REPORT NO. RK-TR-63-20

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KINETICS OF EPOXIDE-CARBOXYLIC ACID REACTION

26 August 1963

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KINETICS OF EPOXIDE-CARBOXYLIC ACID REACTION

by

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Department of Army Project No. 517-06-002

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Redstone Arsenal, Alabama

ABSTRACT

The kinetics of the addition reactions of four structurally different epoxide compounds with glacial acetic acid in dioxane solution have been studied at 90°C, 110°C, and 125°C. The relative order of reactivity of the epoxides is styrene oxide > vinyl cyclohexane monoxide > allyl 9, 10-epoxy stearate > 1,2-epoxy-3-phenoxy propane. The reactions apparently follow the first-order-rate law with respect to epoxide and acid concentrations. For the four epoxides whose rates were determined, $\log_{10}k$ was found to increase linearly with 1/T according to the Arrhenius equation.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Concluded)

KINETICS OF EPOXIDE-CARBOXYLIC ACID REACTION

I. INTRODUCTION

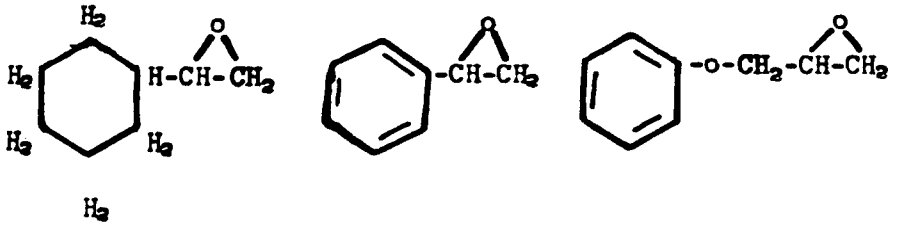
The rapid growth of epoxide compounds into areas other than the protective coating field has directed considerable attention to a field of chemistry in which there has been a real lack of published data. This is particularly true in the field of solid propellant binder systems where a wide variety of epoxide compounds are available for use as curing agents. This interest in epoxide compounds in the area of propellant binder systems has emphasized a fundamental need for additional information on the reactivity of epoxides as well as a simplified method for obtaining kinetic data on reactions involving these materials. This report is concerned with a study of the fundamental nature of these reactions.

Relatively little work in this field was reported prior to 1950; and in most cases, little or no speculation was made concerning the kinetics of these reactions. The most significant work prior to 1950 was reported by Brönsted, Kilpatrick, and Kilpatrick (Reference 1). Brönsted, et al. investigated the hydrolysis of ethylene oxide in dilute aqueous solution of acids. On the basis of their studies, the authors concluded that the reactions lead to the 1,2-glycols and follow the first-order-rate law, in which the specific rate constant, k_1, is directly proportional to the hydrogen ion concentration.

The most recent work in this field has been reported by Shechter, Wynstra, and Kurkjy (References 2,3, and 4) in which the addition reactions of glycidyl ethers with acids, phenols, and alcohols were studied. The authors reported that under condition of base catalyzed reactions the order of reactivity is alcohol > phenol > acid.

The object of the present work was to study quantitatively the addition reactions of four structurally different epoxides--vinyl cychohexane monoxide (I), styrene oxide (II), 1,2-epoxy, 3-phenoxy propane (III), and Allyl 9, 10-epoxy stearate (IV)-

with glacial acetic acid to obtain a quantitative comparison of the effects of structure and temperature on the reactivities of the epoxide compounds.



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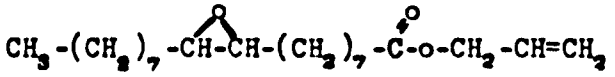

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A. Chemicals

Vinyl cyclohexane monoxide and styrene oxide (98 and 99%) purity by epoxide analysis, supplied by Union Carbide Chemical Company, were used as received. Allyl 9,10-epoxy stearate was a carefully refractionated Union Carbide commercial product. Glacial acetic acid (99.5% purity) and 1,2-epoxy-3-phenoxy propane (99%), supplied by Fisher Scientific Company, were used as received. The dioxane, used as the solvent in the reaction, was purified by the conventional method of refluxing over sodium followed by distillation.

B. Experimental

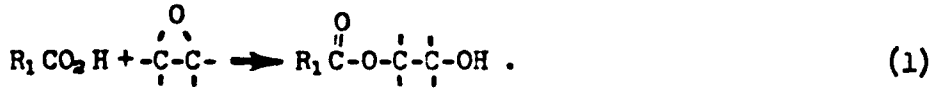
The general experimental method consisted of holding a given set of reactants at a predetermined temperature, sampling frequently, and determining the amount of epoxide remaining at regular time intervals. More specifically, the analysis was carried out as follows: Equimolar quantities of glacial acetic acid and epoxide were weighed separately and diluted to volume with dioxane. The two solutions were then combined and mixed thoroughly. Carefully measured 10-milliliter aliquots of the reaction mixture were placed in 20 x 150 millimeter test tubes which had previously been drawn to a narrow neck for convenience in sealing. After addition of the mixture, the tubes were evacuated, cooled in liquid nitrogen, and sealed with a flame. The sealed samples were allowed to warm to room temperature and then

placed in constant temperature baths, carefully regulated at 90 ± 0.1°, 110±0.1°, and 125± 0.1°C. The reaction was followed by withdrawing samples at regular time intervals, depending on the reaction rate, and titrating the epoxides remaining in the sealed tube with standard hydrogen bromide solution. Crystal violet was used as an indicator.

II. RESULTS AND DISCUSSION

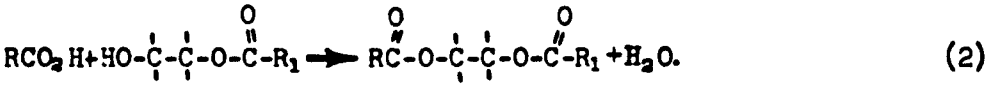
Theoretically, the following epoxide-carboxylic acid reactions are possible.

A. Reaction of the carboxyl group with the epoxide to form a monoester and a hydroxyl group:



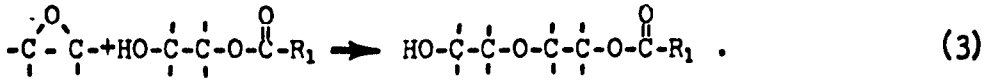
(1)

B. Reaction of the carboxyl group with the newly formed hydroxyl group to form a diester with the elimination of water:



(2)

C. Reaction of the epoxide with the hydroxyl group without the elimination of water:



(3)

This sequence of reactions was investigated by using vinyl cyclohexane monoxide as a model epoxide. Equimolar quantities of the epoxide and glacial acetic acid (1 molar in dioxane) were thoroughly mixed and placed in a constant temperature bath, regulated to 110° ± 1°C for 7 days. Aliquots of the reaction mixture were withdrawn at regular time intervals and the absorption spectra recorded.

The following changes in the absorption were noted: A significant increase in absorption at 3450 cm^{-1}, which can be assigned to the hydroxyl group. Accompanying this increase was a significant decrease in absorption at 1235 cm^{-1}, which can be assigned to the epoxide group. A simultaneous decrease in the absorption at 1724 cm^{-1} and an increase in the absorption at 1198 cm^{-1} which can be associated with the disappearance of the carboxylic acid groups and the formation of the monoester groups, respectively.

To support the above observations, quantitative data on the reaction products of vinyl cyclohexane monoxide and acetic acid were obtained. The reaction mixture was carefully vacuum-distilled and the following fractions were obtained:

(1) b.p. 25-30°/17 mm
(2) b.p. 31-35°/17 mm
(3) b.p. 72-75°/17 mm

Fraction (1) consisted essentially of acetic acid and dioxane, while (2) was identified by epoxide analysis to be largely unreacted epoxide. The greater part of fraction (3) boiled at 74°/17 mm and gave a negative oxerane test. Fraction (3) was further concentrated at 73-74°/17 mm and identified as 2-acetoxy-2-cyclohexyl ethane-1-ol by alkaline hydrolysis saponification equivalent (186), hydroxyl group determination by acetylation in pyridene followed by titrating the excess anhydride after hydrolysis (9.15%), and molecular weight determination by the freezing point depression of cyclohexanol (184).

The results of holding equimolar amounts of 1,2-epoxy-3-phenoxy propane, allyl 9,10-epoxy stearate, vinyl cyclohexane monoxide, styrene oxide, and glacial acetic acid at 90° and 110° C are shown in Figures 1 and 2, respectively. A comparison of the slopes of these rate curves indicate that the order of reactivity is styrene oxide > vinyl cyclohexane monoxide > allyl-9, 10 epoxy stearate > 1,2-epoxy-3-phenoxy propane. This decreasing order of reactivity shows that the rates of epoxide-carboylic acid reactions are influenced significantly by the nature of the epoxide substituents.

The order of reactivity may be explained by assuming that the reaction proceeds through a carbonium ion intermediate complex. Addition of a proton to the oxirane oxygen to form an intermediate complex results subsequently in the rupture of the carbon-oxygen bond with the formation of a carbonium ion:

$$-CH\overset{O}{\diagdown}CH_2 + H^{\oplus} \longrightarrow -CH\overset{OH^{\oplus}}{\diagdown}CH_2 \longrightarrow -CHOH-\overset{\oplus}{C}H_2 \quad \text{. Slow} \qquad (4)$$

Attack of the carbonium ion by an acid:

$$-CHOH-\overset{\oplus}{C}H_2 + \overset{\oplus}{H}\overset{\ominus}{A_c} \longrightarrow -CHOH-CH_2A_c + H^{\oplus} \text{. Fast} \qquad (5)$$

If the ring opening reaction (4) is the rate determining step, the relative order of reactivity of the epoxide compounds shown in Figures 1 and 2 is dependent upon the relative ease of

formation of the carbonium ion. In the case of styrene oxide, the addition of a proton to form the intermediate complex is favored by the close proximity of the aromatic and oxirane oxygen rings, resulting in resonance stabilization of the carbonium ion intermediate. While in the case of 1,2-epoxy-3-phenoxy propane, where no appreciable reaction occured at 90° C, apparently the ether linkage to which the phenyl group is attached acts as an electron withdrawing force resulting in decreased reactivity toward the proton.

Kinetic treatment of the data given in Figures 1 and 2 indicates that the reactions follow the first-order-rate law with respect to the epoxide and acid to approximately one-half lives. A representative plot is shown in Figure 3. If the rate determining step is that shown in Equation 4, then the kinetics would follow the expression:

$$-\frac{dC}{dt} = k \left[H^{+} \right] \left[-\overset{|}{C} \overset{O}{\diagup\diagdown} C \langle \right] \qquad (6)$$

An examination of the results shown in Table I, indicates that the kinetics of the reaction apparently follow this expression.

For the four epoxides whose rates were determined, $\log_{10} k$ was found to increase linearly with 1/T according to the Arrhenius equation:

$$k = PZ\, e^{-E_a/RT} \qquad (7)$$

where:

- k = specific rate constant in sec^{-1}
- PZ = the probability collision factor
- E_a = the activation energy
- R = the molar gas constant
- T = temperature in degrees absolute

The excellent straight line agreement of the experimental point given in Figure 3 appears to conclusively establish the first-order kinetics.

To test the mechanism postulated by Equations 4 and 5, the effect of carboxylic acids of higher strength (K_i) on the rate of reaction was investigated at 125°C. Equimolar quantities of 1,2-epoxy-3-phenoxy propane and benzoic acid in one case and monochloroacetic acid in another were investigated

in dioxane solution. An examination of the results summarized in Table V and Figure 5 indicate that as the available protons are increased, a corresponding increase in the rate of reaction is observed. These data lend substantial support to the carbonium ion intermediate complex concept.

The activation energies (E_a) given in Table I were obtained by plotting the logarithms of the specific rate constants determined at the experimental temperatures against the reciprocal of the absolute temperature according to Equation 7. The slope of the line (Figure 4) is equal to -Ea/R and the intercept is the logarithm of PZ, the probability collision factor.

The activation energies, (E_a) shown in Table I, vary in the manner predicted by the carbonium ion intermediate complex. The activation energies vary in the manner determined by the relative ease of formation of the carbonium ion intermediate. In the case of styrene oxide where resonance stabilization of the carbonium ion is possible, the rate of reaction is approximately 10-fold faster than 1,2-epoxy-3-phenoxy propane where resonance stabilization of the intermediate complex is unlikely.

A. Heat and Entropy of Activation

The Arrhenius parameters, heat and entropy of activation, are related to the specific rate constant by the expression:

$$k = K'T\, e^{\frac{\Delta S^{\ddagger}}{R}} \cdot e^{-\frac{\Delta H^{\ddagger}}{RT}} \qquad (8)$$

where K' is equal to k/h--the Boltzmann and Planck constants respectively, T, the temperature in degrees absolute; $\Delta S^{\ddagger}$, the entropy of activation, and $\Delta H^{\ddagger}$, the enthalpy of activation. The enthalpy or heat of activation is a quantity closely related to the experimental energy of activation by the expression:

$$\Delta H^{\ddagger} = \Delta E_a - nRT \qquad (9)$$

The small difference in the entropy and heat of activation for each compound as shown in Tables II, III, and IV suggests that the reaction product disbribution will not vary significantly with temperature. The large negative entropy values are indictive of the large decrease of entropy accompanying the formation of the activated complex.

B. Base Catalyzed Epoxide-Carboxylic Acid Reactions

The data presented in Table I indicate that the epoxide-carboxylic acid reactions are rather sluggish and an appreciable interval of time is required to reach the reaction half-life. Tertiary amines and amine salts represent an important class of catalyst for the epoxide-carboxylic acid reactions.

To investigate the effect of a quantary ammonium salt on the reaction rate, cetyl dimethyl benzyl ammonium chloride was added to the reaction mixtures of equimolar amounts of 1,2-epoxy-3-phenoxy propane and glacial acetic acid in dioxane solution. Kinetic studies were made at several different concentrations of cetyl dimethyl benzyl ammonium chloride. The results of this study are summarized in Table VI and Figure 6. These data indicate that the reaction proceeds more rapidly when the quaternary ammonium salt is added to the reaction mixture. A measure of the catalyzing effect of the quaternary ammonium chloride on epoxide-carboxylic acid reactions is given by Table VI. Non-catalyzed, the reaction half-life is approximately 53 days, while in the presence of 0.10 mole/liter of cetyl dimethyl benzyl ammonium chloride the reaction half-life is reduced to less than 3 hours. These data indicate that the base catalyzed reaction is apparently first order with respect to the epoxide concentration.

III. SUMMARY

The kinetics of the addition reaction of four structurally different epoxides compounds with carboxylic acids in dioxane solution have been investigated at 90°, 110°, and 125°C. The relative order of reactivity of the epoxides with glacial acetic acid is styrene oxide > vinyl cyclohexane monoxide > allyl 9.10-epoxy stearate > 1,2-epoxy-3-phenoxy propane. A reaction mechanism for these reactions was postulated. The experimental data indicated that the rate of reaction is determined to a large extent by relative ease of formation of the carbonium ion intermediate complex.

The Arrhenius parameters: energy, heat, and entropy of activation were determined and correlated with the structure of the epoxide compounds.

Kinetic treatment of the experimental data indicated the epoxide-carboxylic acid reaction apparently follow the first-order-rate law.

The second phase of this investigation will make use of these data in the study of the cure reactions of the PBAA-ERL binder system.

Table I

RATE CONSTANTS AND ARRHENIUS ACTIVATIONS ENERGIES
FOR EPOXIDES - ACETIC ACID REACTIONS IN DIOXANE

Compound	$10^7 k\ sec^{-1}$			E_a kcal
	90°C	110°C	125°C	
1,2-epoxy-3-phenoxy propane	1.50	2.73	5.49	11.04
Allyl 9,10-epoxy stearate	4.18	7.17	15.80	10.99
Vinyl cyclohexane monoxide	6.87	14.95	23.20	10.05
Styrene oxide	13.64	27.50	48.20	10.29

Table II

RATE CONSTANTS AT 90°C, ENERGIES, HEATS AND ENTROPIES OF ACTIVATIONS
FOR EPOXIDE-ACETIC ACID REACTIONS IN DIOXANE

Compound 90°C	$10^7 k\ sec^{-1}$	$\Delta H^{\ddagger}$ kcal	$\Delta S^{\ddagger}$ E. U.	E_a kcal
1,2-epoxy-3-phenoxy propane	1.50	10.32	-61.74	11.04
Allyl 9,10-epoxy stearate	4.18	10.26	-59.86	10.99
Vinyl cyclohexane monoxide	6.87	9.33	-61.44	10.05
Styrene oxide	13.64	9.57	-59.42	10.29

Table III

RATE CONSTANTS AT 110°C, ENERGIES, HEATS AND ENTROPIES OF ACTIVATIONS FOR EPOXIDE - ACETIC ACID REACTIONS IN DIOXANE

Compound 110°C	$10^7 k\ sec^{-1}$	$\Delta H^{\ddagger}$ kcal	$\Delta S^{\ddagger}$ E.U.	E_a kcal
1,2-epoxy-3-phenoxy propane	2.73	10.28	-62.25	11.04
Allyl 9,10-epoxy stearate	7.17	10.22	-60.47	10.99
Vinyl cyclohexane monoxide	14.95	9.29	-61.44	10.05
Styrene oxide	27.50	9.53	-59.61	10.29

Table IV

RATE CONSTANTS AT 125°C, ENERGIES, HEATS AND ENTROPIES OF ACTIVATIONS FOR EPOXIDE - ACETIC ACID REACTIONS IN DIOXANE

Compound 125°C	$10^7 k\ sec^{-1}$	$\Delta H^{\ddagger}$ kcal	$\Delta S^{\ddagger}$ E.U.	E_a kcal
1,2-epoxy-3-phenoxy propane	5.49	9.64	-61.97	11.04
Allyl 9,10-epoxy stearate	15.80	10.20	-60.01	10.99
Vinyl cyclohexane monoxide	23.20	9.26	-61.59	10.05
Styrene oxide	48.20	9.50	-59.53	10.29

Table V

CARBOXYLIC ACIDS - 1,2-EPOXY-3-PHENOXY PROPANE
REACTION RATES AT 125°C

Acid	10^3k Hrs^{-1}	T. ½ Hr.
Acetic (Glacial)	1.98	350.6
Benzoic	5.10	135.9
Monochloroacetic	34.10	20.32

Table VI

EFFECT OF ADDED CETYL DIMETHYL BENZYL AMMONIUM CHLORIDE
ON THE REACTION HALF-LIFE OF 1,2-EPOXY-3-PHENOXY
PROPANE AND GLACIAL ACETIC ACID AT 90°C

Catalyst Mole Liter	10^4k Hrs^{-1}	T. ½, Hr.
0.0	5.40	1283.3
0.0339	829.1	8.36
0.0507	1512.0	4.583
0.1012	2379.6	2.9123

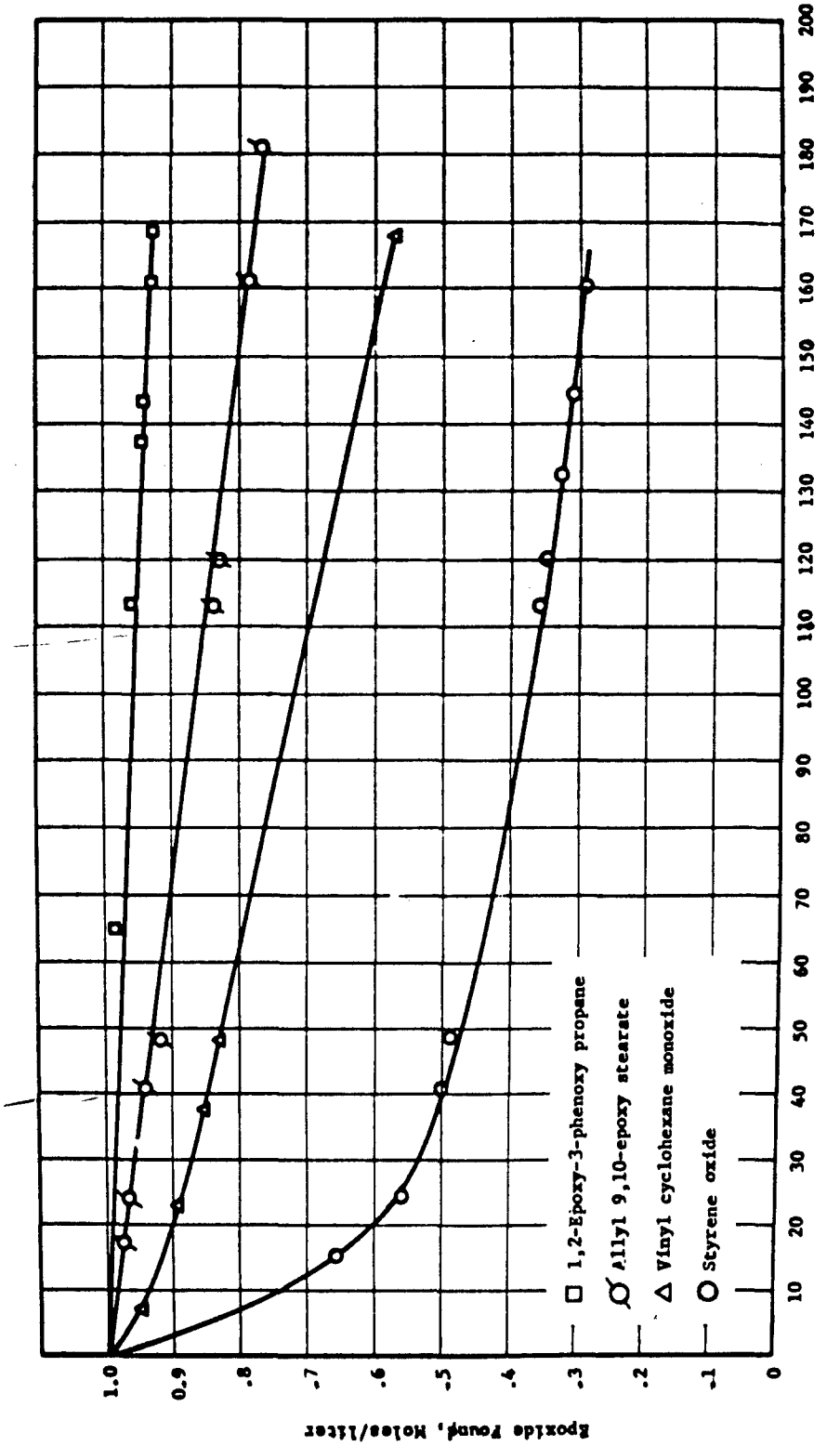


Figure 1. COMPARISON OF EPOXIDE—ACETIC ACID REACTIONS AT 90°C

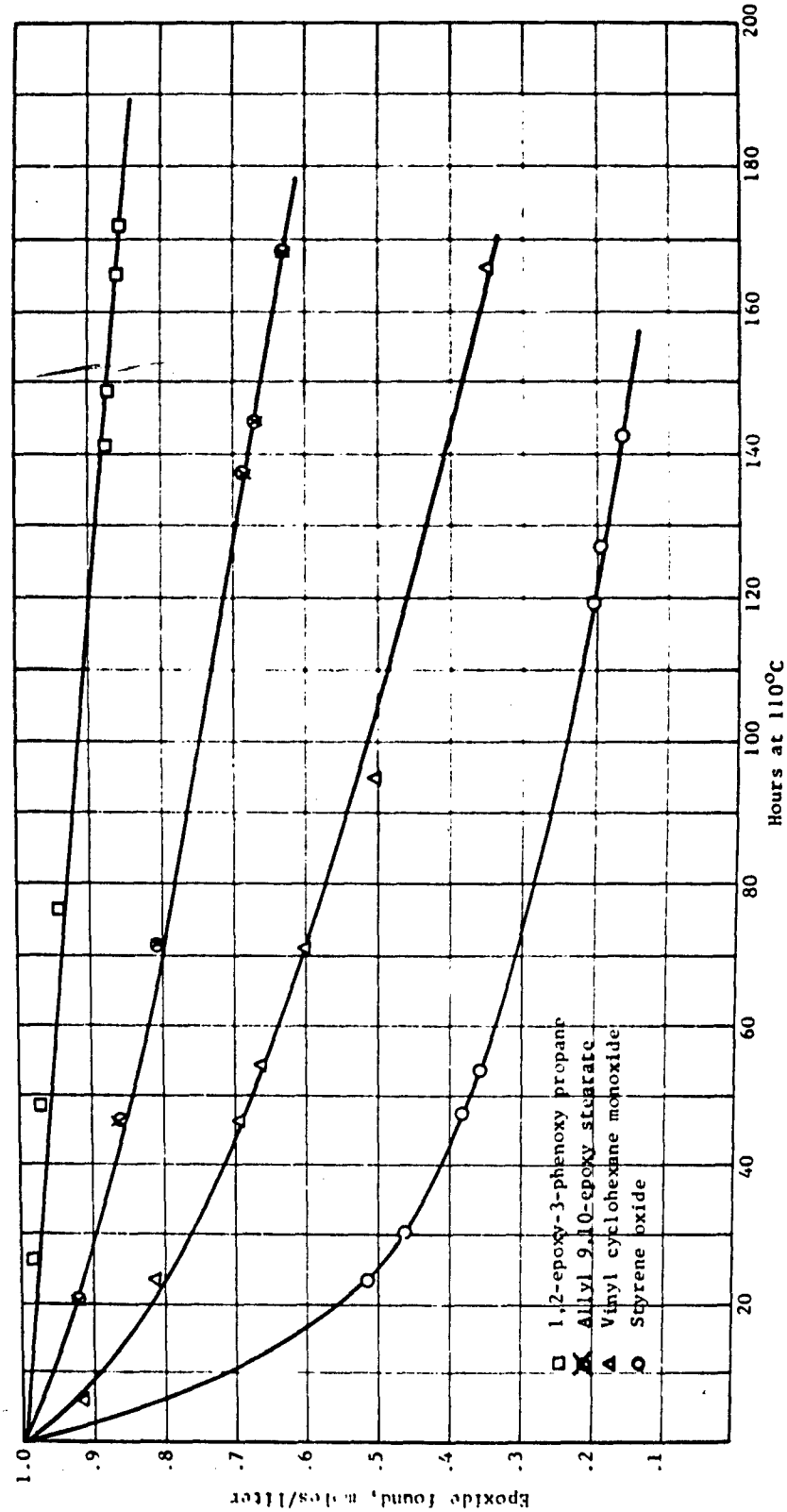


Figure 2. COMPARISON OF EPOXIDE REACTIONS WITH ACETIC ACID at 110°C

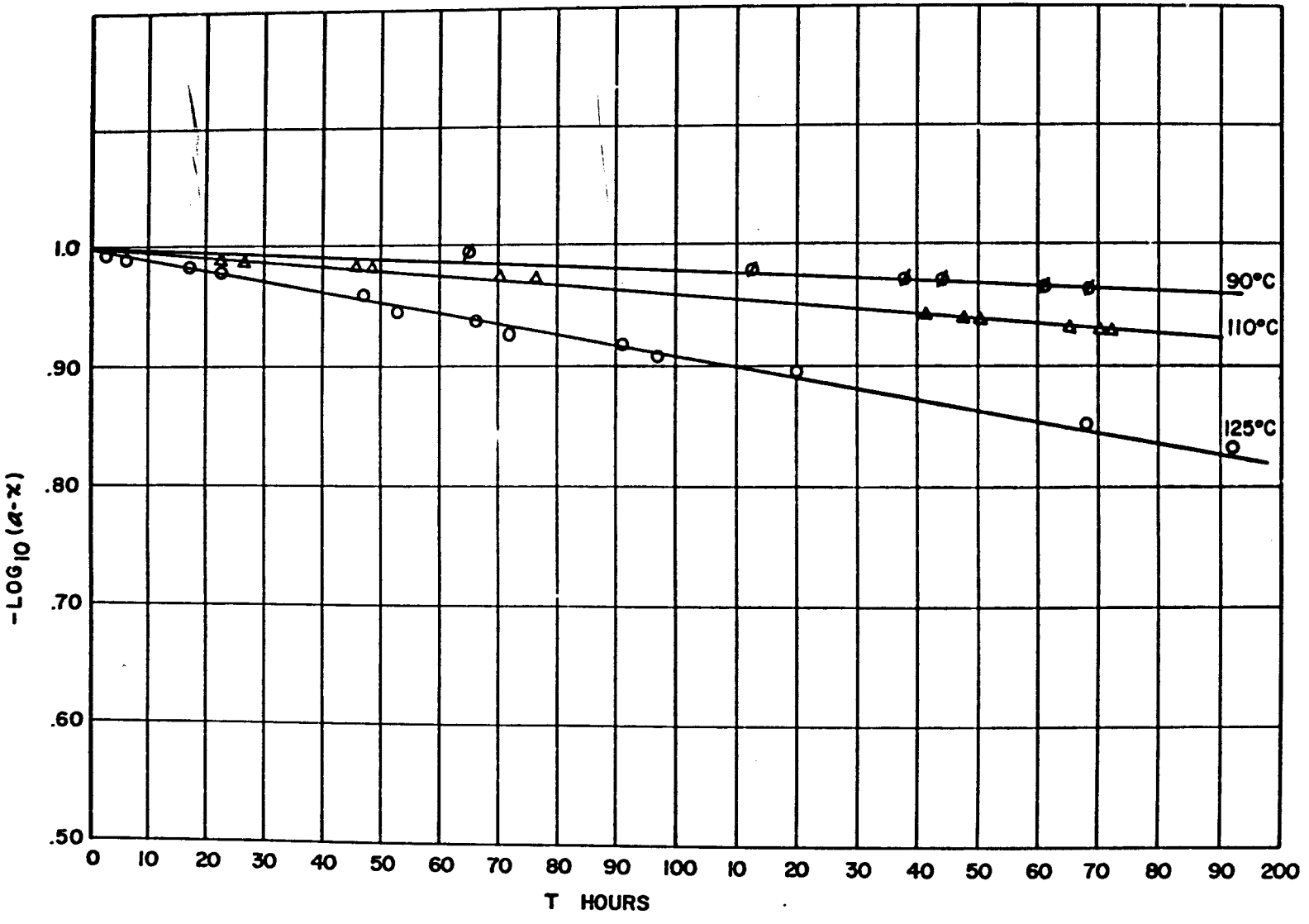


Figure 3. FIRST ORDER PLOT OF 1,2-EPOXY-3-PHENOXY PROPANE - ACETIC ACID IN DIOXANE

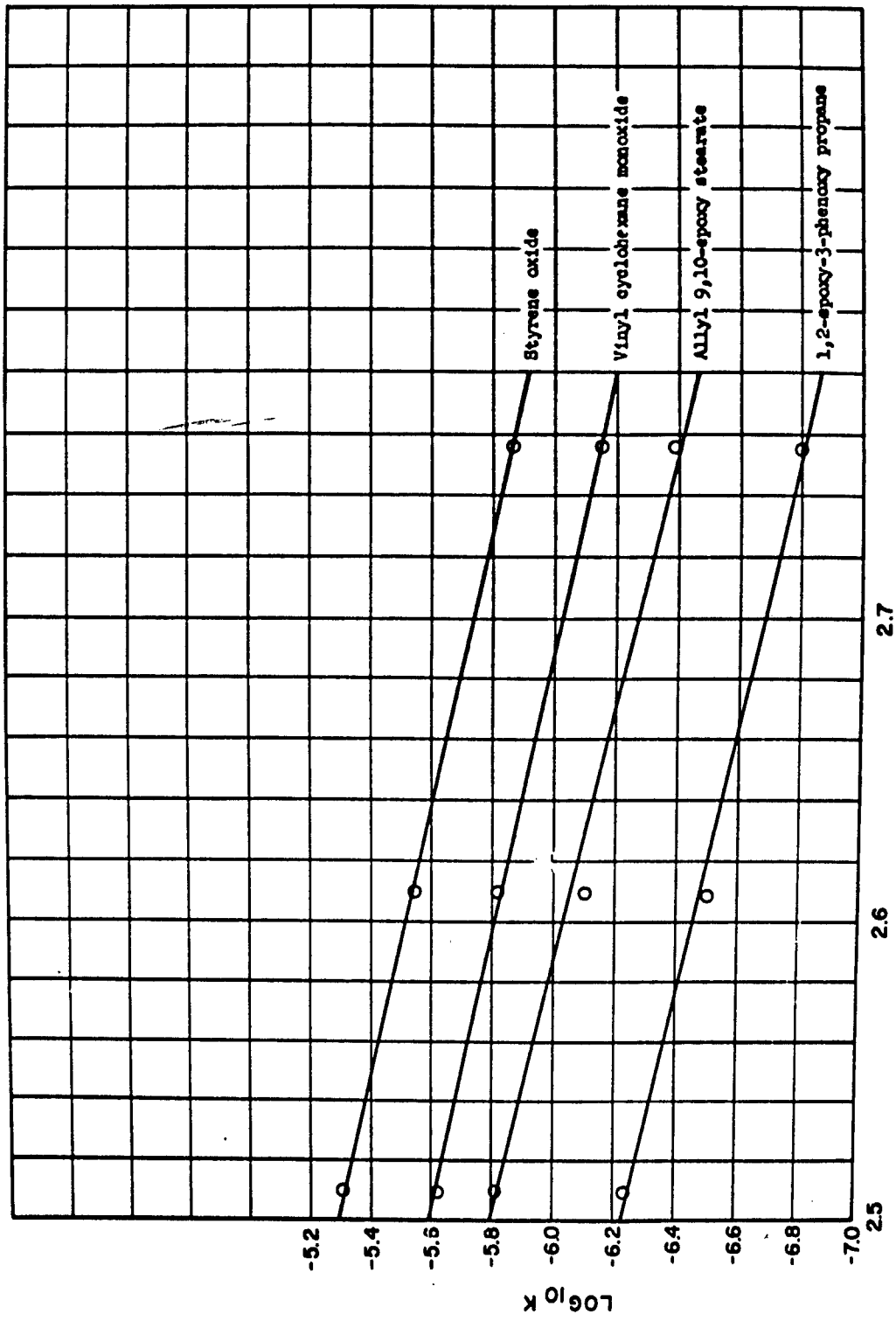


Figure 4. ARRHENIUS PLOT OF EPOXIDE - ACETIC ACID REACTIONS IN DIOXANE

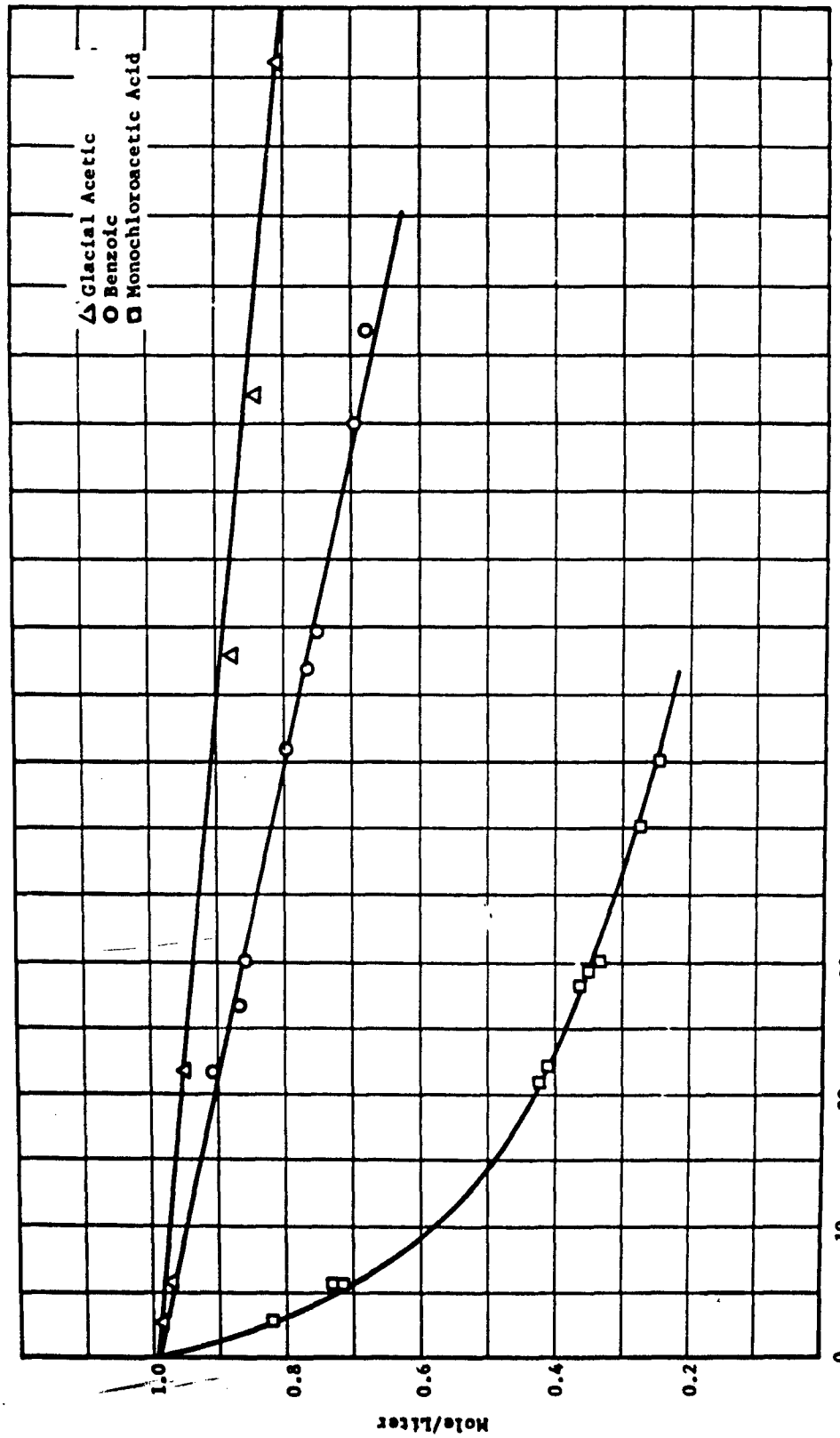


Figure 5. 1,2-EPOXY-3-PHENOXY PROPANE-CARBOXYLIC ACID REACTIONS AT 125°C

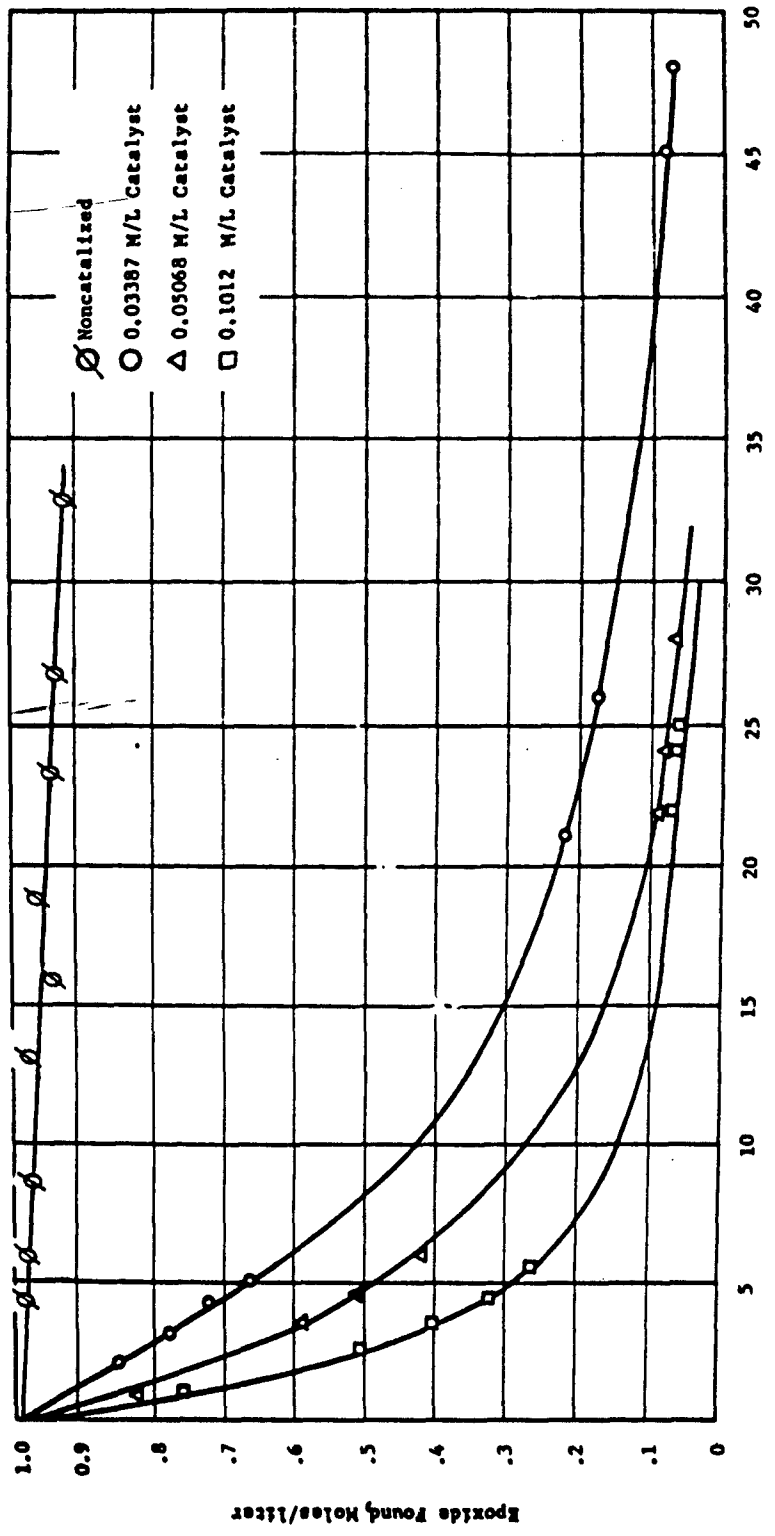


Figure 6. REACTION OF EQUIMOLAR QUANTITIES OF 1,2-EPOXY-3-PHENOXY PROPANE AND ACETIC ACID WITH ADDED CETYL DIMETHYL BENZYL AMMONIUM CHLORIDE AT 90°C

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4. L. Shechter, J. Wynstra, and R. Kurkjy, Industrial Engineering Chemistry 49, 1107, (1957).

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-RBL	138-142
-RFS	143
-RR	144
-RK, Mr. James	145
-RK, Dr. Odom	146-150
-RE	151
-RG	152
-RL	153
-RS	154
-RT	155
-RAP	156
-RKC	157-160
-RFE	161,162

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