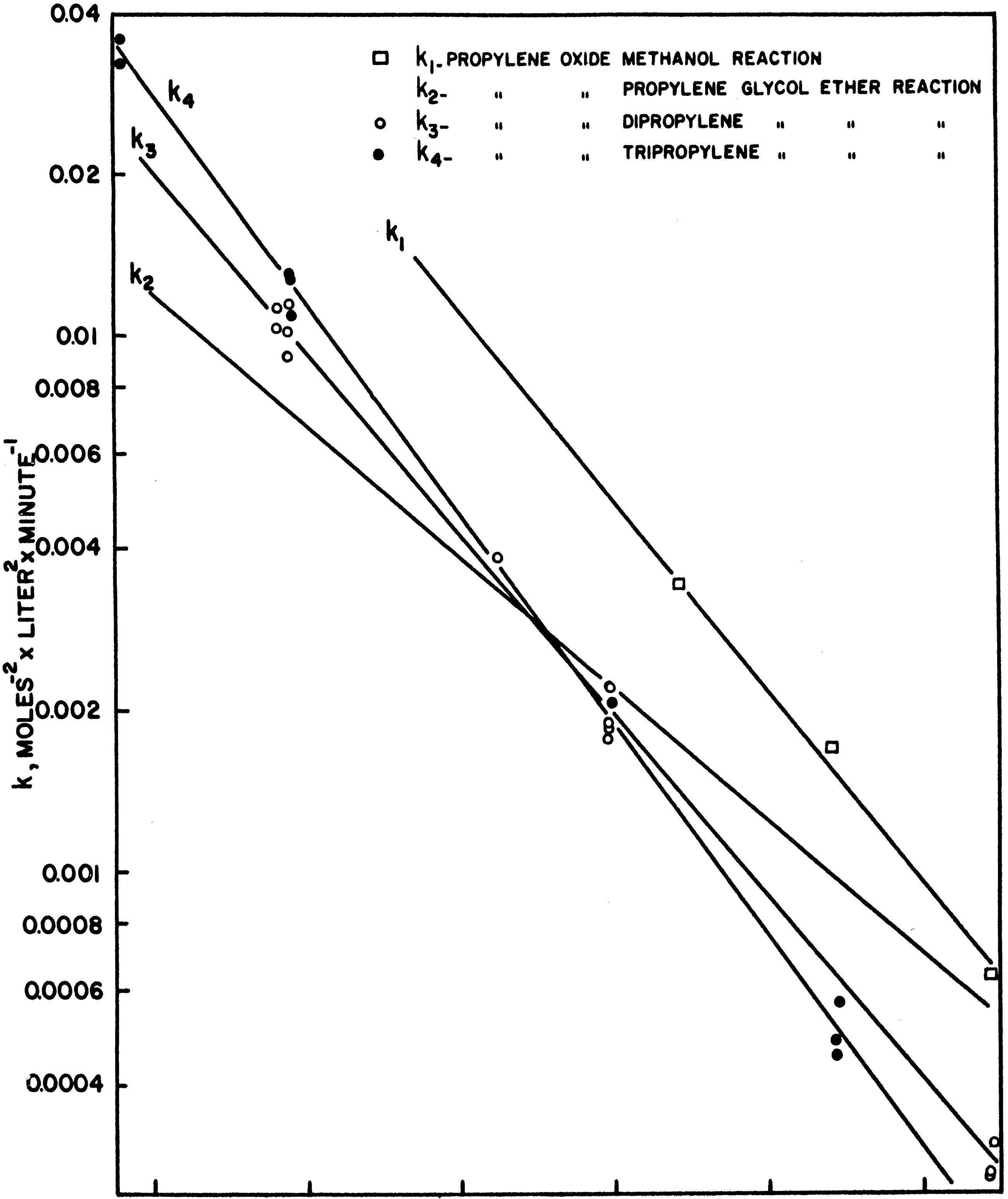


Figure 6. Effect of Temperature on the Catalyzed Reaction Velocity Constants.

TABLE VII

PRODUCT DISTRIBUTION DATA; STARTING MATERIALS: PROPYLENE OXIDE AND METHANOL. TEMPERATURE OF REACTION 45°C.

Run No.	Catalyst Concentration moles/liter	mole ratio methanol/oxide	methanol	monoglycol	diglycol	triglycol
			mole fractions			
1	0.152	10.00	0.90	0.10		
2	0.180	6.25	0.85	0.15		
3	0.325	1.79	0.43	0.52	0.05	
4	0.350	1.067	0.149	0.736	0.115	
5	0.382	0.834	--	0.78	0.20	0.02
6	0.305	0.645	--	0.495	0.32	0.185

The second set of product distribution data was obtained experimentally by reacting propylene glycol methyl ether with various amounts of propylene oxide to completion at 60°C. The results are tabulated in Table VIII.

TABLE VIII

PRODUCT DISTRIBUTION DATA; STARTING MATERIALS: PROPYLENE OXIDE AND MONOPROPYLENE GLYCOL METHYL ETHER. TEMPERATURE OF REACTION 60°C.

			mole fractions				
Run No.	Catalyst Concentration moles/liter	mole ratio alcohol/oxide	mono-glycol	di-glycol	tri-glycol	tetra-glycol	penta-glycol
1	0.215	3.00	0.75	0.222	0.026		
2	0.278	2.00	0.59	0.323	0.087		
3	0.272	1.55	0.525	0.343	0.109	0.0174	
4	0.253	1.15	0.431	0.362	0.162	0.045	
5	0.301	0.835	0.376	0.32	--	--	*
6	0.305	0.665	0.255	0.337	0.23	0.16	0.02

* Higher products unrecovered.

In order to compare experimental with calculated values of product distributions, a set of product distribution equations relating the various product concentrations with the rate constants and concentrations of the initiating reactants are required. In the following derivation we follow closely the treatment presented by previous authors(54,55,76).

For a system of bimolecular consecutive reactions such as represented in page 1 and briefly abbreviated below

$$\begin{aligned} A + B &= AB \\ AB + B &= AB_2 \\ AB_2 + B &= AB_3 \qquad\qquad (44) \\ AB_n + B &= AB_{n+1} \end{aligned}$$

The rate of formation or disappearance of each of the alcohols or alcohol-ethers may be written as

$$\begin{aligned} -\, dC_A/dt &= k_1\, C_A\, C_B \\ dC_{AB}/dt &= k_1\, C_A\, C_B - k_2\, C_{AB}\, C_B \qquad\qquad (45) \\ dC_{AB_2}/dt &= k_2\, C_{AB}\, C_B - k_3\, C_{AB_2}\, C_B \\ &\cdot \\ &\cdot \\ dC_{AB_n}/dt &= k_{n-1}\, C_{AB_{n-2}}\, C_B \quad k_n\, C_{AB_{n-1}}\, C_B \end{aligned}$$

where C_A = alcohol, moles per liter

C_{AB_n} = alcohol-ethers, moles per liter

C_B = propylene oxide, moles per liter

k_n = specific rate constants, liter moles^{-1} min.$^{-1}$

The series of differential Equations (44) can be solved in closed form if the volume is assumed constant and by eliminating the variable time (t).

The units of Equations (44) may therefore be reduced to moles per minute instead of the concentration units of moles per liter per minute by the following substitutions:

$$A = VC_a \tag{46}$$

$$dA = VdC_a \tag{47}$$

where A = moles of component A

C_a = moles per liter of component A

V = volume, liters

Equation (44) may be then rewritten in moles units as follows

$$\begin{aligned} V(dA/dt) &= -k_1\,(A)(B) \\ V(d(AB)/dt) &= k_1\,(A)(B) - k_2\,(AB)(B) \\ V(d(AB_2)/dt) &= k_2\,(AB)(B) - k_3\,(AB_2)(B) \\ &\vdots \\ V(d(AB_n)/dt) &= k_{n-1}\,(AB_{n-2})/dt - k_n(AB_{n-1})(B) \end{aligned} \tag{48}$$

The advantage of using mole units will become apparent if we choose a value for V such that the number of moles of the initiating alcohol is unity. Since the number of moles of alcohols in the reacting mixture is always constant at any time, if all the epoxide were reacted we have

$$\sum_{0}^{n} AB_n = 1 \tag{49}$$

where $AB_o = A$ by definition. The total number of moles of propylene oxide reacted is necessarily

$$B_T = \sum_{0}^{n} n\,(AB_n) \tag{50}$$

The solution of the series of differential Equations (48) gives the composition of each of the alcohols in terms of the amount of propylene oxide consumed, the starting amount of the initiating alcohol and the ratios of the rate constants, k_n/k_1. The solution is

$$\frac{AB_n}{A_o} = (-1)^n \prod_{j=1}^{n+1} k_j \sum_{j=1}^{n+1} \frac{\left(\frac{A}{A_o}\right)^{\frac{k_j}{k_1}}}{\prod\limits_{\substack{j=1 \\ j\neq k}}^{n+1} (k_j - k_k)} \tag{51}$$

where A = the number of moles of the initiating alcohol at any time t.

A_o = number of moles of initiating alcohol at t = 0.

AB_n = number of moles of product.

k_n = rate constants, liter mole^{-1} min.$^{-1}$

The detailed solution of Equations (48) is presented in Appendix IV. Several cases of product distribution of interest were also developed. These include the situation where the initiating alcohol is a mixture of two alcohols and the case where the initiating rate equation is first order while the succeeding ones are second order.

Equation (51) may be used to evaluate the ratios of rate constants when product distribution data and the starting compositions of propylene oxide and alcohol are known. Alternatively, product distributions may be calculated if the ratio of the rate constants and starting amount of propylene oxide and alcohol are available.

In Figure 7 we compare the experimental product distribution initiated by the reaction of propylene oxide with methanol at 45°C (Table VII) and the distribution calculated with the use of Equation (51) and specific rate constants obtained from the single reaction experiments in page 38. The difference of these two distributions is quite striking.

The ratios of the rate constants obtained from single reaction experiments and those obtained from product distributions initiated by the reaction of propylene oxide with methanol at 45°C are compared in Table IX.

It is quite obvious therefore, that specific rate constants calculated from single reaction data are not able to give the product distribution initiated by the reaction of propylene oxide with methanol at 45°C.

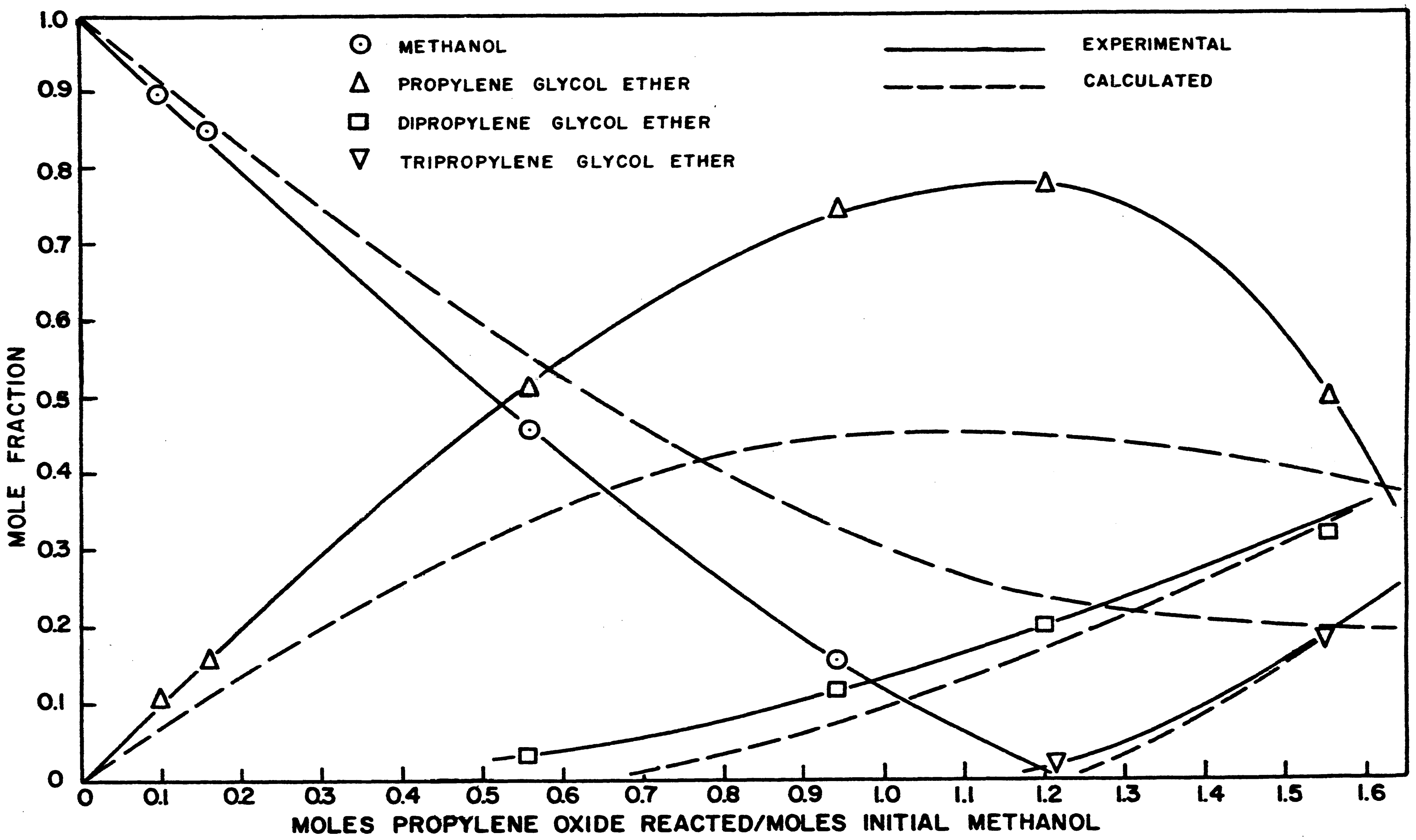


Figure 7. Comparison of Experimental Product Distribution with Calculated Values for the System of Reactions Initiated by the Reaction of Propylene Oxide with Methanol at 45°C.

TABLE IX

COMPARISON OF RATIOS OF RATE CONSTANTS OBTAINED FROM SINGLE REACTION EXPERIMENTS WITH VALUES OBTAINED FROM PRODUCT DISTRIBUTION DATA INITIATED BY THE REACTION OF PROPYLENE OXIDE WITH METHANOL AT 45°C.

$c_n = k_n/k_1$	single reaction	product distribution
c_2	0.571	0.10
c_3	0.427	0.075
c_4	0.282	0.075

On the other hand, the rate constants from single reaction experiments are able to reproduce experimental product distribution data initiated by the reaction of propylene oxide with monopropylene glycol methyl ether at 60°C. In Figure 8 the experimental product distribution is compared with the distribution calculated using Equation (124) and the specific rate constants from page 38. The agreement is very good. Table X compares the ratio of the rate constants obtained from single reaction data and those calculated from the product distribution data initiated by the reaction of propylene oxide with monopropylene glycol methyl ether at 60°C.

TABLE X

COMPARISON OF RATIOS OF RATE CONSTANTS OBTAINED FROM SINGLE REACTION EXPERIMENTS WITH VALUES OBTAINED FROM PRODUCT DISTRIBUTION DATA INITIATED BY THE REACTION OF PROPYLENE OXIDE WITH PROPYLENE GLYCOL METHYL ETHER AT 60°C.

$c_j = k_j/k_2$ $(j>2)$	single reactions	product distribution
c_3	1.00	1.00
c_4	0.933	1.00
c_5	--	1.00

Composition Effects

Up to this point, the experimental results seem to suggest the presence of a composition effect on the rates of reaction, possibly, due to the disproportionate nature of the physical properties of methanol as compared with the other alcohol-ethers.

For any general rate equations to be valid, such effects must be taken into account. The knowledge of the manner in which the concentration of methanol might affect the rates of reaction is therefore highly desirable.

The extent to which the propylene oxide-methanol reaction is sensitive to solvent change, a change of the dielectric constant of the medium in particular, was investigated using dioxane ($D_{25^\circ} = 2.206$) as solvent. The results at 45°C are shown in Figure 9. The rate of reaction increases with increasing dioxane concentration. Although this is an indication of medium effect on the propylene oxide-methanol reaction, we must be cautious in trying to extrapolate it to our system. Figure 9 must therefore be considered only as an indication of a possibility of such an effect also being present in our system.

A study of the effects of composition change on the velocity of reaction can be made by limiting the consecutive reactions to only two succeeding reactions and by making runs using different ratios of the two reacting alcohols.

The nature of the behavior of the rate constants of reaction 1 (methanol-propylene oxide) and reaction 2 (propylene glycol methyl ether-propylene oxide) when both reactions occur simultaneously was therefore

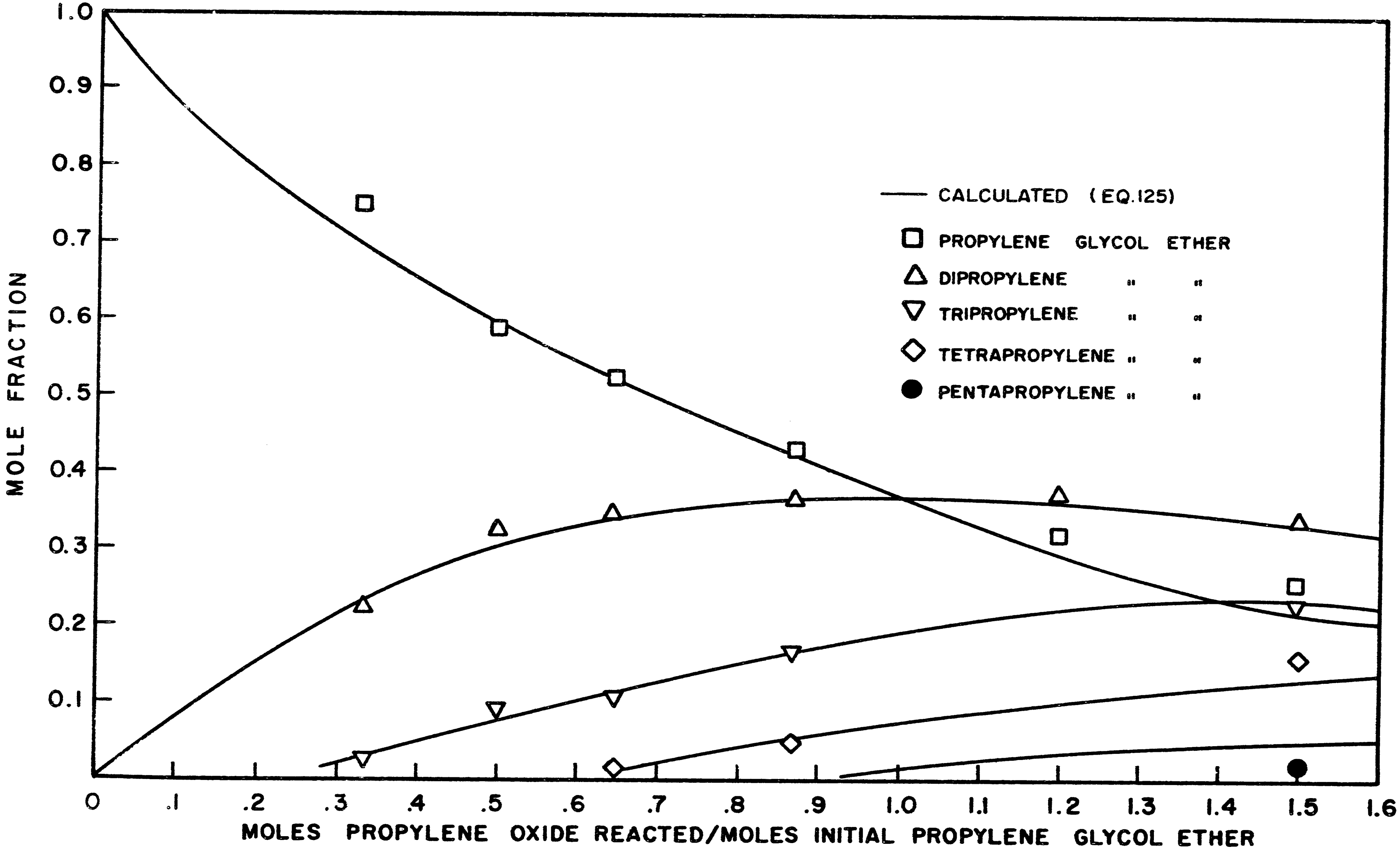


Figure 8. Comparison of Experimental Product Distribution with Calculated Values for the System of Reaction Initiated by the Reaction of Propylene Oxide with Propylene Glycol Methyl Ether at 60°C.

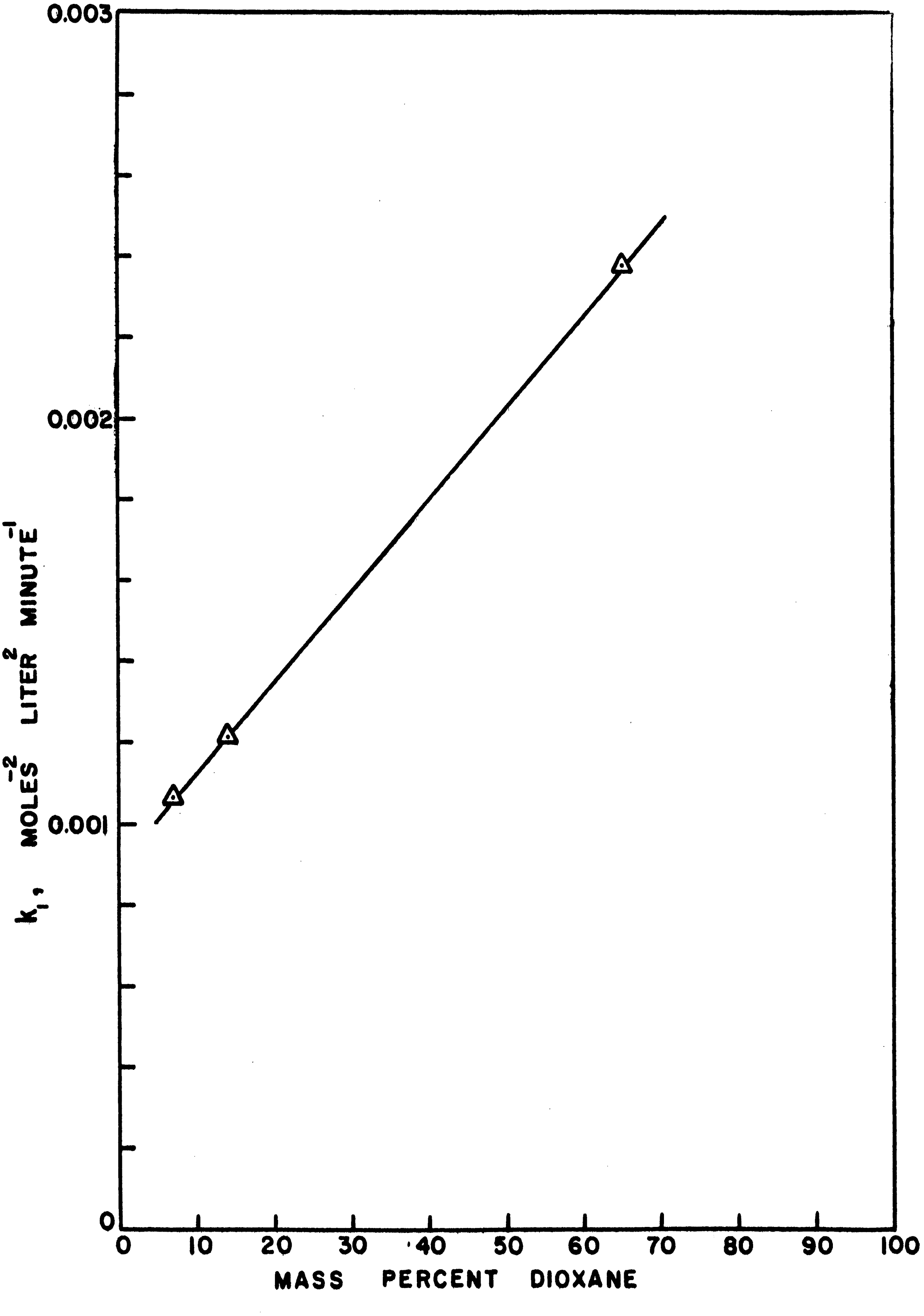


Figure 9. Effect of Dioxane on the Rate Constant of the Reaction of Propylene Oxide with Methanol at 45°C.

investigated by reacting small amounts of propylene oxide with a mixture of the two alcohols. We can write for the rate of disappearance of propylene oxide as

$$- dC_B/dt = \left[k_1 C_A C_B + k_2 C_{AB} C_B\right](NaOH) \tag{52}$$

By using excess amounts of methanol and propylene glycol methyl ether, the quantity $(k_1 C_A + k_2 C_{AB})$ may be considered as a constant and Equation (52) reduces to a pseudo-first order equation

$$- dC_B/dt = G_A C_B (NaOH) \tag{53}$$

where

$$G_A = \left[k_1 C_A + k_2 C_{AB}\right]$$

G_A is a constant for any run but in general is dependent on the starting concentration of methanol or the ratio of methanol to propylene glycol methyl ether.

Equation (53) is easily integrated to give

$$\int_{C_{B_o}}^{C_B} \frac{dC_B}{C_B} = - G_A \int_o^t dt \, (NaOH) \tag{54}$$

$$\ln C_B/C_{B_o} = - G_A (t)(NaOH) \tag{55}$$

If the time composition data of propylene oxide are known, G_A can be readily evaluated. Figures 10 and 11 show composition-time curves for propylene oxide corresponding to different starting mole ratios of methanol to propylene glycol methyl ether at 45°C. In Table XI, the respective values of G_A are tabulated.

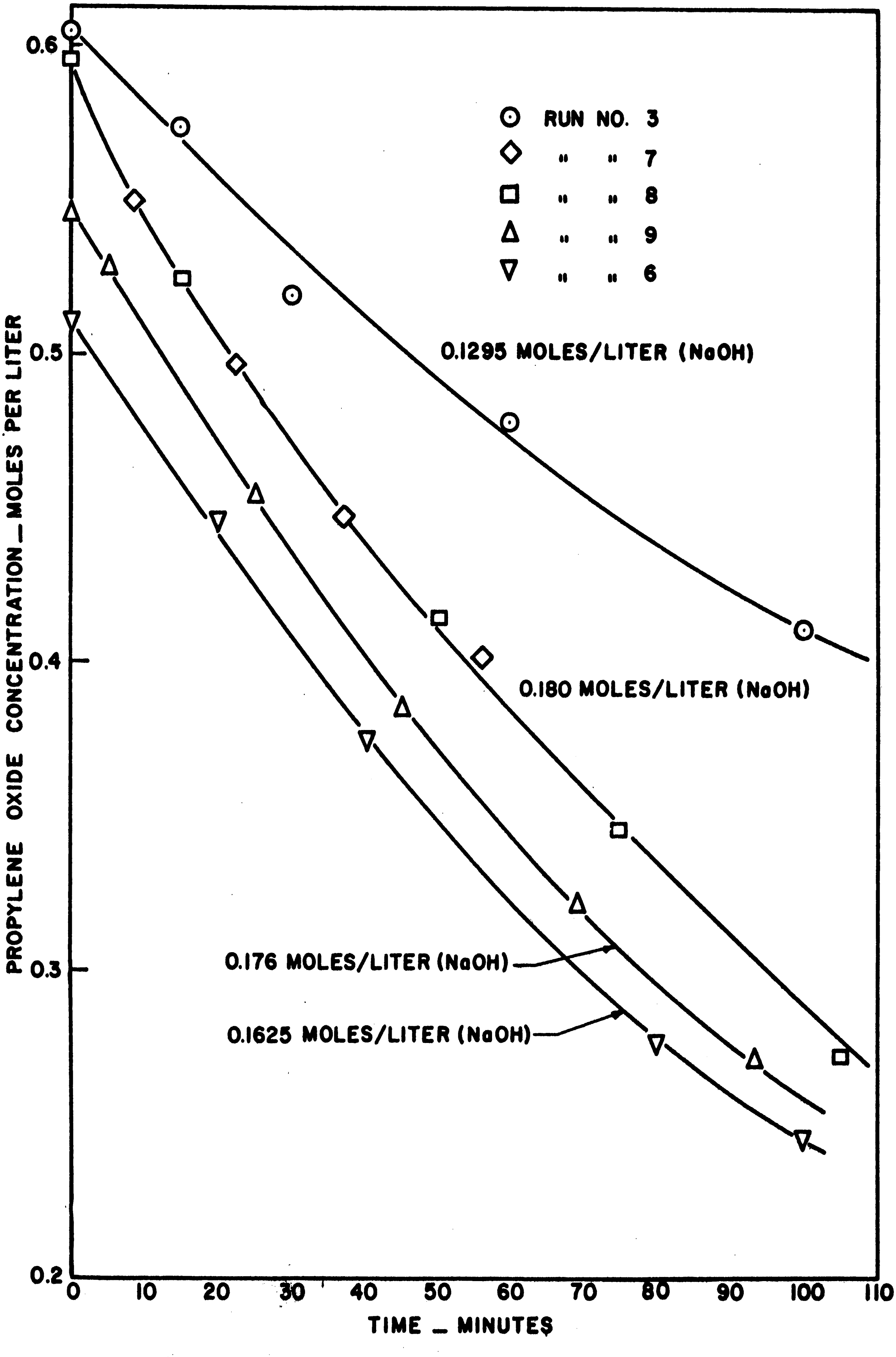


Figure 10. Concentration-Time Curves of Propylene Oxide in the Reaction of Propylene Oxide with Mixtures of Methanol and Propylene Glycol Methyl Ethers at 45°C.

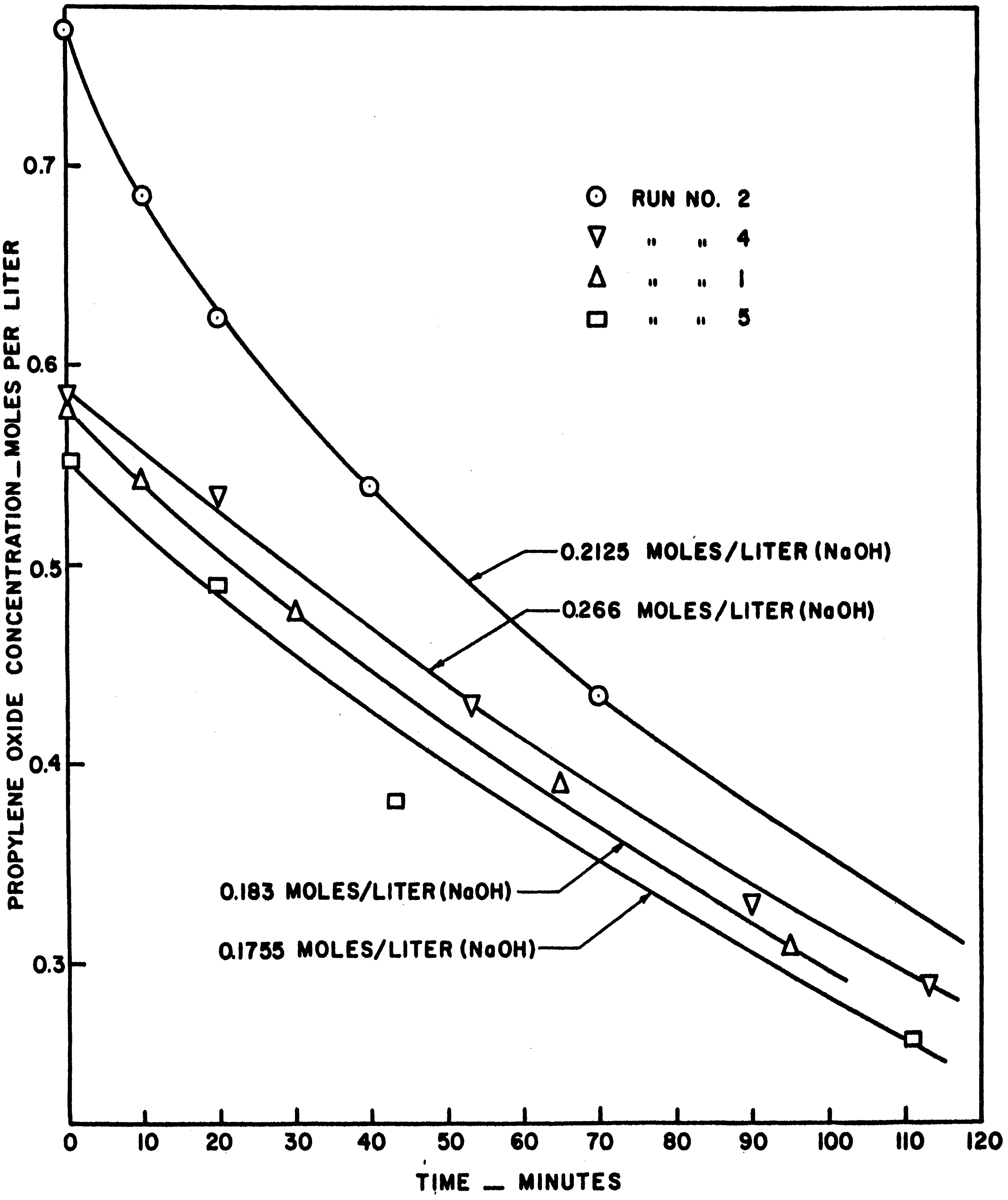


Figure 11. Concentration-Time Curves of Propylene Oxide in the Reaction of Propylene Oxide with Mixtures of Methanol and Propylene Glycol Methyl Ether at 45°C.

TABLE XI

VALUES OF THE PSEUDO-FIRST ORDER CONSTANTS FOR THE REACTION OF PROPYLENE OXIDE WITH A MIXTURE OF METHANOL AND PROPYLENE GLYCOL METHYL ETHER AT 45°C.

Run Number	Methanol C_A mols/lit	Propylene Glycol Ether C_{AB} mols/lit	$\frac{G_A}{(K_1C_A + K_2 C_{AB})}$	(NaOH) moles/lit
1	7.40	6.52	0.0339	0.183
2	8.61	5.95	0.0381	0.213
3	5.24	7.44	0.0305	0.1295
4	3.89	7.89	0.0233	0.266
5	6.5	6.95	0.0324	0.176
6	18.16	2.13	0.0479	0.163
7	9.55	5.65	0.0393	0.190
8	9.55	5.65	0.0393	0.190
9	17.85	2.22	0.0447	0.176

In Figure 12 the values of G_A are plotted versus methanol concentration. The straight line connecting $\underline{k}_2$ C_{AB} and $\underline{k}_1$ C_{AB} represents values of G_A if the rate constants obtained from single reaction experiments listed in page 38 were used. The difference between the experimental values and those calculated using the rate constants listed in page 38 must essentially be a result of composition effects.

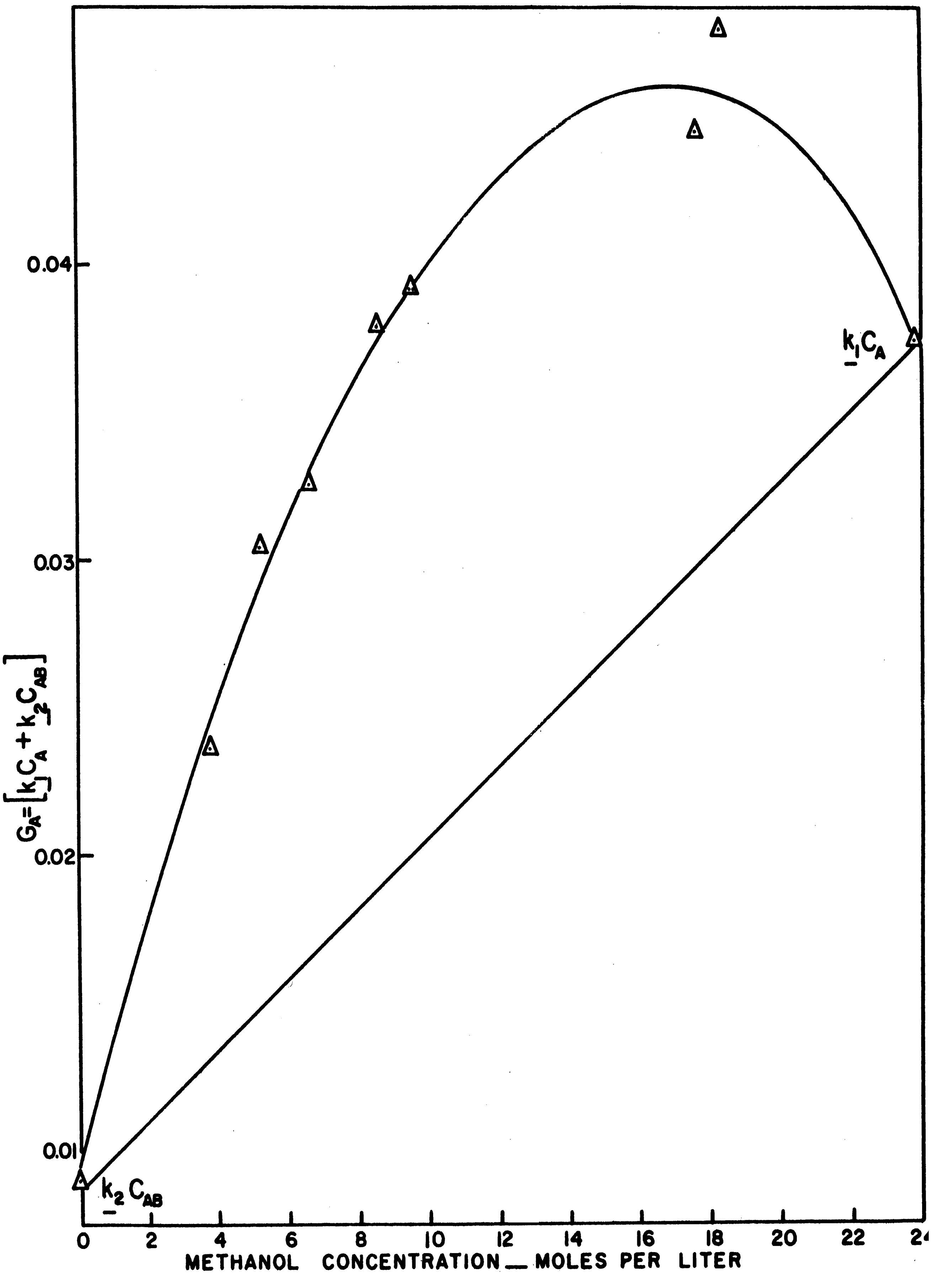


Figure 12. Variation of G_A with Methanol Concentration.

DISCUSSION OF RESULTS

Uncatalyzed Reactions

The values of the measured catalytic rate constants tabulated in Tables IV, V and VI actually represent the sum of the spontaneous rate constant and the specific catalytic constant

$$k = k_u + k_c\,(\mathrm{NaOH}) \qquad (56)$$

The magnitude of the spontaneous rate constant is usually significant only in catalyzed reactions when the catalyst concentration is so low such that k_u and k_c (NaOH) are of the same order of magnitude, e.g.

$$\frac{k_u}{k_c\,(\mathrm{NaOH})} \geqq 0.10 \qquad (57)$$

Pecorini and Banchero(58) have reported experimental data for the uncatalyzed reaction of methanol with propylene oxide. The temperature dependence of the second order rate constants of this reaction is plotted in Figure 13. The Arrhenius Equation for the uncatalyzed rate constant of the reaction of propylene oxide with methanol is

$$k_u = 1.21\,(10^7)\ e^{\frac{-19{,}500}{RT}} \qquad (58)$$

and from Equation (40), the Arrhenius Equation for the rate constant of the catalyzed reaction at unit molar catalyst concentration is

$$k_c = \underline{k}_1 = 1.02\,(10^9)\ e^{\frac{-17{,}200}{RT}} \qquad (59)$$

substituting Equations (58) and (59) into Equation (57), the concentration of the catalyst (NaOH) at which the spontaneous rate would become significant can be calculated as follows

$$\frac{1.21\ (10^{7})}{1.02\ (10^{9})}\ e^{\frac{-19,500+17,200}{RT}} \geqq 0.10\ (\text{NaOH}) \qquad (60)$$

or

$$\frac{1.185\ (10^{-2})}{0.10}\ e^{\frac{-2,300}{RT}} \geqq (\text{NaOH})$$

at RT = 600

$$(\text{NaOH}) \leqq 0.00255 \text{ moles per liter}$$

It is also interesting to compare the uncatalyzed rate constant of the propylene oxide-methanol reaction with that of the ethylene oxide-methanol reaction. The Arrhenius Equation for the ethylene oxide-methanol reaction calculated from data reported by Natta(55) is

$$k_u = 1.0\ (10^{8})\ e^{\frac{-20,100}{RT}} \quad \text{moles}^{-1}\ \text{liter min}^{-1} \qquad (61)$$

as was expected, the activation energy of both reactions is about the same. The fact that the uncatalyzed rate constant for the ethylene oxide-methanol reaction is slightly higher than that of the propylene oxide-methanol reaction (see Figure 13) may be a result of steric effects.

For the reactions of propylene oxide with the glycol ethers, the uncatalyzed rates of reaction are expected to be even slower. When dipropylene glycol methyl ether was mixed with propylene oxide at 85°C for 30 days, no appreciable reaction was observed. The same mixture at 200°C similarly has shown no detectable reaction occurring in 10 hours.

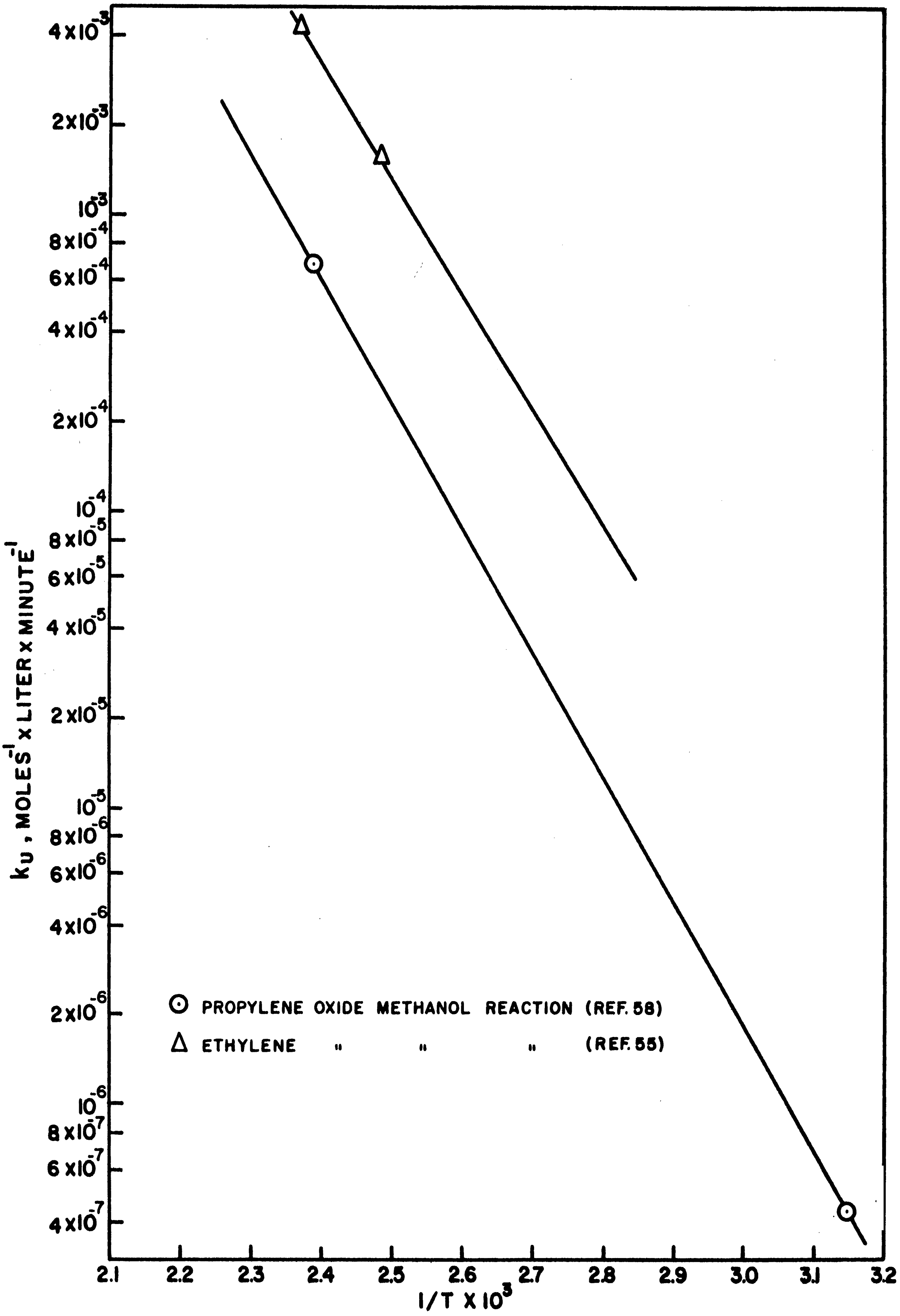


Figure 13. Effect of Temperature on the Uncatalyzed Reaction Velocity Constants.

In view of this, the uncatalyzed rate of reactions for these compounds with propylene oxide may be neglected when studying the catalyzed reactions.

Activation Energy of the Catalyzed Reactions

The presence of catalysts generally lowers the activation energy of chemical reactions. In Table XII the activation energy of the individual reactions are compared. These values are meaningful only when used in context with the composition of the medium.

TABLE XII

ACTIVATION ENERGIES OF INDIVIDUAL REACTIONS

Reaction	Uncatalyzed	Catalyzed	Initial Mole Ratio Alcohol/Oxide
Methanol + propylene oxide	19,500* (5/1)	17,200	45/1
Monopropylene glycol methyl ether + propylene oxide		11,700	5/1
Dipropylene glycol methyl ether + propylene oxide		15,800	10/1
Tripropylene glycol methyl ether + propylene oxide		18,500	7/1

* Calculated from Ref. 57.

It is interesting to note the variation of the activation energies of the alcohol-ether reactions with propylene oxide. Although the relative values of the rate constants for these reactions are about the same in the temperature range investigated, the values of the activation energy, nevertheless, are not the same - the values increasing with increasing molecular weight of the alcohol-ether. However, the collision factors also increase in the same direction (see Equation (40-43)) compensating for the increase of the activation energy. The variation of these quantities is probably due to the increasing complexity of the transition state.

The Influence of the Medium on the Rate of Reaction

The equation relating the rate constant of an ion-dipolar reaction in a medium having a dielectric constant of unity to that existing in the actual solution, according to Laidler(39) (see Appendix III) is

$$\ln k' = \ln k_o + \frac{e^2 Z_a^2}{2\,K\,T}\left[\frac{1}{r_a} - \frac{1}{r_{\neq}}\right]\left[\frac{1-D}{D}\right] \tag{62}$$

where k_o = rate constant referred to the gas phase

e = electronic charge

Z = charge

K = Boltzmann constant

T = absolute temperature °K

r_a = radius of molecule a

$r_{\neq}$ = radius of activated complex

D = dielectric constant of the medium

For any particular reaction

$$\frac{e^2\,Z_a^2}{2\,K}\left[\frac{1}{r_a} - \frac{1}{r_{\neq}}\right] \cong \text{constant} \tag{63}$$

or

$$\ln k' = \ln k_o + C\,\frac{1}{T}\left[\frac{1-D}{D}\right] \tag{64}$$

k_o in Equation (62), the rate constant referred to the gas phase, may be eliminated as follows:

let

$\underline{k'}$ = rate constant where the reacting medium corresponds approximately to that of the pure alcohol

then from Equation (64)

$$\ln \underline{k'} = \ln k_o + C \frac{1}{T} \left[\frac{1-D_o}{D_o}\right] \qquad (65)$$

where D_o is the dielectric constant of the alcohol and the rate constants $\underline{k_n'}$ are represented by Equations (40-43). At any other dielectric constant, the rate constant will vary according to Equation (65). Subtracting Equation (65) from Equation (64).

$$\ln k' - \ln \underline{k'} = \frac{C}{T} \left[\frac{D_o-D}{D\ D_o}\right] \qquad (66)$$

or

$$\ln k' = \ln \underline{k'} + \frac{C}{T\ D_o} \left[\frac{D_o-D}{D}\right] \qquad (67)$$

In most cases, the quantity, $1/TD_o$, is approximately constant since, as temperature increases, dielectric constant usually decreases. Equation (67) may therefore be further simplified to

$$\ln k' = \ln \underline{k'} + C' \left[\frac{D_o-D}{D}\right] \qquad (68)$$

An inspection of Equation (68) indicates that a straight line is obtained if ln k' is plotted against (1/D). Since the dielectric constant of methanol is always greater than the dielectric constant of a mixture of methanol and alcohol ethers, the effect of the medium on the rate of reaction of propylene oxide with methanol in a mixture of methanol and alcohol-ethers is to accelerate the rate of reaction as the concentration of methanol decreases. On the other hand, the presence of methanol in the mixture would slow down the rate of reaction between propylene oxide and the alcohol-ethers.

The use of Equation (68) presuppose the assumption that the polarity of the reacting mixture is a major cause of the anomalous behavior of the rate constants. At best, Equation (68) would give only a qualitative description of the effect on the rate constants, the uncertainty in the calculation of the various ionic and molecular radii and the fact that ionic radius varies from solvent to solvent makes it necessary that the use of equations of this form be supported with experimental data. Furthermore, experimental values of dielectric constant of mixtures are practically nonexistent and additivity of dielectric constants can be assumed only for a limited range of compositions(68). Anomalous behavior of dielectric constants of polar mixtures due to temperature and composition changes and attributed to molecular association has also been observed.

It was therefore found expedient to relate the effect of the medium on the rates of reactions with the concentration of methanol in the reacting mixture rather than with the dielectric constant. Equation (68) then takes the following form

$$\ln k' = \ln \underline{k'} + f(C_A) \qquad (69)$$

where $f(C_A)$ = function of methanol concentration.

Equations for the Rate Constants

The choice of the function $f(C_A)$ was dictated by the following considerations:

1. It must be consistent with Equation (62) e.g., the rate constant should increase with decreasing polarity of the reacting medium.

2. For the glycol-ether reaction $f(C_A) = 0$ when C_A, the concentration of methanol in the reacting medium is zero.
3. The effect of the concentration of propylene oxide in the reacting medium on the rate of reaction is negligible.
4. The ratios of the rate constant for consecutive reactions should correspond to that obtained in the product distribution experiments.
5. The results in Table XI should be satisfied.
6. The effect of temperature on $f(C_A)$ is negligible over the temperature range studied.

The final forms of $f(C_A)$ used were

$$f\,(C_A) = C_1\left(1 - \frac{C_A}{M}\right) \tag{70}$$

for the methanol-propylene oxide reaction and

$$f\,(C_A) = -C_2\,(C_A/M) \tag{71}$$

for the alcohol ethers-propylene oxide reactions where

C_1 and C_2 = constants

C_A = concentration of methanol at any time, moles/liter

M = reciprocal of the molar valume of methanol at the temperature of the reaction.

The final forms of the equations for the rate constants are

$$k_1 = \underline{k}_1\, e^{C_1\,(1 - C_A/M)} \tag{72}$$

$$k_n = \underline{k}_n\, e^{-C_2\,(C_A/M)} \tag{73}$$

for $n \geqq 2$, and k_n reduces to $\underline{k}_n$ when $C_A = 0$. Here C_1 and C_2 are constants to be determined from consecutive reaction data in Tables VII and XI.

In order to evaluate the constants in Equations (72) and (73) we shall define an average rate constant which is a function of methanol concentration as

$$k_n(\text{avg.}) = \frac{\underline{k}_n \int_{C_A}^{M} e^{f(C_A)}\, dC_A}{\int_{C_A}^{M} dC_A} \qquad (74)$$

With the use of Equation (74), the constants in Equations (72) and (73) were evaluated by a successive approximation method as follows: Values of C_1 were assumed and the corresponding C_2 values calculated from the data in Figure 12. The ratio of the rate constants was then evaluated using Equation (74). The correct values of $C_1 = 1.42$ and $C_2 = 2.40$ result in the k_2/k_1 value of 0.10 corresponding to the value obtained in the product distribution studies. In this calculation using Equation (74), A was assumed to have been all reacted.

Table XIII shows the result of the successive approximations for the values of C_1 and C_2. In Figure 14 the variation of k_1 and k_2 with methanol concentration according to Equations (72) and (73) is shown.

TABLE XIII

SUCCESSIVE APPROXIMATION FOR VALUE OF C_1 AND C_2

C_1	C_2	(k_2/k_1) avg.
1.025	0	0.33
1.13	0.8	0.212
1.23	1.17	0.172
1.386	2.19	0.108
1.42	2.40	0.10

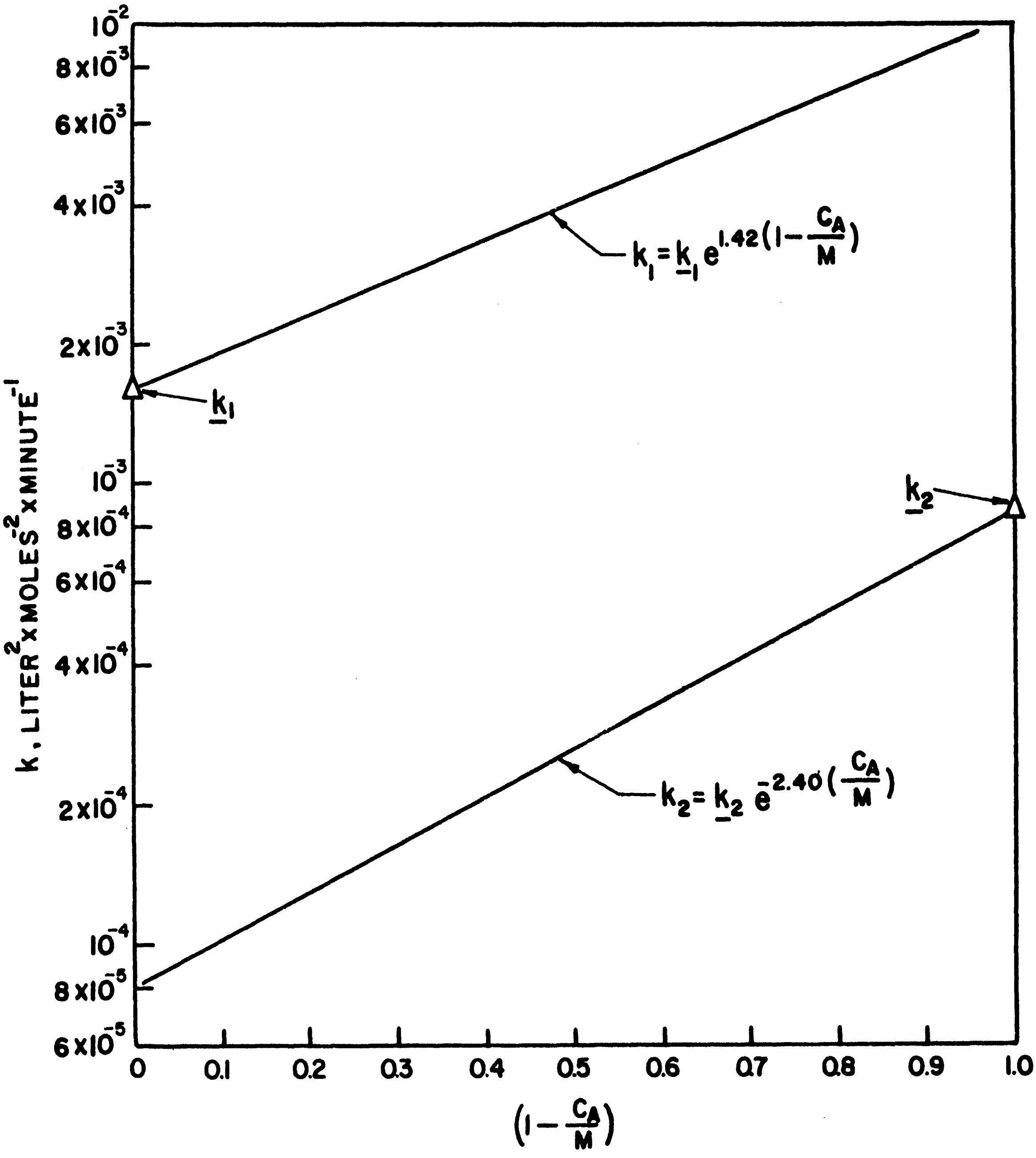


Figure 14. Variation of the Reaction Velocity Constants, k_1 and k_2, with Methanol Concentration.

Temperature Influence on Medium Effects

The influence of the temperature on medium effects may vary widely depending on the nature of the medium. For the present system and over the range of temperature studied it may be assumed to be small. Thermal energies of molecules in the temperature range investigated are about 1500 calories per gram mole while energies of associative links attributed to polar substances such as alcohols are of the order of 5000 calories per gram mole or higher(61).

In Table XIV, the calculated product distribution using Equations (72), (73) and (74) are compared with some experimental data at 55°C and 64°C. The agreement is quite good.

TABLE XIV

COMPARISON OF EXPERIMENTAL PRODUCT DISTRIBUTION DATA WITH CALCULATED RESULTS FOR THE SYSTEM OF REACTIONS INITIATED BY PROPYLENE OXIDE AND METHANOL AT 55°C and 64°C.

Products	Temperature °C	Mole Ratio Oxide Consumed / Initial Methanol	Mole Fraction Experimental	Mole Fraction Calculated
Methanol	55*	0.845	0.235	0.235
Propylene glycol methyl ether			0.696	0.715
Dipropylene glycol methyl ether			0.069	0.050
Methanol	64	0.544	0.505	0.505
Propylene glycol methyl ether			0.453	0.480
Dipropylene glycol methyl ether			0.042	0.015

---

* This set of data obtained from Ref. 57.

Polarity of the Reacting Mediums

A comparison of the dielectric constants in Table XVI indicates the relative "polarity" of the various reactants and products. The large difference of the dielectric constants between methanol and the rest of the compounds may be a factor affecting the rates of reaction of propylene oxide when several of the alcohols are present at the same time.

TABLE XV

DIELECTRIC CONSTANTS AT 25°C

			Ref.
1.	Methanol	32.63	(53)
2.	Propylene oxide	16.0	(68)
3.	Propylene glycol methyl ether	14	*
4.	Dipropylene glycol methyl ether	13	*
5.	Tripropylene glycol methyl ether	12	*
6.	Tetrapropylene glycol methyl ether	12	*
7.	Dioxane	2.209	(53)

*Estimated values based on Ref. 53 and 68.

In the present work we have shown that at least for the NaOH catalyzed reaction of propylene oxide with methanol and with the succeeding products the shifting values of the rate constant may be explained in terms of the changing polarity of the reacting medium, primarily caused by the changing concentration of methanol. The manner in which the rate constants vary is explainable qualitatively by the nature of electrostatic forces in the medium. Specifically, it is shown that the variation of the rate constants can be directly related to the concentration of methanol in the reacting medium. This phenomena is best brought out by the product distribution data which involve a radical change of the composition of the reacting medium. Methods of treatment where the activities of the reacting species are related to the medium properties such as Equation (98) are often used. The effect of the medium on the activities of the reacting species is sometimes denoted as the "primary kinetic effect". Another possible effect of the solvent is its influence on the concentration of the reacting species which naturally will reflect on the rate of reaction. This effect of the solvent designated by some authors as the "secondary kinetic effect" is due to the influence of the medium on the equilibrium constants involved in the mechanism of the reaction. A good example of the latter case is the effect of the solvent in protolytic equilibria(30).

Acidity of the Reactants

The acidity of the various alcohols and alcohol-ether may, to a certain extent be implied from their autoprotolysis constants. The autoprotolysis constant is the product of the concentration of lyonium and lyate ions in the solvent, e.g., $(RCH_2^+)(RO^-) = K_a$. This constant determines the range of values of acidity available in these solvents. The autoprotolysis constant of some solvents of interest are listed in Table XVI (30). The autoprotolysis constant pK of the alcohol-ethers is estimated to be around 22-24.

TABLE XVI

AUTOPROTOLYSIS CONSTANTS

Solvent	Temp. °C	pK
Water	25	14.0
Water	100	12.3
Methanol	25	16.7
Ethanol	25	19.1

Of more direct interest is the relative acidity of these alcohols in a common solvent. Generally, ionization is favored in a solvent of high polarity. However, the ionization of these alcohols in a common solvent is of importance only for the uncatalyzed reactions. For catalyzed reactions, the concentration of the alkoxide ion is dependent only on the concentration of the hydroxyl ion.

Accuracy of Measurements and Errors

In Table XVII the maximum limits of error of the measurements used in the experimental work are tabulated.

TABLE XVII

ESTIMATION OF ACCURACY OF INDIVIDUAL MEASUREMENTS INVOLVED IN THE EXPERIMENTAL WORK

Measurement	Remarks	Accuracy of Measurement	% Error
Weighing	reaction charge of 200-300 gm per batch 4.0% propylene oxide	0.05 gm	0.6
	alcohol	0.5 gm	0.2
Titration analysis	$HCl-CaCl_2$ method periodic-perchloric method		3.25 1.10
Side reactions	negligible		0.50
Time lag		1 min	0.35
Maximum error in measurements			4.90

The maximum deviations from the least-square fit of the individual rate constants are presented in Table XVIII. Here the deviations were assumed to be all due to errors in the activation energy.

TABLE XVIII

ACCURACY OF THE ACTIVATION ENERGIES FOR THE RATE CONSTANTS OF THE INDIVIDUAL REACTIONS

Reactions	Activation energy from least-square fit calories/gm. mole	Maximum deviation calories/gm. mole
Propylene oxide + methanol	17,200	+ 60
Propylene oxide + dipropylene glycol methyl ether	15,800	- 170
Propylene oxide + tripropylene glycol methyl ether	18,500	- 190

The use of average densities in the calculation of the individual rate constants, as was expected contributed comparatively small errors. In Table XIX below, the maximum errors incurred are tabulated.

The assumption of constant volume in the product distribution equations results in larger errors.

Comparison with Work Reported in the Literature

There are very little quantitative data reported in the literature on the base catalyzed alcoholysis of propylene oxide or ethylene oxide. Weibull and Nycander(76) reported the bimolecular rate constant for the base catalyzed reaction of ethylene oxide with ethanol and ethylene oxide with ethylene glycol monoethyl ether at 25°C. These values are compared in Table XX with those obtained in our work involving methanol and propylene oxide and values calculated from Pecorini's data(57)

TABLE XIX

VARIATION OF DENSITY OF REACTING MIXTURE

Initial charge	Initial Mole Ratio	Temp. °C	start	final	average	Dev. from avg. %
Single Reactions						
Methanol + propylene	40/1	35	0.78038	0.78769	0.78403	0.47
		55	0.76117	0.76875	0.76496	0.50
Dipropylene glycol methyl ether + propylene oxide	5/1	35	0.9352	0.94228	0.9387	0.38
		87	0.88460	0.89294	0.8887	0.47
		87	0.87844	0.89568	0.8870	0.97
Tripropylene glycol methyl ether + propylene oxide	7/1	45	0.94228	0.94960	0.9459	0.39
		85	0.90765	0.91559	0.91162	0.44
Methanol + propylene oxide in dioxane	35/1	45	(maximum deviation of all runs)			0.30
Mixed runs: propylene oxide + methanol + monoglycol ether		45	(maximum deviation of all runs)			1.70
Product Distribution						
Methanol + oxide	0.64	45	0.79	0.924	0.957	7.5
Monoglycol + oxide	0.67	60	0.834	0.9265	0.881	5.0

TABLE XX

VELOCITY CONSTANTS AT 25°C. FOR ETHYLENE OXIDE AND PROPYLENE OXIDE WITH VARIOUS ALCOHOLS USING SODIUM HYDROXIDE AS CATALYST

Reactions	Starting Mole Ratio alcohol/oxide	k, moles^{-2} liter min^{-1}	Reference
Ethylene oxide + ethanol	*	1.29×10^{-3}	76
Ethylene oxide + ethylene glycol ethyl ether	*	6.10×10^{-4}	76
Ethylene oxide + diethylene glycol ethyl ether	*	6.10×10^{-4}	76
Propylene oxide + methanol	5/1	3.15×10^{-4}	57
Propylene oxide + methanol	45/1	2.63×10^{-4}	
Propylene oxide + propylene glycol methyl ether	5/1	2.58×10^{-4}	57
Propylene oxide + dipropylene glycol methyl ether	10/1	1.22×10^{-4}	
Propylene oxide + tripropylene glycol methyl ether	7/1	3.95×10^{-5}	

* Reported only as dilute solutions.

While values of the rate constants of some individual reactions of epoxides with alcohols have been reported(55,76) the reason why some of these rate constants are not valid when several consecutive reactions occur at the same time has never been fully explained. Natta(54) introduced the idea of the molecules existing in an activated state at the instant in which they are formed; however, such an assumption is too vague and there is no way in which it may be verified. Weibull(76) mentioned the possibility of an effect of the acidity of the alcohols and the changing condition of the reacting medium on the rate constants but did not pursue the subject further.

Pecorini(57) in his work with the base-catalyzed reactions of propylene oxide with methanol, and with propylene glycol ether, introduced the following empirical rate equation which was shown to correlate his experimental data:

$$[dB]/dt = -k\ [A][B]/n_t \tag{75}$$

where B = Propylene oxide, moles per 100 grams

A = Alcohol, moles per 100 grams

t = Time, hours

n_t = Total number of moles per 100 grams of initial charge.

The Arrhenius Equation for the rate constants of the oxide-methanol reaction (k_1) and the oxide propylene glycol ether reaction (k_2) were

$$k_1 = 3.24\ (10)^{13}\ e^{-17,800/RT}\ \text{hours}^{-1} \tag{76}$$

$$k_2 = 3.15\ (10)^{10}\ e^{-14,600/RT}\ \text{hours}^{-1} \tag{77}$$

It is possible to use the numerical values of the ratio of the rate constants as a basis for comparison with our correlation since they are dimensionless. In this manner, the calculation of k_2/k_1 at 45°C using Pecorini's correlation yields a value of 0.159. In Figure 15, results obtained by the use of Pecorini's and our correlation are compared with experimental composition-time data of propylene oxide obtained at 45°C using an initial mole ratio of alcohol to oxide of 1 to 1(57)

When Pecorini's rate equation was used to correlate the data of the glycol ether reactions obtained in the present work, a larger difference from our results using the present correlation is obtained. In Table XXI the product distribution from the reaction of propylene oxide with propylene glycol methyl ether at 60°C obtained by various methods are compared.

TABLE XXI

COMPARISON OF PRODUCT DISTRIBUTION INITIATED BY THE REACTION OF PROPYLENE OXIDE WITH PROPYLENE GLYCOL METHYL ETHER AT 60°C.

Products	Initial Mole Ratio Glycol Ether / Propylene Oxide	Experimental	This Correlation	Pecorini's Rate Equation
			mole fraction	
Propylene glycol methyl ether	1.15	0.431	0.43	0.43
Dipropylene glycol methyl ether		0.362	0.36	0.40
Tripropylene glycol methyl ether		0.161	0.16	0.17
Tetrapropylene glycol methyl ether		0.046	0.050	0.0

Pecorini's correlation therefore predicts the results for the reactions of methanol with propylene oxide and the reaction of propylene oxide with propylene glycol methyl ether fairly well, both when they occur singly and consecutively. However, at the high initial mole ratio of methanol to oxide of 45 to 1, the values predicted by his rate equation are about 40 percent higher than the experimental results obtained in this work. In the case of the reaction of propylene oxide with methanol and propylene glycol methyl ether initially present in the mixture and with consecutive reactions involving glycol ethers only, his correlation is less accurate.

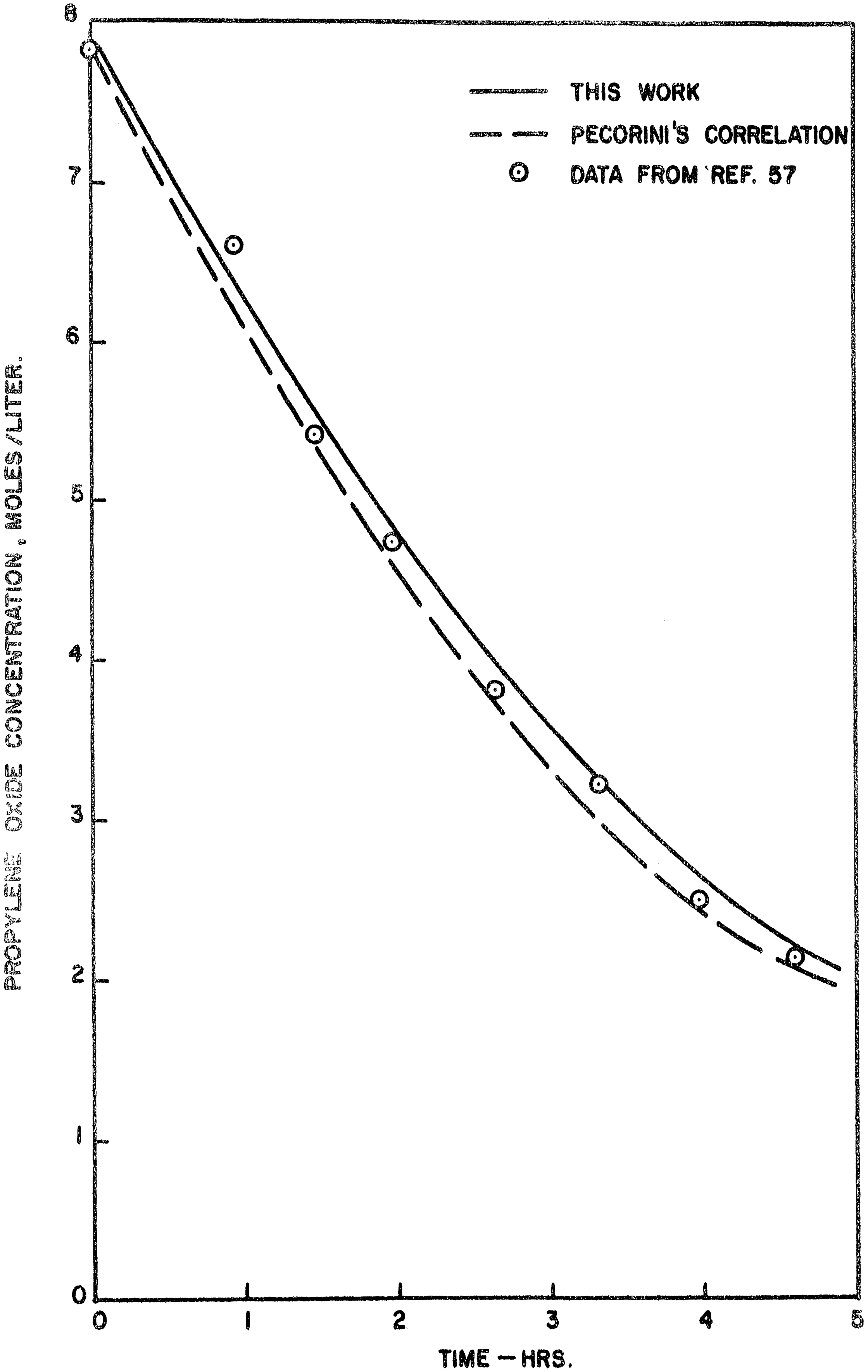


Figure 15. Comparison of Experimental Time-Composition Data of Propylene Oxide with Calculated Values at 45°C.

CONCLUSIONS

1. The reaction velocity of each of the reactions is directly proportional to the sodium hydroxide concentration. The reaction velocity constant can be expressed as:

$$k = k_u + k_c\,(\mathrm{NaOH}) \tag{56}$$

where k = the measured rate constant

k_u = the uncatalyzed rate constant

k_c = the catalyzed rate constant

(NaOH) = catalyst concentration, moles/liter

For the methanol reaction, k_u becomes significant only at a catalyst concentration of less than 0.0025 moles/liter. For the reactions with the alcohol-ethers, k_u is negligible.

2. The reaction velocities of these reactions are sensitive to composition changes of the medium which affect the polarity of the reacting mixture.

3. The effect of the reacting mixture on the various rate constants could be directly related to the concentration of methanol in the mixture. The following equations for the rate constants are able to correlate experimental data obtained in this work under varying conditions, e.g., whether the reactions occurred independently or consecutively.

a. For the propylene oxide-methanol reaction

$$k_1 = \underline{k_1}\, e^{1.42\,(1-C_A/M)} \tag{79}$$

$$\underline{k_1} = 1.02\,(10^9)\, e^{-\frac{17,200}{RT}} \quad \text{moles}^{-2}\ \text{lit}^{2}\ \text{min}^{-1}$$

b. For the propylene oxide-propylene glycol methyl ether reaction

$$k_2 = \underline{k_2}\, e^{-2.40\,(C_A/M)} \tag{80}$$

$$\underline{k_2} = 0.97\,(10^5)\, e^{\frac{-11,700}{RT}} \text{ moles}^{-2}\text{lit}^2 \text{ min}^{-1}$$

c. For the propylene oxide-dipropylene glycol methyl ether reaction

$$k_3 = \underline{k_3}\, e^{-2.40\,(CA/M)}$$

$$\underline{k_3} = 4.75\,(10^7)\, e^{\frac{-15,800}{RT}} \text{ moles}^{-2}\text{lit}^{2}\text{min}^{-1} \tag{81}$$

d. For the propylene oxide-tripropylene glycol methyl ether reaction

$$k_4 = \underline{k_4}\, e^{-2.40\,(C_A/M)}$$

$$\underline{k_4} = 2.25\,(10^9)\, e^{\frac{-18,500}{RT}} \text{ moles}^{-2} \text{ lit}^{2}\text{min}^{-1} \tag{82}$$

where A = concentration of methanol at time t in moles per liter

M = the reciprocal of the molar volume of methanol at the temperature of the reaction

APPENDIX I

PHYSICAL PROPERTIES

Densities

The use of concentration units in the rate equations necessitates the accurate knowledge of the densities of the reaction mixtures. Pecorini(57) found that the densities of the reacting mixture are additive with respect to the compositions in mass fractions. Figure 16 presents the densities of the four alcohol-ethers as a function of temperature. The values for the first three alcohol-ethers were obtained from several sources(16,57) while the values for the tetrapropylene glycol methyl ether were extrapolated from an experimental value obtained at 25°C.

The densities of propylene oxide and methanol at various temperatures are well investigated. Pecorini(57) has summarized the various values for the densities of these two compounds in his work.

Refractive Indices

In order to analyze the relative amounts of the two alcohol-ethers in the binary fractions obtained from distilling samples from the product distribution runs, binary refractive index calibration curves were prepared at 25°C. They were found to be additive with respect to the mass fractions of the pure compounds. The curves are shown in Figure 17. The measurements were obtained using a Bausch and Lomb Abbe-56 refractometer. Pecorini(57) has reported similar results on the refractive indices of binary mixtures as well as ternary mixtures.

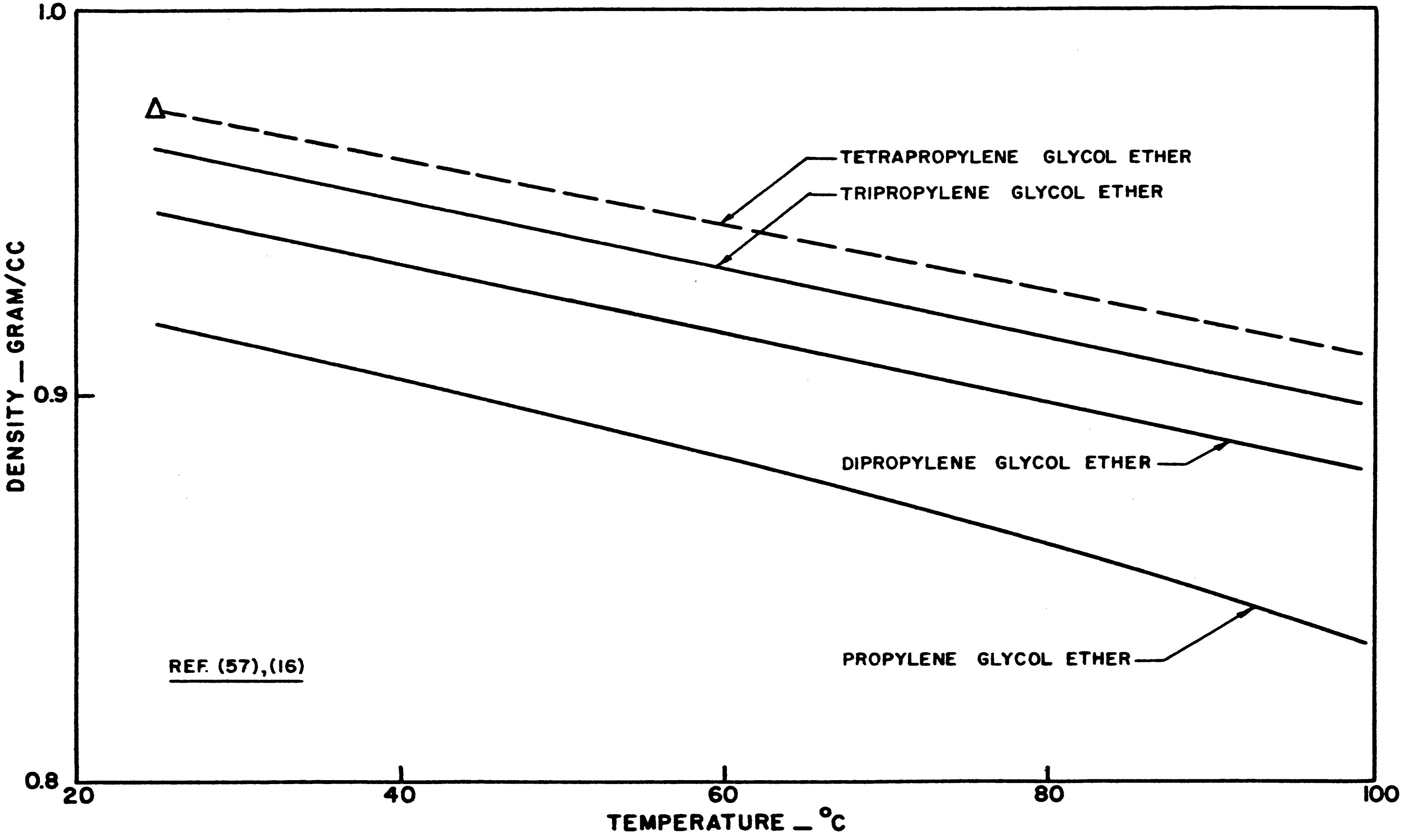


Figure 16. Effect of Temperature on the Density of Alcohol-Ethers.

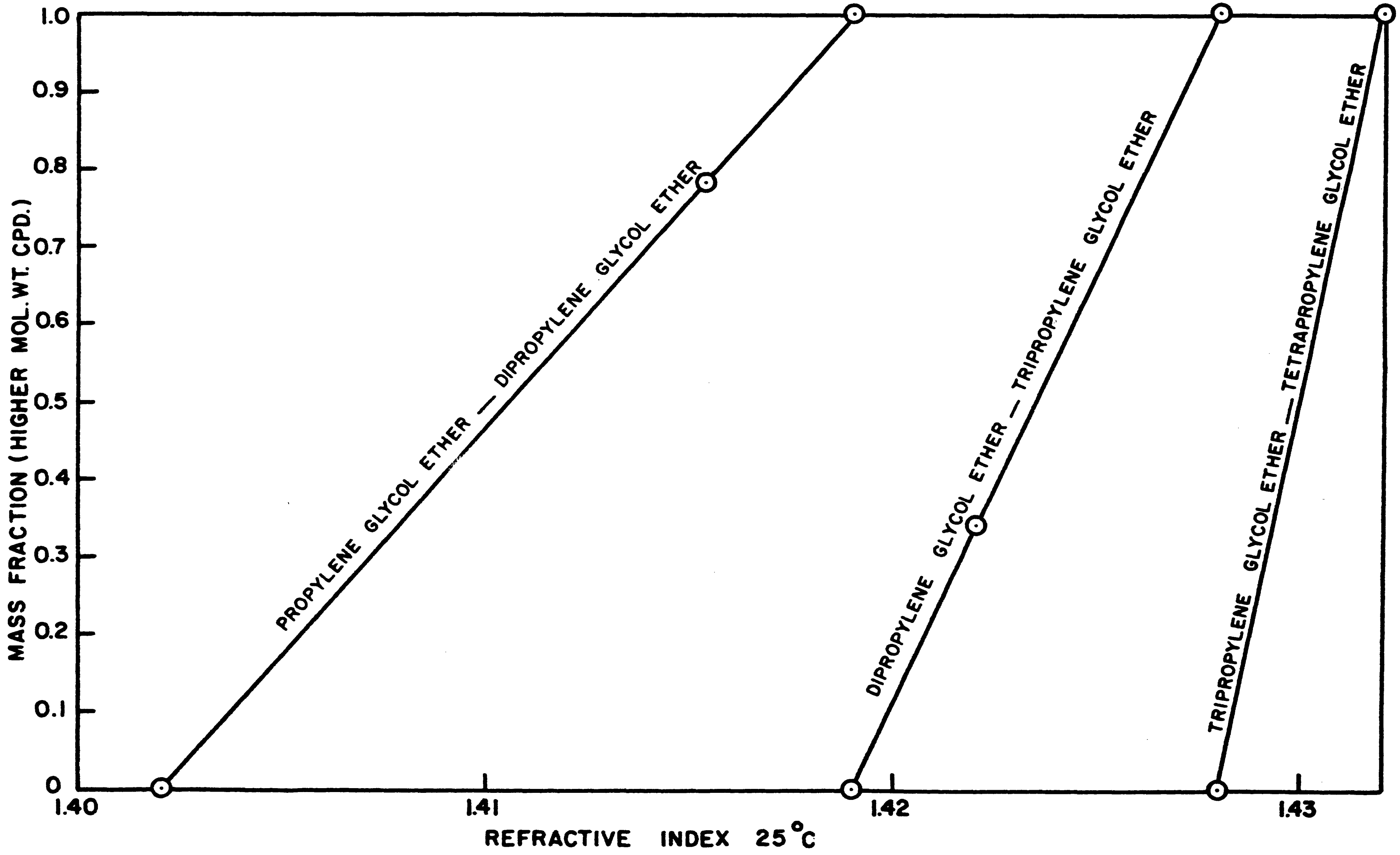


Figure 17. Binary Refractive Index of Alcohol Ethers at 25°C.

Infrared Spectrograms

The infrared spectrograms of methanol, propylene oxide, and isomers of propylene glycol methyl ether have been reviewed, analyzed and presented in Pecorini's work. No spectrograms for the dipropylene glycol methyl ether or for the tripropylene glycol methyl ether have so far been reported in the literature. In order to have a permanent record of these two alcohol-ethers used in our work, their infrared spectrogram was obtained using a Baird Model B double beam recording spectrophotometer. The spectrograms are shown in Figure 18.

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.			
DATE Aug. 30,1954	INDEX		
SAMPLE DIPROPYLENE GLYCOL METHYL ETHER			
FROM Dow Chemical Co.			
SAMP. CELL# 0.1 MM	CMS.		
REF. CELL 0.1 MM	CMS.		
CHEM. 2500 MG.	MG.		
SOLV. CS$_2$			
VOL. 25 C.C.	%	C.C.	%
F.S. SOLID	°C.	GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.			
DATE Aug. 30,1954	INDEX		
SAMPLE TRIPROPYLENE GLYCOL METHYL ETHER			
FROM Dow Chemical Co.			
SAMP. CELL# 0.1 MM	CMS.		
REF. CELL 0.1 MM	CMS.		
CHEM. 2500 MG.	MG.		
SOLV. CS$_2$			
VOL. 25 C.C.	%	C.C.	%
F.S. SOLID	°C.	GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9

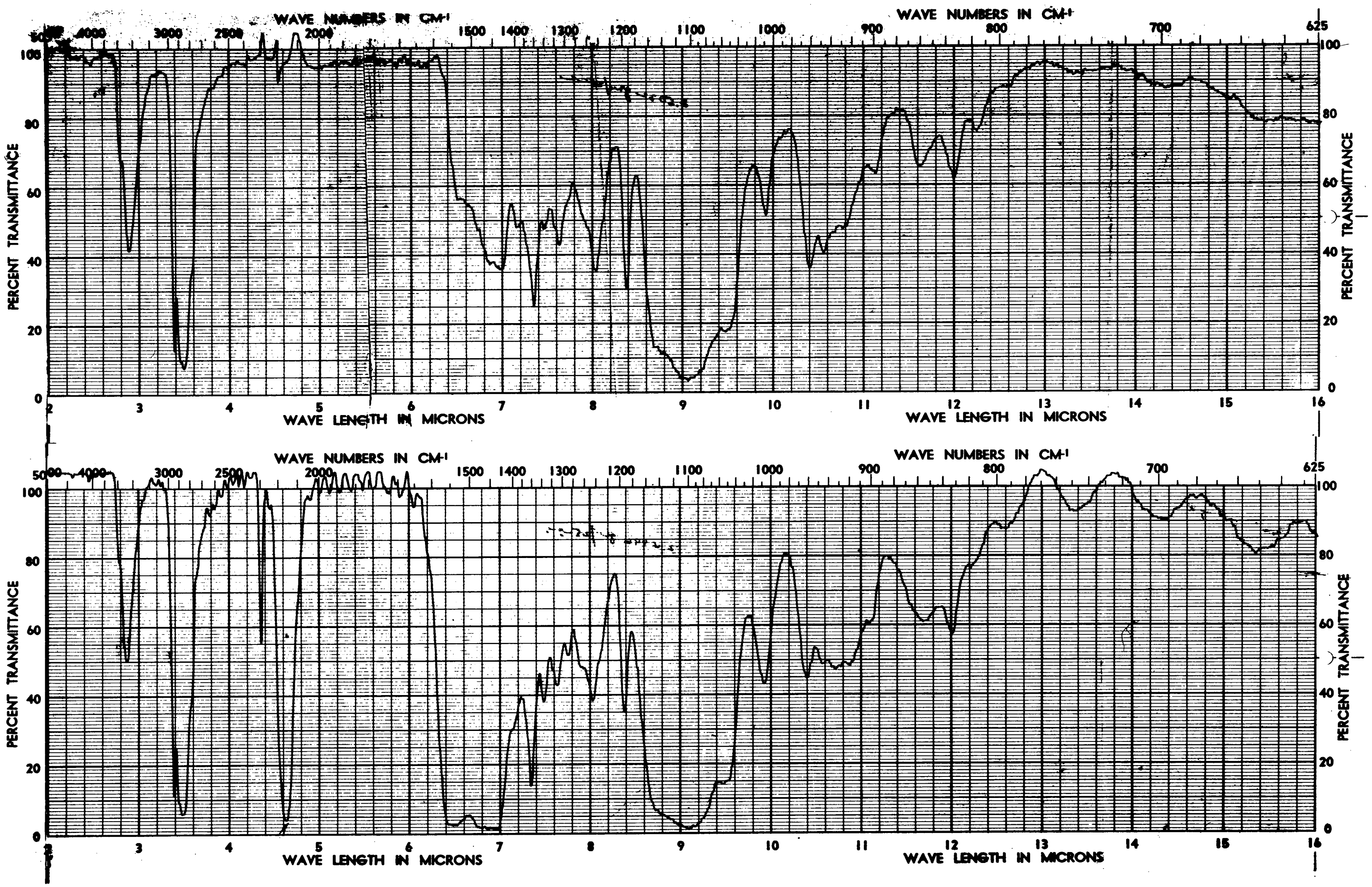


Figure 18. Infrared Spectrogram of Dipropylene Glycol Methyl Ether and Tripropylene Glycol Methyl Ether.

APPENDIX II

ANALYTICAL METHODS

Chemical Analysis of Propylene Oxide

Numerous methods for the analysis of epoxides have been reported in the literature(50). Some were specifically developed for the analysis of a particular epoxide compound in the presence of other materials while others are only adaptable to the analysis of low molecular weight epoxides. The effectiveness of the method depends to a large extent on the concentration of the analytical reagent (a factor sometimes overlooked), on the time required for reaction, and sometimes on the temperature. A constant trouble spot is interference by other substances in the sample resulting in side reactions. Mitchell(50) has summarized available methods for analyzing epoxy compounds. Table XXII below presents a condensation of methods for analyzing low molecular weight epoxides. It should be pointed out, however, that this table may be used only as a rough guide. It has been our experience that results vary considerably depending on the condition of analysis and the particular substance analyzed.

A description of the two methods used for the analysis of propylene oxide in this investigation is presented below:

1. Aqueous HCl-$CaCl_2$ Method(43,44)

Preparation of the Reagent-- A saturated aqueous solution of calcium chloride at room temperature was prepared by dissolving reagent grade anhydrous calcium chloride in distilled water. The saturated solution was acidified with hydrochloric acid to make up an acid strength of about

TABLE XXII

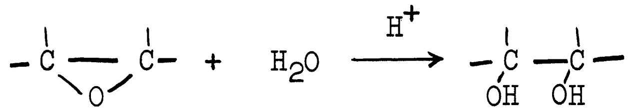
METHODS OF ANALYSIS FOR PROPYLENE AND ETHYLENE OXIDES

	Methods	Reagents	Reaction Temperature	Reaction Time	Titrant	Precision	Ref.
1.	Aqueous $MgCl_2$-HCl	0.1N HCl, sat. soln. $MgCl_2$	room temp.	30 mins.	0.1N NaOH	- 0.5%	(15)
2.	Aqueous $CaCl_2$-HCl	0.15N HCl, sat. soln. $CaCl_2$	room temp.	30 mins.	0.1N NaOH	- 0.8%	(43, 44)
3.	Alcohol $MgCl_2$-HCl	0.5N HCl in ethanol	room temp.	30 mins.	0.1N NaOH	- 0.2%	(34)
4.	Cellosolve-HCl	0.2N HCl in Cellosolve	65°C	3 hours	0.1N NaOH	--	(50)
5.	Ethyl ether-HCl	0.2N HCl in anhyd. ether	room temp.	3 hours	0.1N NaOH	--	(73)
6.	Pyridinum Chloride-Pyridine	0.2N HCl in Pyridine	reflux	30 mins.	0.1N NaOH	- 0.5%	(18)
7.	Pyridinum Chloride-Chloroform	Mix (6) in Chloroform	reflux	30 mins.	0.1N NaOH	- 0.5%	(50)
8.	Dioxane-HCl	0.2N HCl in dioxane	room temp.	30 mins.	0.1N NaOH	- 0.5%	(35)
9.	Periodic-Perchloric	1% HIO_4 in 0.4N $HClO_4$	room temp.	1 hour	KI, 0.1N $Na_2S_2O_3$	- 0.2%	(17)
10.	Sodium Thiosulfate	0.2M $Na_2S_2O_3$ in 50% acetone	65°C	30 mins.	0.2N acetic acid	--	(12)
11.	Sodium Sulfite	sat. soln. of Na_2SO_3	room temp.	30 mins.	0.2N HCl	- 0.5%	(71)

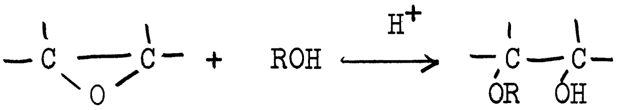
0.15 N. The prepared solution was stable over a period of several months. Standard 0.1 N sodium hydroxide was used as the titrant.

Procedure--15 c.c. of the analytical reagent was pipetted into an erlenmeyer flask with a glass stopper. The samples to be analyzed were withdrawn from the reacting mixture with a calibrated 2 c.c. hypodermic syringe with exactly 1 c.c. of the sample being delivered into the erlenmeyer flask. The mixture was allowed to stand for thirty minutes and then titrated to neutral with a standard base. The hydrochloric acid consumed, corrected for the catalyst, was the measure of the epoxide in the sample.

Calibration--The simple procedure and the stability of the reagent made this method a very desirable one, especially, when a large number of analyses had to be made. Several undesirable effects, however, were uncovered when the method was being calibrated for our materials. One of these is the presence of competing side reactions according to the following equations:



(19)



(83)

which are catalyzed by hydrogen ions. This made it impossible to account for all the epoxides by Equation (18) page 21. Furthermore, Equation (19) and (83) indicate that less and less epoxide will react by the way of Equation (18) as the concentration of hydrogen ion is increased. In Table XXIII the percentage of epoxide analyzed by this

TABLE XXIII

ANALYSIS OF PROPYLENE OXIDE IN ALCOHOL-ETHER BY THE AQUEOUS HCl-$CaCl_2$ METHOD

	HCl strength of reagent	Concentration of oxide in sample, gm/gm	Oxide analyzed	Fraction analyzed	Deviation from average
1.	0.15 N	0.0115	0.0112	0.974	+ 0.0065
		0.0125	0.0120	0.96	- 0.0075
		0.0130	0.0130	1.00	+ 0.0325
		0.0152*	0.0150	0.987	+ 0.0195
		0.0160	0.0158	0.989	+ 0.0215
		0.025	0.0243	0.972	+ 0.0045
		0.0264*	0.0240	0.909	- 0.0585
		0.0267	0.0262	0.981	+ 0.0135
		0.0290	0.0282	0.972	+ 0.0045
		0.0330*	0.0310	0.939	- 0.0285
		0.0440	0.0425	0.966	- 0.0015
		0.0500	0.0465	0.93	- 0.0375
		0.0500	0.0485	0.97	+ 0.0025
		0.0520*	0.0500	0.962	- 0.0055
		0.0550	0.0540	0.982	+ 0.0145
		0.0875*	0.0760	0.968	+ 0.0005
		0.0875	0.0845	0.966	- 0.0015
		0.0940	0.0920	0.979	+ 0.0115
		0.1040	0.1015	0.976	+ 0.0085
			average	0.967	
2.	0.25 N	0.0260	0.0230	0.885	- 0.0048
		0.0335	0.0295	0.881	- 0.0088
		0.0565	0.0500	0.885	- 0.0048
		0.0975	0.0885	0.908	+ 0.0182
			average	0.889	

---

* Samples consist of propylene oxide and tripropylene glycol ether. The rest are mixtures of propylene oxide and dipropylene glycol ether.

method are tabulated. Fairly consistent results were obtained and the actual concentration of the epoxide in the sample can be obtained by using the necessary correction factor. This method was used for Runs 1 to 14 inclusive, for the dipropylene glycol methyl ether - propylene oxide runs.

2. Periodic - Perchloric Acid Method(17)

Preparation of Reagent--The analytical reagent was prepared by dissolving 1 weight percent periodic acid in an aqueous solution of a 0.4 N perchloric acid. Iodine is liberated from the excess periodic acid by the addition of 10 c.c. of 15 percent potassium iodide solution. The free iodine was titrated with a 0.1 N standard sodium thiosulfate solution. The periodic acid reagent was found to be stable over a period of one month.

Procedure--25 c.c. of the reagent was pipetted into an erlenmeyer flask fitted with a glass stopper. Samples to be analyzed were withdrawn from the reacting mixture with a calibrated 2 c.c. hypodermic syringe and exactly 1 c.c. of the sample was introduced into the flask. The mixture was allowed to stand for one hour after which 10 c.c. of 15 percent potassium iodide solution was added to the mixture together with 1 c.c. of concentrated acetic acid. The free iodine liberated in the mixture was then immediately titrated with standard 0.1 N sodium thiosulfate. The difference of sodium thiosulfate used between a blank and the sample is a measure of the propylene glycol present in the sample. From this, the concentration of propylene oxide can be calculated.

Calibration--Results using the periodic-perchloric acid method on known samples are tabulated in Table XXIV. As can be seen, low values are obtained when an insufficient amount of the reagent was used.

The results in Table XXIV agree quite well with values reported by Latremouille(17) for pure ethylene oxide. Fleury(22) reported that methanol and acetic acid are reactive with the periodic reagent. However, blanks with and without these two compounds had failed to indicate that this is so. It may be pointed out here also that this method is known to be specific only for adjacent hydroxyl groups(50).

Chemical Analysis of Hydroxyl Group(50)

Acetylation with Acetic Anhydride in Pyridine--As mentioned in page 22, the analysis of the hydroxyl concentration is necessary to give a complete description of the experimental product distribution. The analytical method used was the acetylation of the hydroxyl group using acetic anhydride in pyridine. This method is essentially that described by Mitchell(50) with slight modification.

Preparation of reagent--The analtyical reagent consisted of 10 percent acetic anhydride in reagent grade pyridine. Standard 0.5 N NaOH was used as a titrant with phenolphthalein as indicator. This reagent is not too stable and should be prepared fresh.

Procedure--A sample of about 500 mg. was weighed into a glass stoppered erlenmeyer flask with 25 c.c. of the reagent. The glass stopper was moistened with pyridine and seated loosely on the flask. The flask was then placed on a steam bath and heated for one hour. After the heating

TABLE XXIV

ANALYSIS OF PROPYLENE OXIDE IN ALCOHOL-ETHER USING THE PERIODIC-PERCHLORIC ACID METHOD

c.c. of reagent used	Concentration of propylene oxide in sample gm/gm	Oxide analyzed	Fraction Analyzed	Deviation from average
15	0.03565*	0.0342	0.96	- 0.0066
	0.03565	0.034	0.954	- 0.0126
	0.03565	0.0344	0.965	- 0.0016
	0.0254	0.0241	0.9488	- 0.0178
	0.0294	0.0288	0.9799	+ 0.0133
	0.03495	0.0338	0.9668	+ 0.0002
	0.01527	0.01504	0.985	+ 0.0184
	0.0286*	0.02748	0.9608	- 0.0058
	0.03858	0.0374	0.9699	+ 0.0033
	0.01293	0.01233	0.953	- 0.0136
	0.0386*	0.0378	0.978	+ 0.0114
	0.0386*	0.0378	0.978	+ 0.0114
	0.0386	0.0376	0.972	+ 0.0054
	0.0386	0.03714	0.961	- 0.0056
		average	0.9666	
25	0.03565	0.03547	0.995	- 0.0017
	0.03565*	0.03558	0.998	+ 0.0013
	0.0386	0.0388	1.005	+ 0.0083
	0.0386*	0.0382	0.99	- 0.0067
	0.0155	0.01538	0.992	- 0.0047
	0.0270	0.02727	1.01	+ 0.0133
	0.0129*	0.01277	0.99	- 0.0067
	0.0456*	0.0451	0.989	- 0.0077
	0.0456	0.04596	1.008	+ 0.0113
	0.0245	0.03426	0.99	- 0.0067
		average	0.9967	

---

* Samples consist of propylene oxide and tripropylene glycol ether. The rest are mixtures of propylene oxide and dipropylene glycol ether.

period, about 50 c.c. of distilled water was added to the mixture to hydrolyze the unreacted anhydride. The mixture was then titrated with the standard base. Simultaneously, a blank was also prepared and titrated. The difference in the titrating base between the blank and the sample is a measure of the hydroxyl group concentration of the sample.

This method was found to be satisfactory and in general, gave quantitative results. Care should be taken that the acetic anhydride concentration in the reagent should be at least 10 percent, as low results will be obtained at lower concentrations. In Table XXV results of this method on pure glycol ethers are tabulated.

TABLE XXV

ANALYSIS OF HYDROXYL GROUP IN ALCOHOL-ETHERS BY THE ACETIC ANHYDRIDE-PYRIDINE METHOD

	Theoretical molecular weight	Molecular weight by analysis of OH group
dipropylene glycol methyl ether	148.16	148.25 148.30
tripropylene glycol methyl ether	206.24	206.8 206.0

APPENDIX III

THEORETICAL AND EMPIRICAL TREATMENT OF REACTION RATE IN THE LIQUID PHASE

Theoretical treatment of chemical reaction kinetics in the liquid phase has always been hampered by the fact that the theories of liquids and solutions are still in the developmental stage. The extension of gas kinetics methods to the liquid phase has met with relatively little success except in systems that can be considered as ideal solutions.

For non-ideal systems, the common approach is to relate some bulk properties of the solution to the activity of the reacting species. For reactions involving ions and polar molecules, the important parameter is the ionic atmosphere or electrostatic potential between the reacting species. A summary of this treatment is presented below. The inherent simplifying assumptions involved, however, make such a treatment valid only as a rough guide. Sometimes, the results obtained are not too consistent(2,39).

For non-electrolytes in general, the recent extension of strictly regular solution theory to kinetics in the liquid phase indicates some promising results(29,52).

Relationship Between Rate Constants and Activity of the Reacting Species

By considering the electrostatic forces among ions and assuming complete dissociation of strong electrolytes in solution, Debye and Huckel (14) satisfactorily solved the problem of calculating activity coefficients of ions and electrolytes, expressing them in terms of the ionic strength of the solution:

$$- \ln\gamma_i = \frac{Z_i^2 A \sqrt{\mu}}{1 + \beta a_i \sqrt{\mu}} \tag{84}$$

where a_i = distance of closest approach of another ion to the ith ion

γ_i = activity coefficient of the ith ion

μ = ionic strength
= $1/2 \sum c_i Z_i$

Z = charge

c_i = concentration of the ith ion

and

$$A = \frac{e^3}{DKT} \sqrt{\frac{2\pi N}{1000\ DKT}} \tag{85}$$

$$\beta = \sqrt{\frac{8\pi N e^2}{1000\ DKT}} \tag{86}$$

where e = electronic charge

N = Avogadro's number

K = Boltzmann's constant

D = dielectric constant

T = absolute temperature °K

The activity coefficient for the electrolyte defined as

$$\gamma_{\pm} = \gamma_+ + \gamma_- \tag{87}$$

is then related as follows:

$$- \ln \gamma_{\pm} = \frac{Z_+ Z_- A \sqrt{\mu}}{1 + \beta a_i \sqrt{\mu}} \tag{88}$$

The above equations hold rigorously for very dilute solutions or very low ionic strengths; for moderately higher ionic strengths or a change of the dielectric constant of the solution, additional terms had to be added to Equation (84) to account for deviations (2).

For reactions involving ions only and where the dielectric constant of the reacting medium is unchanged, the Debye and Huckel expression for the activity coefficients may be used. For a bimolecular ion-ion reaction in solution, the substitution of the Debye and Huckel terms for the activity coefficients in Equation (33) yields the following expression for the specific rate constant:

$$\ln k = \ln k' + \frac{e^2 Z_a Z_b}{DKT} \left(\frac{\kappa}{1 + \kappa a} \right) \qquad (89)$$

where

$$\kappa^2 = \frac{8 N \pi e^2}{1000 \ DKT} \mu \qquad (90)$$

The assumption of a double-sphere activated complex was made to facilitate the calculation of $\gamma^{\neq}$.

In the case where one of the reactants is a neutral molecule, $Z_a Z_b = 0$, and according to Equation (89), the specific rate constant is independent of the ionic strength of the reacting medium.

In the above treatment, the dielectric constant of the reacting medium was considered to be unchanged. In reactions in the liquid phase the dielectric constant of the reacting medium may play an important role. The dielectric constant of the medium affects markedly the ability of reactant particles to contact each other. This is especially true with ion-ion and ion-dipole reactants. The work required to separate two unlike charges varies inversely as the dielectric constant of the medium.

The Debye and Huckel theory predicts activity coefficients for ions as less than unity in the range where the theory holds. This implies that the variation of activity coefficients is attributed to forces of attraction between the oppositely charged ions, which are more important than the repulsions between the like charged ions. By the same reasoning a decrease in the dielectric constant of the medium leads to an increase in the activity coefficient of the ion.

The effect of the dielectric constant of the medium on the rate of ionic reactions may be similarly treated by the method of Debye and Huckel(14) By relating the rate constant at infinite dilution, k', in Equation (89) to that in the gas phase

$$k' = k_o \frac{\alpha_a \alpha_b}{\alpha^{\neq}} \tag{91}$$

where

k_o = is a true constant independent of the dielectric constant and ionic strength

$\alpha_{a,b,}$ = activity coefficient of reactants relating the infinitely dilute solution to the ideal gas

or

$$\ln k' = \ln k_o + \ln \frac{\alpha_a \alpha_b}{\alpha^{\neq}} \tag{92}$$

Following Scatchard's treatment(67), where the concentration of the activated complex was calculated in terms of the concentration of A ions, the concentration of B ions at a distance r from A, and the electrostatic potential, the following relationship is obtained:

$$\ln \frac{\alpha_a \alpha_b}{\alpha^{\neq}} = \frac{e^2 Z_a Z_b}{K\ T\ r} \left(1 - \frac{1}{D}\right) \tag{93}$$

substituting this into Equation (92) gives

$$\ln k' = \ln k_o + \frac{e^2 Z_a Z_b}{K\ T\ r_{\neq}}\left(1 - \frac{1}{D}\right) \qquad (94)$$

where $r \neq$ = ionic radius of the activated complex

which relates the rate constant in solutions of different dielectric constants.

Equation (94) may be written in a more useful form

$$\frac{d \ln k'}{d\ (1/D)} = - \frac{e^2 Z_a Z_b}{K\ T\ r} \qquad (95)$$

Laidler and Eyring$^{(39)}$, treating the activated complex as a sphere instead of a double sphere, arrived at a similar equation for the effect of the dielectric constant on the rates of ionic reactions

$$\ln k' = \ln k_o + \frac{e^2}{2KT}\left(\frac{1}{D} - 1\right)\left(\frac{Z_a^2}{r_a} \quad \frac{Z_b^2}{r_b} \quad \frac{(Z_a + Z_b)^2}{r^{\neq}}\right) \qquad (96)$$

or

$$\frac{d \ln k'}{d(1/D)} = \frac{e^2}{2KT}\left(\frac{Z_a^2}{r_a} + \frac{Z_b^2}{r_b} - \frac{(Z_a + Z_b)^2}{r^{\neq}}\right) \qquad (97)$$

Equations (97) and (95) are identical when $r_a = r_b = r^{\neq}$. An examination of Equations (97) or (95) shows that the effect of the dielectric constant on the rate of ion-ion reactions is dependent on the charge type of the reactants.

For the reaction of an ion with a polar molecule, Equation (94) is not applicable. Equation (97), however, reduces to

$$\frac{d \ln k'}{d(1/D)} = \frac{e^2 Z_a^2}{2KT}\left(\frac{1}{r_a} - \frac{1}{r^{\neq}}\right) \qquad (98)$$

Since the radius of the activated complex $r^{\neq}$, is always greater than that of the ion r_a, the effect of the dielectric constant of the medium on ion-dipolar reactions is to decrease the rate of reaction as the dielectric constant increases.

Deviations from Equation (98), frequently found at low dielectric constant, have been attributed to the tendency of the more polar component to cluster around ions such that the bulk dielectric constant is very much lower than the dielectric constant around the ions. Here the rate constant should conform more to that of a medium of a higher dielectric constant than to the apparent one(27).

Recently, Landskroener(40) presented an improved version of Equation (98) which was applied to reactions such as the hydrolysis of esters, reactions which have failed to be treated satisfactorily by Equation (98). The final form of the Landskroener equation is

$$\ln k' = \ln k_o + \frac{e^2}{2KT}\left(\frac{1}{D} - 1\right)\left(\frac{Z_a^2}{r_a} + \frac{Z_b^2}{r_b} - \frac{(Z_a + Z_b)^2}{r^{\neq}}\right)$$

$$+ \frac{3\,e^2}{8KT}\left(\frac{2}{D} - 1\right)\left(\frac{G_a}{r_a^3} + \frac{G_b}{r_b^3} - \frac{G^{\neq}}{r^{\neq 3}}\right) \qquad (99)$$

Here G_i is the distance separating the two point charges of the molecule forming the dipole. For an ion, $G = 0$ and evaluation of $G^{\neq}$ is possible if the configuration of the activated complex is known. Additional terms may be added to Equation (99) to account for higher multipole moments of the molecule(36).

Equation (99) is equivalent to Equation (98) except for the last term on the right hand side. It was pointed out that for ion-ion reactions the final term of Equation (99) might be negligible while for dipole-dipole reactions the effect of the solvent is solely given by the last term. For ion-dipole reactions the final term may be more important than the second term thereby accounting for the failure of Equation (98) in its application to some reactions.

Molecular Association and its Influence on the Kinetics of Liquid-Phase Chemical Reactions

Associative phenomena occur widely in non-ideal liquid mixtures and when hydroxylic compounds are involved, hydrogen bonding is invariably the cause. The result of such interaction is the formation of stable complexes which definitely affects the rate of reaction of such a system. Lutskii(45) and Knorre(37) have studied organic reactions in solutions and the effect of hydrogen bonding on their rates. Anomalous behaviors on the rates of reaction were observed and some of the data were shown to be explainable in terms of the dielectric constant of the solutions. In general, it was observed that the activation energy is decreased by hydrogen bonding. In another direction, Prigogine(61) has summarized recent efforts in calculating activity coefficients of associated solutions (due to hydrogen bonding) from spectroscopic data.

Medium Effects on the Arrhenius Equation

According to the transition state theory and thermodynamics, the specific rate constant k is expressable as

$$k = \frac{K\,T}{h}\, e^{\Delta S^{\neq}/R}\, e^{-\Delta H^{\neq}/RT} \qquad (100)$$

and since for reactions in the liquid state

$$E = \Delta H^{\neq} + RT \qquad (101)$$

$$k = \frac{e\,K\,T}{h}\, e^{\Delta S^{\neq}/R}\, e^{-E/RT} \qquad (102)$$

where K = Boltzmann constant

following equation(75)

$$\frac{d \ln k}{dT} = \left\{\frac{\partial \ln k}{\partial T}\right\}_D + \left\{\frac{\partial \ln k}{\partial D}\right\} \frac{dD}{dT} \qquad (104)$$

leads to

$$E_c = E_D + 2.3\ RT^2 \left\{\frac{\partial \log k}{\partial D}\right\} \frac{dD}{dT} \qquad (105)$$

where E_c is the apparent energy of activation measured in media of constant composition and E_D is the activation energy at constant dielectric constant.

Harned and Samaras(31) derived equations relating the work required to displace a solvent by another of different polarity in the presence of an electric field and showed that the specific rate constant can be represented as

$$k = \underline{k}\, c' e^{-w/KT} \qquad (106)$$

where k = is the velocity constant in the medium in question

$\underline{k}$ = velocity constant in the original medium before the change was effected

c' = concentration of the catalyst

$e^{-w/KT}$ = a Boltzman factor, where w is the work term

Evans and Jenkins(21) have shown that the activation energies of some organic reactions in solvents of different dielectric constants can be correlated by the simple relationship

$$E = E_B + E_x/D_{20^\circ} \qquad (107)$$

where E = the measured Arrhenius activation energy

E_B = the activation energy obtained by extrapolation to $1/D = 0$

E_x/D = $E - E_B$, the repulsion energy, characteristic of the solvent.

APPENDIX IV

MATHEMATICAL DERIVATIONS

Equations Describing Product Distribution Of Consecutive Reactions

Case 1: All the steps are bimolecular and volume change is assumed negligible.. The rate equations are

$$V \frac{d(A)}{dt} = - k_1 (A)(B) \tag{48a}$$

$$V \frac{d(AB)}{dt} = k_1 (A)(B) - k_2 (AB) (B) \tag{48b}$$

$$V \frac{d(AB_2)}{dt} = k_2 (AB)(B) - k_3 (AB_2)(B) \tag{48c}$$

where the AB_ns' and B are in number of moles and the units of k_ns' are in liter mole^{-1} min.$^{-1}$. Dividing ~~Equation~~ 48a by 48b.

$$\frac{d(A)}{d(AB)} = - \frac{k_1 (A)}{k_1 (A) - k_2 (AB)} \tag{108}$$

rearranging,

$$d(AB) - \frac{k_2 (AB)}{k_1 (A)} d(A) = - d(A)$$

Equation (108) is a linear equation of the first order whose solution is

$$(AB) = k_1 (A) \left\{ \frac{1}{k_2 - k_1} + \frac{1}{k_1 - k_2} \left(\frac{A_o}{A} \right)^{\frac{k_1 - k_2}{k_1}} \right\} \tag{109}$$

similarly, by dividing Equation 48a by Equation 48c and substituting the values of (AB) obtained from Equation (109), a similar first order linear equation is obtained, and the solution is

$$(AB_2) = k_1 k_2 (A) \left\{ \frac{1}{(k_2 - k_1)(k_3 - k_1)} + \frac{1}{(k_1 - k_2)(k_3 - k_2)} \left[\frac{A_o}{A}\right]^{\frac{k_1 - k_2}{k_1}} \right.$$

$$\left. + \frac{1}{(k_1 - k_3)(k_2 - k_3)} \left[\frac{A_o}{A}\right]^{\frac{k_1 - k_3}{k_1}} \right\} \qquad (110)$$

repeating this procedure, it can be shown that the solution is symmetrical and can be written in terms of the mole ratio AB_n/A_o, as

$$\frac{AB_n}{A_o} = (-1)^n \prod_{j=1}^{n} k_j \sum_{j=1}^{n+1} \frac{\left(\frac{A}{A_o}\right)^{\frac{k_j}{k_1}}}{\prod\limits_{\substack{j=1 \\ j \neq k}}^{n+1} (k_j - k_k)} \qquad (51)$$

In terms of distribution constants c, the general solution may be written as

$$\frac{AB_n}{A_o} = (-1)^n \prod_{j=1}^{n} c_j \sum_{j=1}^{n+1} \frac{\left(\frac{A}{A_o}\right)^{c_j}}{\prod\limits_{\substack{j=1 \\ j \neq k}}^{n+1} (c_j - c_k)} \qquad (111)$$

Equations (111) do not hold when two or more alcohols are present at the start of the reaction. For the case where both (A_o) and $(AB)_o$ are present at the start of the reaction, the boundary condition $\left[(A) = (A_o); (AB) = (AB)_o; \text{ at } t = 0\right]$ must be satisfied. Equation (109) then becomes

$$AB = \frac{k_1}{k_2 - k_1} (A) + (AB)_o \left(\frac{A}{A_o}\right)^{\frac{k_2}{k_1}} - \frac{k_1}{k_2 - k_1} \left(\frac{(A)^{k_2/k_1}}{(A_o)^{k_2/k_1 - 1}} \right) \qquad (112)$$

and Equation (110) becomes

$$AB_2 = \frac{k_1\, k_2}{(k_2 - k_1)(k_3 - k_1)} \left[\frac{(A)^{1 - k_3/k_1} - A_o^{\,1 - k_3/k_1}}{A^{-\,k_3/k_1}} \right]$$

$$+ \frac{k_1 k_2 - k_2((AB)_o)(k_2 - k_1)}{(k_2 - k_1)(k_2 - k_3)} \left[\frac{A_o^{1 - k_2/k_1}}{A - k_2/k_1} - \frac{A_o^{1 - k_3/k_1}}{A - k_3/k_1} \right] \tag{113}$$

The number of moles of the higher products can be obtained by the same procedure. In the case where

$$k_1 \neq k_n \; ; \; n > 1$$

$$k_n = k_{n+1} \; ; \; n > 1$$

Equation (111) reduces to

$$\frac{AB_n}{A_o} = \frac{c^{n - 1}}{(c - 1)^n} \left\{ \left(\frac{A}{A_o}\right) - \left(\frac{A}{A_o}\right)^c \sum_{j=0}^{n-1} \frac{1}{j!} \left[(c - 1) \ln \frac{A_o}{A} \right]^j \right\} \tag{114}$$

where

$$c_n = \frac{k_n}{k_1} \; ; \; n > 1$$

Case 2: Distribution of products of consecutive second order reactions with equal velocities. The system of differential equations is identica with Equations (48) except that $k_1 = k_2 = \ldots = k_n$. The rate of change of B may be written as

$$\frac{d\,(B)}{dt} = -\sum_{n=0}^{n} k\,(AB_n)(B) = -k\,(B) \sum_{n=0}^{n} (AB_n) \tag{115}$$

where $AB_o = A$.

We note also that

$$\sum_{n=0}^{n} (AB_n) = A_o, \quad \text{the initial concentration of the propagating alcohol} \tag{116}$$

substituting Equation (116) into Equation 115) gives

$$\frac{d\,(B)}{dt} = -\,k\,A_o\,(B) \qquad (117)$$

solving Equation (117) in the following manner:

$$-\int_{B_0}^{B} d\,(B) = A_o\,k \int_{0}^{t} (B)\,dt \qquad (118)$$

or

$$\frac{B_o - B}{A_o} = k \int_{0}^{t} (B)\,dt \qquad (119)$$

Letting

$$v = \frac{B_o - B}{A_o}, \quad \text{the mole ratio of oxide consumed to that of the initial alcohol} \qquad (120)$$

we have

$$dv = k\,(B)\,dt \qquad (121)$$

from Equation (45a)

$$d(A) = -\,k\,(A)(B)\,dt = -A\,dv \qquad (122)$$

similarly from Equation (45b) and (121)

$$\frac{d\,(AB)}{dt} = k\,(A)(B) - k\,(AB)(B) \qquad (123)$$

$$d\,(AB) = k\,(A - AB)(B)\,dt \qquad (124)$$

$$= (A - AB)\,dv$$

The general solution to Equations (45) is

$$AB_n = \frac{(A_o)v^n\,e^{-v}}{n'\,!} \qquad (125)$$

or in terms of the mole ratio of the product to that of the initial alcohol, Equation (125) becomes

$$\frac{AB_n}{A_o} = \frac{v^n e^{-v}}{n\,!} \tag{126}$$

This equation is the well-known Poisson distribution equation. The amount of B at any time t may be obtained from Equation (119). The result is

$$B = B_o e^{-k(A)t} \tag{127}$$

An interesting result is obtained by differentiating AB_n/A_o (Equation (126)) with respect to v and equating the expression to 0, . e.g.,

$$\frac{d\ (AB_n/A_o)}{dv} = \frac{1}{n\,!}\left[v^n\ (-e^{-v}) + e^{-v}\ (nv^{n-1})\right] = 0 \tag{128}$$

simplifying, we have

$$v = n \tag{129}$$

implying that the maximum mole fraction of any AB_n is reached at v = n.

Case 3: The initiating reaction is first order and the succeeding reactions are second order. The system may be represented by the following rate equations assuming negligible volume change.

$$V\ dA/dt = k_1\ (B) \tag{130a}$$

$$V\ d(AB)/dt = k_1\ (B) - k_2\ (AB)(B) \tag{130b}$$

$$V\ d(AB_2)/dt = k_2\ (AB)(B) - k_3\ (AB_2)(B) \tag{130c}$$

$$V\ d(AB\ )/dt = k_3\ (AB_2)(B) - k_4\ (AB_3)(B) \tag{130d}$$

and so on

where the AB_ns and B are in number of moles and the units of the k_n's are in liter mole^{-1} sec.$^{-1}$.

$n > 1$ and the units of k_1 is sec.$^{-1}$

dividing Equation(130a) by Equation (130b)

$$dA/d(AB) = \frac{k_1}{k_1 - k_2\ (AB)} \tag{131}$$

or

$$k_1\ dA - k_2(AB)\ dA = k_1\ d(AB) \tag{132}$$

Equation (132) is a linear differential equation of the first order, solving the equation for AB in terms of A and k_1/k_2 we have

$$(AB) = k_1/k_2 - (k_1/k_2)\ e^{(-k_1/k_2)\ A} \tag{133}$$

likewise, using Equation (130a and c) the relationship of AB_2 in terms of the rate constants and the concentration of the starting alcohol (A) is

$$(AB_2) = k_1/k_2 - \frac{k_1}{k_3 - k_2}\ e^{-(k_2/k_1)(A)}\ \frac{k_2\ e^{(-k_3/k_1)A}}{k_3(k_3 - k_2)} \tag{134}$$

similarly, $(AB_3, AB_4, \ldots)$ can be obtained.

Application of the least Squares Method to the Arrhenius Equation

The Arrhenius Equation for the reaction velocity constant is

$$k = A\ e^{-E/RT} \tag{39}$$

This equation may be written in the logarithmic form as

$$\ln k = \ln A + E/RT = 0 \tag{135}$$

The method of least squares specifies that the sum of the square of deviations of Equation (135) by a minimum or

$$(\ln k - \ln A + E/RT)^2 = \text{minimum} \qquad (136)$$

Let the left hand side of Equation (136) be represented by φ, then to evaluate the two constants A and E we partial differentiate φ with respect to the two constants and equate the two equations to zero, resulting in two equations in two unknowns.

$$\partial\varphi/\partial A = (\ln k - \ln A + E/RT)(-1/A) = 0 \qquad (137)$$

$$\partial\varphi/\partial E = (\ln k - \ln A + E/RT)(1/RT) = 0 \qquad (138)$$

or

$$\ln A = \frac{\sum_i \ln k + \sum_i E/RT}{i} \qquad (139)$$

$$E = \frac{\sum_i \ln A/RT - \sum_i \ln k/RT}{\sum_i 1/R^2T^2} \qquad (140)$$

where i is the number of experimental observations. From these two equations, the constants A, and E can be readily calculated.

APPENDIX V

EXPERIMENTAL DATA

TABLE XXVI

REACTION VELOCITY CONSTANTS FOR METHANOL-PROPYLENE OXIDE REACTION FROM PROPYLENE OXIDE CONCENTRATION DATA

Run Number	Temp. °C	Mole Ratio methanol/oxide	Cat. Conc. mols/lit.	Time min.	Oxide conc. mols/lit.	k lit./mols.min.
1	35	48.1	0.139	0	0.488	--
				15	0.470	--
				85	0.410	0.0000879
				150	0.357	0.0000894
				205	0.327	0.0000840
				295	0.262	0.0000904
				365	0.228	0.0000895
					average	0.0000884
2	45	38.4	0.172	0	0.595	--
				25	0.489	0.000344
				65	0.380	0.000300
				95	0.314	0.000295
				150	0.216	0.000296
				235	0.142	0.000268
				370	0.075	0.000248
					average	0.000292
3	55	48.8	0.252	0	0.465	--
				11	0.380	0.000806
				30	0.2539	0.000894
				55	0.1569	0.000878
				85	0.0856	0.000885
				131	0.0447	0.000796
					average	0.000852

TABLE XXVII

REACTION VELOCITY CONSTANTS FOR THE DIPROPYLENE GLYCOL METHYL ETHER-PROPYLENE OXIDE REACTION FROM PROPYLENE OXIDE CONCENTRATION DATA

Run Number	Mole Ratio alcohol/oxide	Temp. °C	Cat. Conc. mols/lit.	Time mins.	Oxide conc. mols/lit	k $\frac{\text{lit.}}{\text{mol.min.}}$
1	10	87	0.1764	0	0.573	--
				20	0.487	--
				40	0.364	0.00202
				75	0.240	0.00210
				135	0.172	0.00163
				195	0.089	0.00177
					average	0.00179
2	10	87	0.1764	0	0.573	--
				50	0.340	0.00186
				95	0.218	0.00184
				145	0.129	0.00189
				215	0.050	0.00212
					average	0.00192
3	10	87	0.1764	0	0.573	--
				20	0.495	--
				48	0.352	0.00181
				93	0.215	0.00191
				143	0.124	0.00196
				213	0.049	0.00216
					average	0.00194
4	5	87	0.1764	0	1.102	--
				45	0.683	0.00200
				106	0.342	0.00226
				167	0.160	0.00237
				261	0.050	0.00249
					average	0.00227

TABLE XXVII (CONT'D)

Run Number	Mole Ratio alcohol/oxide	Temp. °C	Cat. Conc. mols/lit.	Time mins.	Oxide conc. mols/lit	k $\frac{\text{lit.}}{\text{mol.min.}}$
5	10	85	0.0556	0	0.578	--
				70	0.491	0.000394
				130	0.410	0.000464
				190	0.340	0.000494
				290	0.288	0.000429
					average	0.000445
6	10	85	0.1109	0	0.576	--
				90	0.341	0.00111
				185	0.246	0.00107
				270	0.109	0.00115
				360	0.057	0.00118
					average	0.00112
7	10	85	0.1109	0	0.576	--
				90	0.347	0.00100
				150	0.246	0.00102
				240	0.169	0.00093
					average	0.00099
8	10	85	0.2207	0	0.573	--
				25	0.388	0.00278
				60	0.252	0.00247
				120	0.121	0.00237
				180	0.048	0.00257
					average	0.00255
9	10	85	0.3295	0	0.570	--
				20	0.379	0.00365
				60	0.165	0.00378
				105	0.068	0.00377
				145	0.027	0.00398
					average	0.00379

TABLE XXVII (CONT'D)

Run Number	Mole Ratio alcohol/oxide	Temp. °C	Cat. Conc. mols/lit.	Time mins.	Oxide conc. mols/lit	k lit./mol.min.
10	10.1	69	0.2746	0	0.575	--
				43	0.438	0.00120
				83	0.373	0.00097
				113	0.306	0.00103
				143	0.256	0.00104
				191	0.183	0.00110
					average	0.00106
11	10	60	0.11378	0	0.391	--
				105	0.529	0.000181
				195	0.474	0.000199
				315	0.427	0.000199
					average	0.000194
12	10	60	0.1195	0	0.599	--
				185	0.478	0.000203
				243	0.420	0.000246
				296	0.399	0.000236
				380	0.377	0.000210
					average	0.000224
13	10	60	0.2227	0	0.583	--
				123	0.360	0.000429
				158	0.323	0.000431
				293	0.220	0.000415
					average	0.000425
14	10	60	0.2264	0	0.588	--
				60	0.469	0.000646
				105	0.441	0.000455
				165	0.390	0.000431
				245	0.302	0.000476
					average	0.000503

TABLE XXVII (CONT'D)

Run Number	Mole Ratio alcohol/oxide	Temp. °C	Cat. Conc. mols/lit.	Time mins.	Oxide conc. mols/lit	k lit./mol.min.
15	10	60	0.3380	0	0.585	--
				60	0.490	0.000506
				140	0.358	0.000612
				270	0.226	0.000624
				360	0.152	0.000671
					average	0.000602
16	10	35	0.1168	0	0.607	--
				350	0.566	0.0000328
				140	0.546	0.0000394
				577	0.547	0.0000297
				1070	0.495	0.0000319
					average	0.0000315
17	10	35	0.2323	0	0.604	--
				60	0.582	--
				210	0.554	0.000681
				315	0.526	0.000723
				735	0.432	0.000768
					average	0.000723
18	10	35	0.3469	0	0.600	--
				120	0.563	0.000878
				180	0.542	0.000950
				315	0.507	0.000897
					average	0.000908

TABLE XXVIII

REACTION VELOCITY CONSTANTS FOR THE TRIPROPYLENE GLYCOL METHYL ETHER-PROPYLENE OXIDE REACTION FROM PROPYLENE OXIDE CONCENTRATION DATA

Run Number	Mole Ratio alcohol/oxide	Temp. °C	Cat. Conc. mols/lit.	Time mins.	Oxide conc. mols/lit	k lit./mols.min.
1	9.25	100	0.1895	0	0.457	--
				14.5	0.307	0.00662
				26.0	0.271	0.00487
				39.0	0.171	0.00566
				57.0	0.114	0.00625
				69.0	0.078	0.00644
					average	0.00597
2	10.25	100	0.1900	0	0.414	--
				9	0.321	0.0067
				19	0.264	0.0057
				29	0.193	0.0064
				62	0.100	0.00568
					average	0.00612
3	7	85	0.05683	0	0.605	--
				45	0.494	0.00108
				130	0.411	0.000728
				190	0.368	0.000635
				305	0.308	0.000539
					average	0.00742
4	7	85	0.11340	0	0.604	--
				30	0.475	0.00193
				90	0.368	0.00134
				150	0.263	0.00138
				270	0.153	0.00129
					average	0.00133

TABLE XXVIII (CONT'D)

Run Number	Mole Ratio alcohol/oxide	Temp. °C	Cat. Conc. mols/lit	Time mins.	Oxide conc. mols/lit	k lit./mols.min.
5	7	85	0.22560	0	0.604	--
				45	0.336	0.00312
				150	0.104	0.00300
					average	0.00306
6	7	85	0.33684	0	0.598	--
				30	0.361	0.00415
				75	0.191	0.00386
				105	0.135	0.00364
				135	0.075	0.00400
					average	0.00386
7	7	60	0.05683	0	0.620	--
				30	0.571	0.000064
				180	0.549	0.000150
				365	0.506	0.000130
				995	0.407	0.000103
				1665	0.336	0.000088
				2480	0.278	0.000078
					average	0.000106
8	7	60	0.11620	0	0.619	--
				575	0.345	0.000326
				840	0.280	0.000229
				1040	0.239	0.000223
				1370	0.181	0.000224
					average	0.000224
9	7	60	0.23114	0	0.616	--
				120	0.474	0.000515
				285	0.342	0.000496
				405	0.267	0.000500
				690	0.150	0.000510
					average	0.000502

TABLE XXVIII (CONT'D)

Run Number	Mole Ratio alcohol/oxide	Temp. °C	Cat. Conc. mols/lit	Time mins.	Oxide conc.. mols/lit	k lit./mols.min.
10	7	60	0.34505	0	0.612	--
				110	0.425	0.00079
				180	0.347	0.00075
				410	0.177	0.00075
					average	0.00076
11	7	45	0.05897	0	0.628	--
				585	0.578	0.000032
				1115	0.543	0.000030
				2100	0.493	0.0000266
				3630	0.436	0.0000234
				4445	0.371	0.0000278
					average	0.0000276
12	7	45	0.1177	0	0.	--
				840	0.511	0.000056
				1110	0.476	0.000057
				2085	0.410	0.000048
				2655	0.343	0.0000535
					average	0.0000536
13	7	45	0.23413	0		--
				300	0.564	0.000081
				1120	0.361	0.000116
				1410	0.304	0.000120
					average	0.000106
14	7	45	0.3495	0	0.620	--
				60	0.600	0.000127
				155	0.543	0.000190
				275	0.489	0.000202
				530	0.386	0.000212
				680	0.343	0.000208
					average	0.000205

TABLE XXIX

REACTION VELOCITY CONSTANTS FOR METHANOL-PROPYLENE OXIDE REACTION IN DIOXANE FROM PROPYLENE OXIDE CONCENTRATION DATA AT 45°C.

Run Number	Mole Ratio Methanol/Oxide	Cat. Conc. Mols/Lit.	Dioxane Conc. Mols/Lit.	Time Mins.	Oxide Conc. Mols/Lit	k $\frac{\text{lit.}}{\text{Mols.Min}}$
1	12.51	0.202	6.90	0	0.677	--
				10	0.645	0.000555
				40	0.585	0.000429
				92	0.445	0.000487
				131	0.390	0.000464
				190	0.305	0.000476
					average	0.000482
2	47.00	0.234	1.988	0	0.437	--
				30	0.395	--
				50	0.329	0.000279
				80	0.282	0.000268
				110	0.222	0.000300
				140	0.191	0.000290
					average	0.000284
3	37.20	0.1839	0.575	0	0.585	--
				20	0.571	--
				50	0.492	0.000157
				80	0.416	0.000197
				100	0.378	0.000202
				140	0.311	0.000209
				170	0.270	0.000211
				225	0.207	0.000215
					average	0.0001985

TABLE XXX

EXPERIMENTAL TIME-COMPOSITION DATA AND PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE REACTION OF PROPYLENE OXIDE WITH A MIXTURE OF METHANOL AND PROPYLENE GLYCOL METHYL ETHER AT 45°C.

Run Number	Mole Ratio Methanol/Oxide	Mole Ratio Monoglycol/Oxide	Cat. Conc. Mols/Lit	Time Mins.	Oxide Conc. Mols/Lit	$(2.303)\frac{1}{t}\log\frac{B_o}{B}$
1	12.85	11.35	0.183	0	0.574	--
				10	0.542	0.00537
				30	0.475	0.00622
				65	0.393	0.00583
				95	0.305	0.00666
				170	0.213	0.00580
2	11.28	7.78	0.2125	0	0.765	--
				10	0.687	0.01043
				20	0.625	0.01117
				40	0.539	0.00868
				70	0.435	0.01271
				100	0.323	0.00859
				130	0.288	0.00751
				160	0.243	0.00714
3	8.62	12.25	0.1295	0	0.608	--
				15	0.574	0.00389
				30	0.518	0.00530
				60	0.479	0.00398
				100	0.407	0.00405
				150	0.362	0.00346
				205	0.293	0.00355
4	6.67	13.50	0.266	0	0.583	--
				20	0.536	0.00412
				53	0.434	0.00560
				91	0.331	0.00622
				113	0.292	0.00610
				143	0.236	0.00633

TABLE XXX (CONT'D)

Run Number	Mole Ratio Methanol/Oxide	Mole Ratio Monoglycol/Oxide	Cat. Conc. Mols/Lit	Time Mins.	Oxide Conc. Mols/Lit	$(2.303)\frac{1}{t}\log\frac{B_o}{B}$
5	11.86	12.70	0.1755	0	0.547	--
				20	0.494	0.00183
				43	0.385	0.00813
				81	0.342	0.00580
				111	0.262	0.00684
				136	0.218	0.00679
6	35.20	4.12	0.1625	0	0.517	--
				20	0.444	0.00762
				40	0.376	0.00797
				80	0.275	0.00541
				100	0.246	0.00484
7	16.00	9.47	0.190	0	0.596	--
				15	0.524	0.00875
				50	0.414	0.00730
				75	0.344	0.00735
				105	0.272	0.00746
				127	0.238	0.00721
8	16.00	9.47	0.190	0	0.597	--
				8	0.549	0.01020
				23	0.498	0.00795
				37	0.446	0.00781
				56	0.401	0.00707
				90	0.312	0.00712
				126	0.237	0.00735
9	32.70	4.06	0.176	0	0.548	--
				5	0.528	0.00783
				25	0.453	0.00760
				45	0.384	0.00788
				69	0.320	0.00778
				93	0.270	0.00755

APPENDIX VI

SAMPLE CALCULATIONS

A. Single Reactions

In the following sample calculations, the steps involved in the conversion of experimental raw data to the final rate constants are presented. The raw data used here were taken from Run 1 of the reaction of tripropylene glycol ether with propylene oxide (see Table XXVIII).

TABLE XXXI

RAW DATA FROM RUN 1 OF THE REACTION OF TRIPROPYLENE GLYCOL ETHER WITH PROPYLENE OXIDE AT 100°C. AND A STARTING MOLE RATIO OF ALCOHOL TO OXIDE OF 9.25/1

Reactor Charge

Tripropylene Glycol Ether	248.3 grams
Propylene Oxide	8.33 grams
NaOH	2.08* grams
Total Charge	258.63 grams

Reactor Temperature °C	Time Minutes	$Na_2S_2O_7$ used per sample, c.c
100.1	0	
99.9	1	
100.0	14.5	102.0
100.1	26.0	102.5
100.2	39.0	103.9
100.0	57.0	104.7
100.0	69.0	105.2

* Dissolved in the glycol-ether.

For this particular run, the weight of each sample was 0.94 grams and 25 c.c. of the periodic-perchloric reagent was used (see analytical methods in page 81). The blank titration of 25 c.c. of this periodic-perchloric reagent corresponded to 106.3 c.c. of the sodium thiosulfate solution used. The normality of the thiosulfate titrant was 0.149 N.

The amount of propylene oxide in the sample may now be calculated from Table XXXI. The differences of the amount of thiosulfate solution used in the blank and that used on the sample, properly adjusted by the correction factor in Table XXIV, is a measure of the propylene oxide content of the sample.

Conversion of the number of c.c of sodium thiosulfate to grams of propylene oxide may be effected by the following relationship:

$$(\text{c.c. } Na_2S_2O_7)(\text{Normality}) = \text{Milli-equivalents} \qquad (141)$$

$$\frac{\text{grams propylene oxide}}{\text{milli-equivalents}} = \frac{58.08}{2000} = 0.002904 \qquad (142)$$

Table XXXII gives the result of the calculation for the concentration of propylene oxide in the samples reported in Table XXXI.

TABLE XXXII

RESULTS FROM THE CONVERSION OF c.c. $Na_2S_2O_7$ TO MOLES PER LITER OF PROPYLENE OXIDE FOR THE DATA IN TABLE XXXI.

Time Mins.	$Na_2S_2O_7$ (c.c. Blank - c.c. for Sample)	Propylene Oxide Moles per Liter.
0		0.457
14.5	4.3	0.307
26.0	3.8	0.271
39.0	2.4	0.171
57.0	1.6	0.114
69.0	1.1	0.078

The time-composition data of propylene oxide shown in Table XXXII can now be used to calculate the specific rate constant according to Equation (38a).

$$k = \frac{1}{t\ (C_{A_o} - C_{B_o})} \ln \frac{C_{A_o}\ \ C_B}{C_{A_o}\ \ C_B} \qquad (38a)$$

The results of the calculation are tabulated in Table XXXIII.

TABLE XXXIII

RESULTS OF THE CALCULATION FOR THE SPECIFIC REACTION VELOCITY CONSTANT USING THE DATA IN TABLE XXXII

Time Minutes	C_A, Triglycol Moles per Liter	C_B, Oxide Moles per Liter	k_3 Liter Moles^{-1}Min.
0	4.22	0.457	--
14.5	4.07	0.307	0.0066
26.0	4.04	0.271	0.00487
39.0	3.94	0.171	0.00566
57.0	3.88	0.114	0.00625
69.0	3.85	0.078	0.00644

B. Product Distributions

In the case when the distribution constants are to be calculated from experimental distribution data, the calculational steps involve a successive approximation of the distribution constants until the calculated product distribution matches the experimental results. On the other hand, if the values of the distribution constants are already known, the product distribution maybe immediately calculated using Equations (111)(114) and (126). The calculations, although a bit tedious, are straightforward. In Figure 19, calculated product distrubution results using Equation (114) and various values of c (c = 1, 0.5 and 0.10) are plotted.

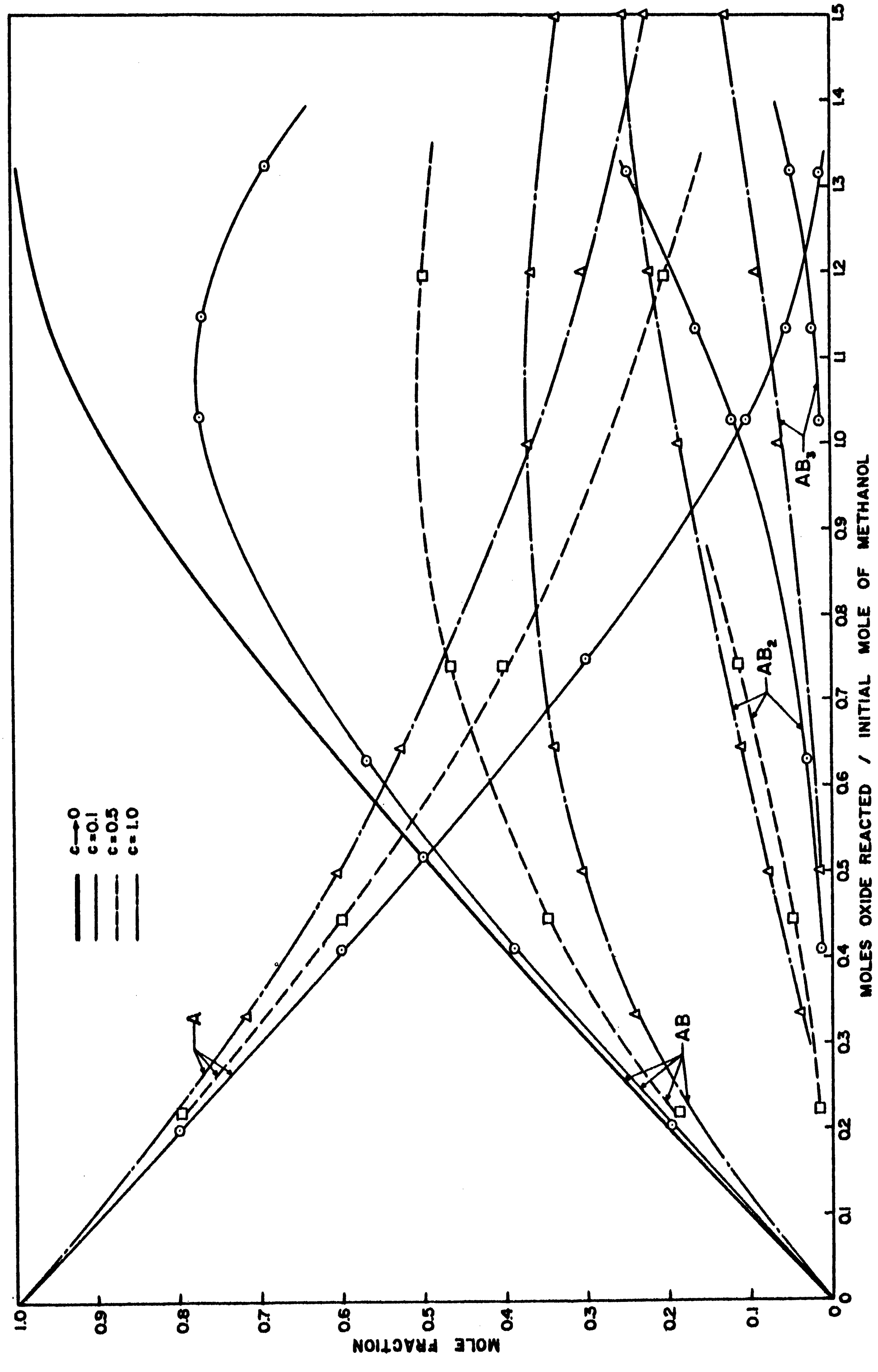


Figure 19. Calculated Product Distribution Curves (C = 1, 0.5 and 0.10).

BIBLIOGRAPHY

1. Abel, E. Z., Physik Chem., 56, 558 (1906).

2. Amis, E. S., "Kinetics of Chemical Change in Solution", pp. 19-89, 178-197; 234-265; Macmillan, 1949.

3. Barlett, P. D., Ross, S. D., J. Am. Chem. Soc., 70, 926-929 (1948).

4. Bell, R. P., "Acid Base Catalysis", Oxford University Press, (1941)

5. Bell, R. P., "Annual Reports on the Progress of Chemistry", The Chemical Society, 1939.

6. Benham, A., Kurata, F., J. Am. Inst. Chem. Engr., 1, 118 (1956).

7. Boyd, D. R., Marle, E. R., J. Chem. Soc., 105, 2117 (1914).

8. Branch, G. E., Calvin, M., "The Theory of Organic Chemistry", pp. 183-269; 393-443, Prentice Hall, 1941.

9. Bronsted, J. N., Kilpatrick, M., J. Am. Chem. Soc., 51, 428 (1929).

10. Carbide and Carbon Chemicals Corporation, New York, Catalog, "Ethers and Oxides" (1956).

11. Chitwood, H. C., Freure, B. J., J. Am. Chem. Soc., 68, 680 (1946).

12. Culvenor, C. C., Davies, W., Heath, N. S., J. Am. Chem. Soc., 71, 278 (1949).

13. Davis, P. C., Von Waaden, C. E., Kurata, F., Chem. Eng. Prog. Symposium Series, 48, 91 (1951).

14. Debye, P., Huckel, E., Physik Z., 24, 185 (1923).

15. Deckert, W., Z. Anal. Chem., 82, 297 (1930); 109, 166 (1937).

16. Dow Chemical Co., Midland, Mich., Catalog, "Dowanols" (1949).

17. Eastham, A. M., Latremouille, G. A., Can J. Research, B28, 264 (1950).

18. Eastham, A. M., J. Chem. Soc., 1952 (1936).

19. Elderfield, R. C., "Heterocyclic Compounds", Chap. I, "Ethylene and Trimethylene Oxides" by S. Winstein and R. B. Henderson, John Wiley, New York, 1950.

20. Ellis, Carleton, "Chemistry of Petroleum Derivatives", Vol. I, p. 537, Chemical Catalog Co., New York, 1947.

21. Evans, D. P., Jenkins, H. O., Trans. Faraday Soc., 36, 818 (1940).

22. Fleury, P. F., Boisson, R., J. Pharm. Chim., 30, 145, 307, (1939).

23. Flory, P. J., J. Am. Chem. Soc., 62, 1561 (1940).

24. Flory, P. J., "Principles of Polymer Chemistry", pp. 69-102; 317-345, Cornell University Press, New York, (1953).

25. Frost, A. A., Pearson, R. G., "Kinetics and Mechanism", pp. 113-146; 191-223; 243-256, John Wiley, New York, 1953.

26. Fuoss, R. M., J. Am. Chem. Soc., 65, 2406 (1943).

27. Glasstone, S., Laidler, K. J., Eyring, H., "The Theory of Rate Processes", pp. 400-476, McGraw Hill, New York, (1941).

28. Grisby, W. E., Hind, J., Chanley, J., Westheimer, F. H., J. Am. Chem. Soc., 64, 2606 (1942).

29. Guggenheim, E. A., "Mixtures", Oxford University Press, (1952).

30. Hammett, L. P., "Physical Organic Chemistry", McGraw Hill, New York, (1940).

31. Harned, H. S., Samaras, N. N. T., J. Am. Chem. Soc., 54, 9 (1932).

32. Ingold, C. K., "Structure and Mechanism in Organic Chemistry", pp. 206-418; 722-750, Cornell University Press, New York, (1953).

33. Kadesch, R. G., J. Am. Chem. Soc., 68, 41 (1945).

34. Kerchov, F. W., Z. Anal. Chem., 108, 249 (1937).

35. King, G., Nature, 164, 706 (1949).

36. Kirkwood, J. G., J. Chem. Phys., 2, 351 (1934).

37. Knorre, D. G., Emmanuel, D. M., Uspekhii Khim., 24, 275 (1955).

38. Laidler, K. J., "Chemical Kinetics", pp. 111-144, McGraw Hill, New York, 1950.

39. Laidler, K. J., Eyring, H., Ann. N. Y. Acad. Sci., 39, 303 (1940).

40. Landskoener, P. A., Ph.D. Thesis, The Catholic University of America, (1954).

41. Lichtenstein, H. J., Twigg, G. H., Trans. Faraday Soc., 44, 905 (1948).

42. Long, F. A., Pritchard, J. G., J. Am. Chem. Soc., 78, 2663 (1956).

43. Lubatti, O. F., J. Soc. Chem. Ind., 51, 361T (1932).

44. Lubatti, O. F., J. Soc. Chem. Ind., 54, 424T (1935).

45. Lutskii, A. E., Sbornik Statei po Obshchei Khim., Acad. Nauk, (U. S.S.R.) 2, 1202 (1953).

46. Maget, H., CM 210 report, University of Michigan, 1956.

47. Martin, F., Fuchs, O. Z., Elektrochem., 27, 150 (1921).

48. Matignon, C., Moureau, H., Dode, M., Bull. Soc. Chim. France, (5) 1, 1308 (1934).

49. Miller, S. A., Bann, B., Thrower, R. D., J. Chem. Soc., 3623 (1950).

50. Mitchell, J., "Organic Analysis", vol. 1, Interscience, New York, 1953.

51. Moelwyn-Hughes, E. A., "The Kinetics of Reactions in Solution", pp. 183-252, Oxford University Press, (1952).

52. Mueller, C. R., J. Chem. Phys., 28, 846 (1958).

53. National Bureau of Standards, "Table of Dielectric Constants of Pure Liquids", Circular 514 (1951).

54. Natta, G., Mantica, E., J. Am. Chem. Soc., 74, 3152 (1952).

55. Natta, G., Simonetta, M., Rend. Inst. Lombardo Sci., 78, 336 (1944-5).

56. Patat, F., Cremer, E., Bobleter, O., Monatsh., 83, 322 (1952).

57. Pecorini, H. A., Ph.D. Thesis in Chemical Engineering, University of Michigan, (1953).

58. Pecorini, H. A., Banchero, J. T., Ind. Eng. Chem., 48, 1287 (1956).

59. Petrov. A. A., J. Gen. Chem., (U.S.S.R.), 14, 1038 (1944).

60. Potter, C., Macdonald, W. C., Can J. Research, 25B, 415 (1947).

61. Prigogine, I., "The Molecular Theory of Solutions", North Holland Publishing Co., 1957.

62. Pritchard, J. G., Long, F. A., J. Am. Chem. Soc., 78, 2667 (1956).

63. Reeve, W., Sadle, A., J. Am. Chem. Soc., 72, 1251 (1950).

64. Roithner, G., Monathsh., 15, 674 (1894).

65. Ross, W. C., J. Chem. Soc., 2257 (1950).

66. Satkowski, W. B., Hsu, C. G., Ind. Eng. Chem., 49, 1875 (1957).

67. Scatchard, G., Chem. Revs., 10, 229 (1932).

68. Smyth, C. P., "Dielectric Behavior and Structure", p. 79, McGraw Hill, 1955.

69. Spark, C. E., Nelson, R. E., J. Am. Chem. Soc., 58, 671 (1936).

70. Schwab, G. M., Editor, "Handbuch Der Katalyse", Bnad II Katalyse in Losungen, Springer Vienna, (1940).

71. Swan, J. D., Anal. Chem., 26, 879 (1954).

72. Swern, D., Billen, G. N., Knight, H. B., J. Am. Chem. Soc., 71, 1152 (1949).

73. Swern, D., Findley, T. W., Billen, G. N., Scanlan, J. T., Anal. Chem., 19, 414 (1947).

74. Todd, F., Ind. Eng. Chem., Anal. Edit., 17, 175 (1945).

75. Warner, J. C., Svirbely, W. J., J. Am. Chem. Soc., 57, 1883 (1935).

76. Weibull, B., Nycander, B., Acta Chemica Scand., 8, 847 (1954).