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The Reaction of Ethylene Oxide with Oleic Acid

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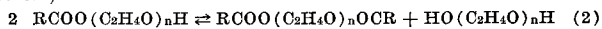
Abstract

The base-catalyzed reaction of ethylene oxide with oleic acid can be divided into two stages. The first stage consists of a slow reaction of oleic acid with ethylene oxide to form principally ethylene glycol monooleate; other reactions such as esterification, transesterification and polyglycol formation lag behind. In the second stage, after the addition of approximately one mole of ethylene oxide, the reaction accelerates and transesterification equilibrium is rapidly attained. The composition of products containing several molecules or more of ethylene oxide can be calculated satisfactorily on the assumption of random addition of ethylene oxide and random esterification of the hydroxyl groups. The uncatalyzed reaction is much slower and transesterification equilibrium is attained slowly, if at all. A reaction mechanism based on the difference in basicities of the carboxylate and alkoxide ions (and the relative rates of the competitive ethylene oxide reactions) is presented for the base-catalyzed reaction.
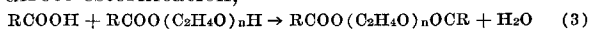
Introduction

THE ALKALI-CATALYZED reactions of ethylene oxide with long-chain fatty acids are used for the production of a number of commercially important emulsifiers and nonionic detergents (1,2). A simplified representation of the reaction is

$$RCOOH + n\ C_2H_4O \longrightarrow RCOO(C_2H_4O)_nH \qquad (1)$$

The reaction is customarily conducted with an alkaline catalyst and other reactions such as transesterification,

$$2\ RCOO(C_2H_4O)_nH \rightleftharpoons RCOO(C_2H_4O)_nOCR + HO(C_2H_4O)_nH \qquad (2)$$

and direct esterification,

$$RCOOH + RCOO(C_2H_4O)_nH \rightarrow RCOO(C_2H_4O)_nOCR + H_2O \qquad (3)$$

have been observed (2–4).

Polyoxyethylene (8) stearate (MYRJ 45—Atlas Chemical Industries, Inc.), which is the reaction product of 8 moles of ethylene oxide per mole of stearic acid, is approximately a 1:2:1 molar mixture of free polyol, monoester and diester (3). This distribution is the one expected (10) if ester interchange equilibrium (Equation 2) is reached rapidly. Larger mole ratios of mono- to diester have been reported for early stages of oxyethylation (4–7). In view of the interest in polyoxyethylene glycol esters in foods, pharmaceuticals, etc., it seemed desirable to make a thorough study of the effects of reaction conditions, including extent of oxyethylation on the composition of the products. Oleic acid was chosen for the study rather than stearic acid because the oleate esters are liquids and easy to handle and to observe for homogeneity.

Experimental

Starting Materials

Oleic acid was Emersol 233LL (Acid No., 202; average mole weight, 278), obtained from Emery Industries, Inc. Commercial ethylene oxide and sodium hydroxide were used without purification.

Procedure

Fatty acid-catalyst mixtures were prepared by dissolving powdered sodium hydroxide in oleic acid at elevated temperatures and decanting the mixture from the small quantity of aqueous phase which settled out upon standing. The ethylene oxide reactions were conducted in a one-liter stirred autoclave under a nitrogen atmosphere. Ethylene oxide was added incrementally maintaining autoclave pressure constant to ±3 psig. Details of the equipment and procedure were given previously (11). In order to obtain samples representative of operating conditions, small quantities were removed rapidly from the autoclave into a flask cooled in a solid carbon dioxide-isopropanol bath.

Separation of Reaction Products and Analysis

The products are for the most part homogeneous. Those containing between 1.0 and 2.5 moles of ethylene oxide per mole acid yielded a small quantity of a second liquid phase, largely glycols, upon standing at room temperature. Before sampling for analysis, the products were mixed by shaking. The mole ratio of epoxide reacted with acid was estimated from the oxyethylene content of the product, determined by the method of Siggia et al. (8). The products were analyzed for acid value, hydroxyl value and saponification value by methods essentially those of the American Oil Chemists' Society. Free and total ethylene glycol were determined by periodate oxidation before and after saponification of the oleate ester. Water content was determined by Karl Fischer reagent or by gas-liquid chromatography.

Samples were processed to yield (a) free polyols, (b) combined mono- and diesters, and (c) total (free and combined) polyols. The procedure utilized to obtain the total polyols was similar to that described by Birkmeier and Brandner (3), except that samples were concentrated under controlled conditions to prevent loss of the lower glycols. The separation of free polyols from the combined esters was accomplished by extracting a benzene solution with aqueous 10% sodium sulfate solution. In some of the extractions, emulsions were obtained, which were broken by the addition of small quantities of isopropanol. The free polyols (and the total polyols obtained after saponification) were recovered as aqueous solutions, concentrated and the chain length of the glycols estimated from the hydroxyl number. Alternatively, GLC was used to estimate free polyols directly using a column
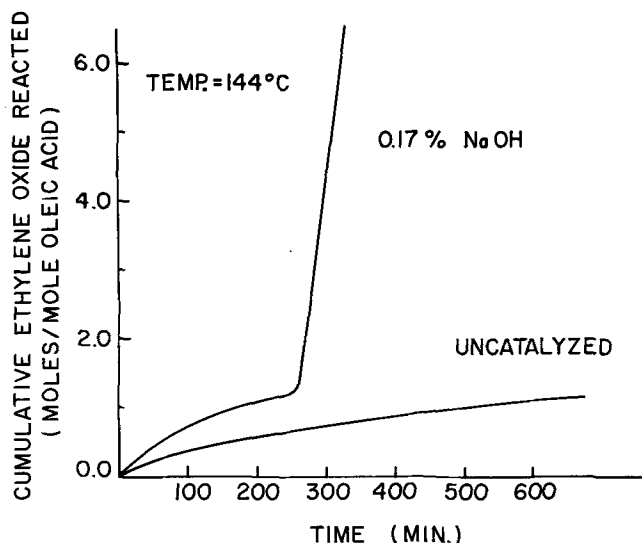
FIG. 1. Rate of consumption of ethylene oxide by reaction with oleic acid.

FIG. 2. Rate of consumption of oleic acid by reaction with ethylene oxide.

of Carbowax 20M on Chromosorb W, and esterified polyols were transmethylated before injection into the GLC.

The following calculations were used to determine the product composition:

Mole Fraction Acid Reacted, $X = 1 - [(278 + 44.1 \, n) \text{ Acid No.}]/56{,}100$

where n is moles of combined ethylene oxide per mole of acid charged.

Mole Ratio Mono-/Diester, $R = 2/[(E/H) - 1]$ where E and H are ester number and hydroxyl number of ester portion, respectively.

Mole Fraction Diester, $D = X/(R + 2)$

Mole Fraction Monoester, $M = DR$

Mole Fraction Free Polyol, $P = T - (M + D)$ where T is moles total polyols found per mole acid charged.

Results and Discussion

A typical rate curve obtained upon addition of ethylene oxide to oleic acid using sodium hydroxide as catalyst is shown in Figure 1. The reaction occurs in two distinct kinetic stages, as was reported previously (5,9). Stage one is a slow reaction which lasts until approximately 1.1 moles of epoxide per mole of acid have reacted. Stage two is characterized by a much faster reacton, which persists for the duration of the ethylene oxide addition. The uncatalyzed reaction at a slightly higher pressure is shown to be much slower. No evidence was found in any uncatalyzed run for an abrupt increase in reaction rate comparable with that observed in base-catalyzed reactions.

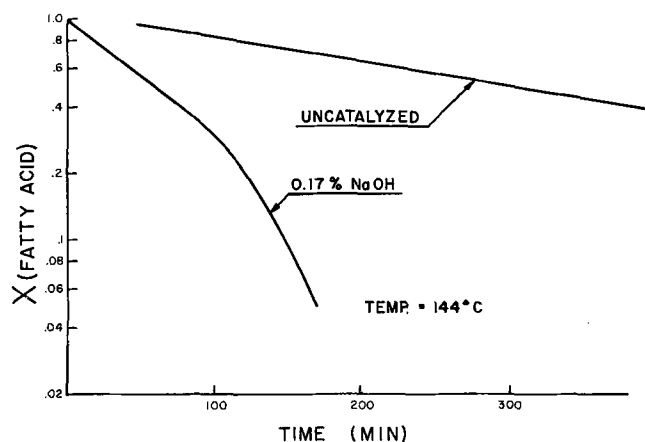Figure 2 shows the rate of consumption of fatty acid both for the base-catalyzed and the uncatalyzed

reaction of ethylene oxide with oleic acid. The logarithm of the mole fraction of acid plotted vs. time yields a straight line for the first portions of the base-catalyzed reaction. The base-catalyzed reaction rate constant increases as the reaction of fatty acid approaches completion, presumably due to direct esterification as a competitive route for consumption of oleic acid. The uncatalyzed reaction appears to be linear throughout.

Catalyst concentration was varied in order to determine the effect on rate of reaction. The reaction rate constant k_1, defined as $-d[\text{Fatty Acid}]/dt = k_1 [\text{Fatty Acid}]$, is shown in Table I as a function of catalyst concentration. k_2, defined as $k_1/[\text{NaOH}]$, decreases somewhat with increasing catalyst concentration, presumably because of the decrease in the fraction of catalyst ionized.

The effect of ethylene oxide pressure on the rate constant for consumption of fatty acid is presented in Table II. Within experimental error, the rate constant k_3, defined as $k_2/[\text{ETO}]$, is constant over a range of ethylene oxide pressures.

Variation of product composition with moles of ethylene oxide reacted per mole of oleic acid is shown in Figure 3. An abrupt change in the product distribution occurs at the point where the kinetic change is observed. As had been reported previously (3), during the initial reaction, the mole fraction of acid decreases linearly to zero which shows that the preferred reaction is between ethylene oxide and fatty acid. During this period, the mole fraction of monoester increases to a maximum of about 0.7. Although in the initial stage monoester is the predominant product, ester interchange or transesterification takes place slowly, resulting in small but steadily increasing amounts of free polyol and diester. The slight excess of diester over polyol is probably due to direct esterification of monoester with free fatty acid.

After addition of slightly more than one mole of ethylene oxide per mole of acid, the monoester concentration decreases suddenly and the concentrations

TABLE I
Reaction Rate vs. Catalyst Concentration

	Temperature, 120C Average ETO pres., 52.5 psi	
NaOH (wt. %)	$k_1 \cdot 10^3$, min.$^{-1}$ ($\Delta \ln X_{FA}/\Delta t$)	k_2, min.$^{-1}$ (k_1/X_{NaOH})
0.069	2.80	0.58
0.14	5.15	0.54
0.22	6.84	0.50
0.28	8.41	0.44
0.42	10.9	0.38
0.61	12.3	0.30

TABLE II
Reaction Rate vs. Ethylene Oxide Pressure

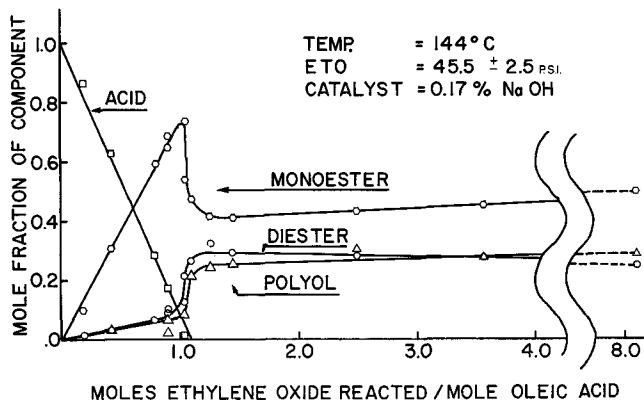|	Temperature, 120C Catalyst, 0.42% NaOH		
Avg. ETO pres., P (psi)	$k_1 \cdot 10^3$, min.$^{-1}$ ($\Delta \ln X_{FA}/\Delta t$)	k_2, min.$^{-1}$ (k_1/X_{NaOH})	k_3, min.$^{-1}$ (k_2/X_{ETO})
52.5	10.9	0.38	2.0
37.5	8.6	0.30	2.5
17.5	3.7	0.13	2.3
where $X_{ETO} = P/P_o$; $P_o = 310$ psi at 120C			

Fig. 3. Variation of product composition with moles of ethylene oxide reacted.

of diester and polyol increase sharply. Addition of several more moles of epoxide results in a slight increase in monoester and free polyol and a slight decrease in diester. After eight moles of ethylene oxide have reacted, the product contains a mole ratio of free polyol, monoester and diester of 1.16:2.00:1.00, in agreement with previous work on polyoxyethylene (8) stearate and oleate (3,6).

Chain growth is at a minimum in the initial stage since the average chain length of the total polyols recovered after saponification is constant at about 1.15. Figure 4 shows the chain length of the polyol as a function of moles of ethylene oxide reacted per mole of oleic acid. At mole ratios of ethylene oxide to fatty acid reacted greater than about 1, the average ethylene oxide polymer length is the same in that portion of the polyol which is free as in the portion esterified.

Figure 5 shows the variation of ethylene glycol content with the number of moles of ethylene oxide reacted per mole of oleic acid. The total ethylene glycol content (both free and esterified) rises to a maximum at approximately one mole of ethylene oxide reacted per mole of oleic acid and then drops rapidly to zero by the time eight moles of ethylene oxide have reacted.

Additional evidence for direct esterification in the initial stage is given in Figure 6 which shows the water content of the base-catalyzed and uncatalyzed reaction product. In the case of the base-catalyzed reaction, water content increases to a maximum at about 0.8 moles ethylene oxide reacted per mole of fatty acid, and by the time about one mole of ethy-
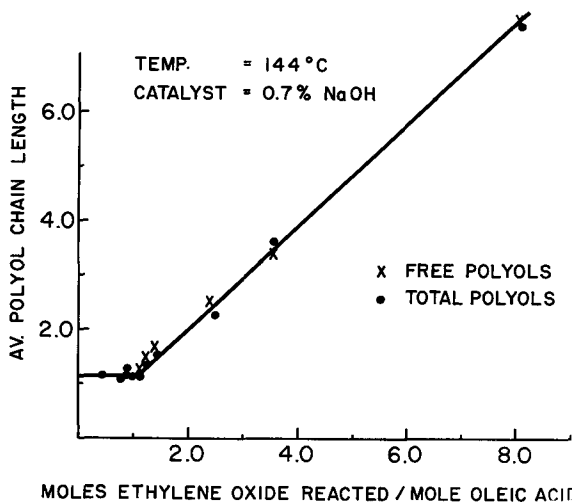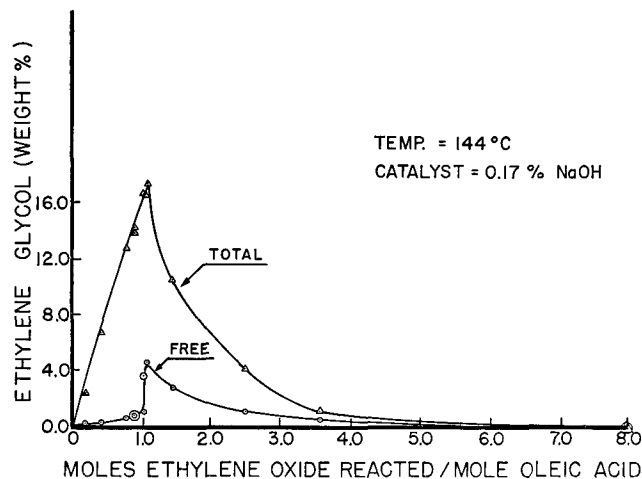

Fig. 5. Variation of ethylene glycol content with moles of ethylene oxide reacted.

lene oxide per mole of fatty acid has reacted the water content has decreased to a low value by reaction to form ethylene glycol. The uncatalyzed reaction shows an increase of water during the addition of the first mole of ethylene oxide and no precipitous reduction of water content thereafter.

Qualitatively, the observed change of the kinetics and product composition when the fatty acid content reaches zero can be explained by (a) the almost exclusive reaction of ethylene oxide with fatty acid, accompanied by slow transesterification and slow direct esterification in the initial stage, followed by (b) oxyethylene chain growth and rapid transesterification after the fatty acid has all reacted. In the present work and in earlier work (4,5), it was observed that immediately following the kinetic change, the mole ratio of monoester to diester passes through a minimum. As more ethylene oxide is reacted the composition approaches the 1:2:1 mole ratio of free polyol to monoester to diester, corresponding with ester interchange equilibrium.

Samples were separated and analyzed by countercurrent extraction using a procedure described previously (6). The data which are given in Table III support the observation of a minimum in the ratio. A likely explanation for the minimum in the mole fraction of monoester lies in the observation, mentioned earlier, that a small quantity of a second liquid phase was observed in products containing from about
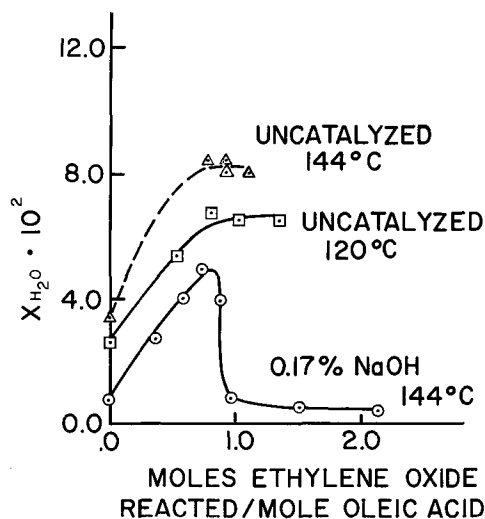

Fig. 4. Variation of polyol chain length with moles of ethylene oxide reacted.

Fig. 6. Variation of water content with moles of ethylene oxide reacted.

TABLE III

Countercurrent Extraction Analysis
of Polyoxyethylated Oleic Acid

Autoclave reaction conditions: 144C, 0.17% NaOH			
Mole ratio $\dfrac{C_2H_4O}{Acid}$ reacted	0.81	1.40	8.45
Product mole fractions			
Free fatty acid	0.202	0.002	0.006
Free polyol	0.034	0.277	0.259
Monoester	0.671	0.351	0.501
Diester	0.079	0.356	0.221
Mole ratio mono-/diester	8.51	0.99	2.27

TABLE IV

The Reaction of Ethylene Oxide with
Oleic Acid in Dimethyl Sulfoxide

Catalyst = 0.17% NaOH Solvent = 50% of initial charge Temperature = 144C				
Mole ratio (ETO/acid) reacted	0.61	0.97	1.16	1.79	1.95
Product mole fractions					
Fatty acid	0.14	0.06	0.001	0.002	0.002
Monoester	0.79	0.84	0.63	0.52	0.55
Diester	0.038	0.10	0.19	0.24	0.23
Mole ratio mono-/diester	21	8.4	3.3	2.2	2.4

1.0 to 2.5 moles of ethylene oxide reacted per mole of fatty acid. This lower phase at room temperature constitutes 1% to 2% of the product, and according to GLC, is a mixture of ethylene glycol and polyethylene glycols. If the polyols are insoluble in the ester at reaction temperature, transesterification equilibrium will be displaced resulting in an excess of diester and less monoester than otherwise predicted. Several experiments using dimethyl sulfoxide as a solvent are reported in Table IV. The mono- to diester ratio does not appear to go through a minimum but approaches the theoretical ratio of 2:1.
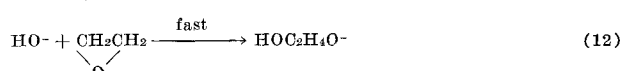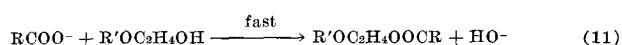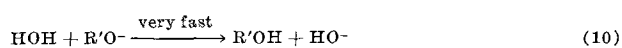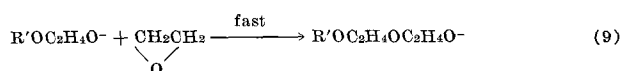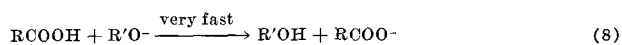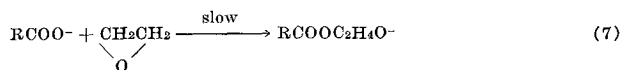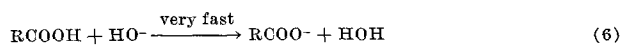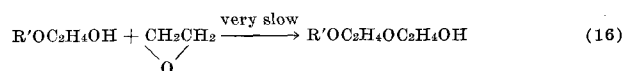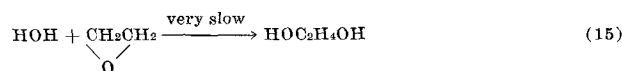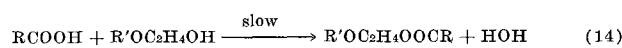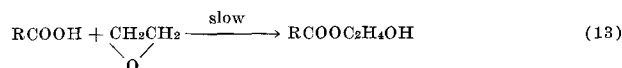
The effect of NaOH catalyst on the ratio of mono- to diester is shown by the data in Table V. At mole ratios of ethylene oxide to oleic acid reacted of less than 1 the mono- to di- ratio increases with catalyst concentration.

Data on the uncatalyzed reaction of ethylene oxide with oleic acid at 144C are shown in Figure 7. The fatty acid curves are similar for the base catalyzed and uncatalyzed reactions. The monoester content increases and reaches a mole fraction of about 0.5 when all of the fatty acid has reacted. The diester content increases simultaneously to a mole fraction of about 0.25. The free polyol content increases slowly, presumably as a result of the sluggish reaction between water and ethylene oxide already noted. Transesterification equilibrium is not achieved rapidly in the uncatalyzed reaction even after all of the fatty acid has reacted.

The effect of temperature on the rate of the base-catalyzed and of the uncatalyzed reaction is shown in Table VI.

The energy of activation of the base-catalyzed reaction, 17 kcal/g mole, is higher than that for the uncatalyzed reaction, 14 kcal/g mole, which indicates that the two processes have different rate-controlling steps.

Based upon all of the foregoing data, the following mechanism can be written for the base-catalyzed reactions of ethylene oxide with fatty acids.

$$RCOOH + HO^- \xrightarrow{\text{very fast}} RCOO^- + HOH \tag{6}$$

$$RCOO^- + CH_2CH_2{\diagdown}O{\diagup} \xrightarrow{\text{slow}} RCOOC_2H_4O^- \tag{7}$$

$$RCOOH + R'O^- \xrightarrow{\text{very fast}} R'OH + RCOO^- \tag{8}$$

$$R'OC_2H_4O^- + CH_2CH_2{\diagdown}O{\diagup} \xrightarrow{\text{fast}} R'OC_2H_4OC_2H_4O^- \tag{9}$$

$$HOH + R'O^- \xrightarrow{\text{very fast}} R'OH + HO^- \tag{10}$$

$$RCOO^- + R'OC_2H_4OH \xrightarrow{\text{fast}} R'OC_2H_4OOCR + HO^- \tag{11}$$

$$HO^- + CH_2CH_2{\diagdown}O{\diagup} \xrightarrow{\text{fast}} HOC_2H_4O^- \tag{12}$$

where R' is $H(OC_2H_4)_n$ or $RCO(OC_2H_4)_n$

The initial reaction proceeds through the carboxylate ion which is formed rapidly from the base by reaction 6; the carboxylate ion then reacts slowly with ethylene oxide according to Equation 7. The strongly basic alcoholate ion which is formed reacts rapidly with more fatty acid, regenerating the carboxylate ion (Equation 8). These are the predominant reactions which occur in the first stage. As long as fatty acid is present, alcoholate ion concentration is low and there is limited opportunity for chain growth (Equation 9). Free polyols and diester are formed to a limited extent, probably by reactions represented by Equations 11, 12 and 8. The reaction represented by Equation 12 is competitive with reaction 7. As the concentration of unreacted fatty acid becomes low the next strongest acid, namely water, can compete successfully with the carboxyl group for the alkoxide ion. Thus, the water content increases initially, and then decreases nearly to zero by the time all of the fatty acid has reacted.

After all of the fatty acid has reacted and Equation 8 is no longer operable, the concentration of strongly basic alcoholate ion increases. As has been reported (9,11), this is an excellent catalyst for polyoxyethylation and chain growth (Equation 9) becomes rapid. The strongly basic catalyst permits rapid transesterification. Thus, the product composition (free polyol, monoester and diester) approaches the equilibrium concentration and the oxyethylene chain length is equal in free polyol, mono- and diester.

The uncatalyzed reaction is represented by the following equations:

$$RCOOH + CH_2CH_2{\diagdown}O{\diagup} \xrightarrow{\text{slow}} RCOOC_2H_4OH \tag{13}$$

$$RCOOH + R'OC_2H_4OH \xrightarrow{\text{slow}} R'OC_2H_4OOCR + HOH \tag{14}$$

$$HOH + CH_2CH_2{\diagdown}O{\diagup} \xrightarrow{\text{very slow}} HOC_2H_4OH \tag{15}$$

$$R'OC_2H_4OH + CH_2CH_2{\diagdown}O{\diagup} \xrightarrow{\text{very slow}} R'OC_2H_4OC_2H_4OH \tag{16}$$
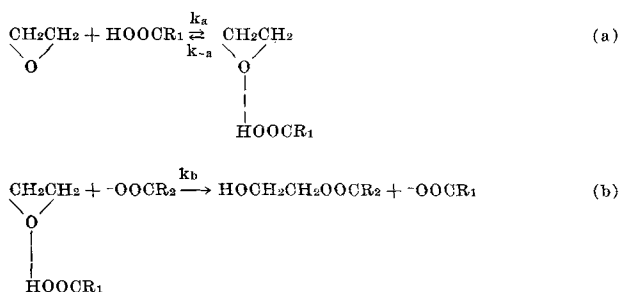
Fatty acid reacts slowly with ethylene oxide to form monoester (Equation 13). Simultaneously, there is a slow reaction of fatty acid with monoester to form diester (Equation 14). The uncatalyzed reactions of ethylene oxide with water (Equation 15) and with monoester (Equation 16) are even slower according to these data.

A detailed picture of the mechanism of the base-catalyzed reaction of ethylene oxide with fatty acid must take into account the fact that the reaction rate is proportional to the catalyst concentration, the ethylene oxide pressure and fatty acid concentration. It is obviously an oversimplification of the process

TABLE V

Effect of Catalyst Concentration
on Mono-/Diester Ratio

Temperature, 144C
Catalyst, NaOH

Moles ethylene oxide per mole oleic acid reacted	Catalyst concentration—wt%	Mole ratio mono-/diester
0.49	0.0	2.5
	0.17	8.1
	0.66	10
0.81	0.0	2.4
	0.17	8.3
	0.66	19
0.94	0.0	2.4
	0.17	7.0
	0.66	14
1.5	0.0	2
	0.17	1.4
	0.66	1.1

to indicate the reaction according to Equation 7, in which the rate depends only on ethylene oxide concentration and catalyst concentration. The process may occur in the following manner:

$$CH_2CH_2 + HOOCR_1 \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} \underset{\text{O}}{\overset{\text{CH}_2\text{CH}_2}{}} \quad (a)$$

$$\text{HOOCR}_1$$

$$CH_2CH_2 + {}^-OOCR_2 \xrightarrow{k_b} HOCH_2CH_2OOCR_2 + {}^-OOCR_1 \quad (b)$$

$$\text{HOOCR}_1$$

where the subscripts are used to denote that the acid group which enters first (R_1COOH) makes a complex with ethylene oxide; this is attacked by the carboxylate ion (R_2COO^-) to form the product and generate a carboxylate ion of the original fatty acid molecule (R_1COO^-).
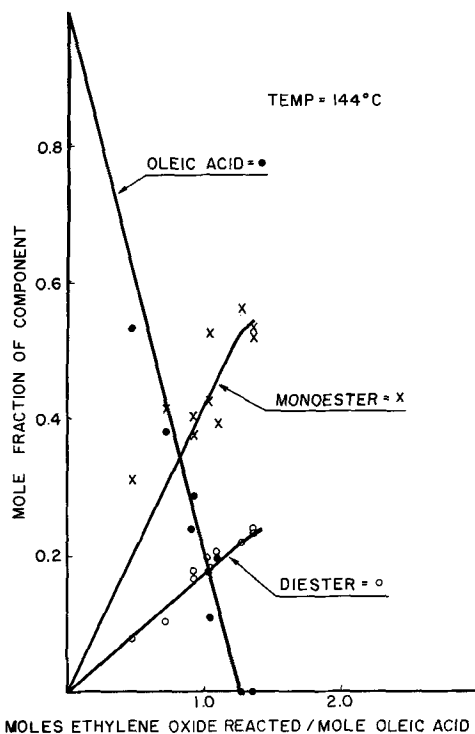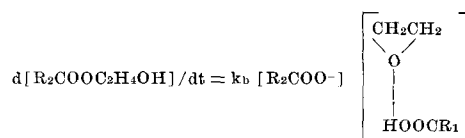

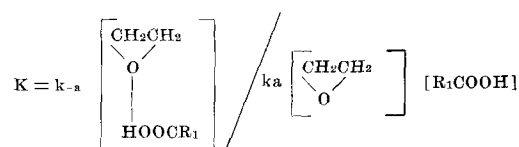FIG. 7. Variation of product composition for uncatalyzed reaction.

TABLE VI

Reaction Rate vs. Temperature

Temp. C	0.15% NaOH		Uncatalyzed	
	ETO pres (PSI)	k_3, min.$^{-1}$	ETO pres (PSI)	k_3, min.$^{-1}$
164	37.5	27.8	27.5	0.0537
144	45.5	10.2	52.5	0.0229
120	52.5	3.16	52.5	0.00846

The rate of formation of product determined by reaction (b) is as follows:

$$d[R_2COOC_2H_4OH]/dt = k_b [R_2COO^-] \begin{bmatrix} CH_2CH_2 \\ O \\ HOOCR_1 \end{bmatrix}$$

The concentration of complex is determined by equilibrium in reaction (a).

$$K = k_{-a} \begin{bmatrix} CH_2CH_2 \\ O \\ HOOCR_1 \end{bmatrix} / k_a \begin{bmatrix} CH_2CH_2 \\ O \end{bmatrix} [R_1COOH]$$

Rearranging and substituting the concentration of complex in the rate equation (b) one obtains

$$d[R_2COOC_2H_4OH]/dt = k_3[R_2COO^-] \begin{bmatrix} CH_2CH_2 \\ O \end{bmatrix} [R_1COOH]$$
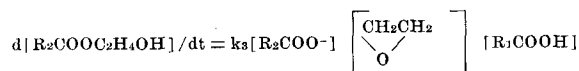
The foregoing mechanism is similar to one proposed recently to explain the kinetics of the reaction of ethylene oxide with phenols (12,13).

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