KINETICS OF THE CATALYZED AND UNCATALYZED LIQUID-PHASE HYDRATION OF PROPYLENE OXIDE

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The kinetics of the catalytic and noncatalytic hydration of propylene oxide were studied in a continuous reactor. Both the catalytic and noncatalytic reaction were studied over a temperature range of 100° to 300°F. The feed ratios ranged from 2.5 to 10 lb. water/lb. propylene oxide. In the case of catalytic reaction, the catalyst concentration of sulfuric acid ranged up to 0.25 wt. % of the total feed.

The study showed the noncatalytic reaction to be pseudo first order with respect to propylene oxide, and an equation was found for the rate constant. The catalytic reaction was found to be pseudo second order with respect to propylene oxide, and the effect of the catalyst concentration is shown graphically.

Propylene glycol (1-, 2-propanediol), which was first prepared by Wurtz(*10*) in 1859 by hydrolysis of propylene glycol diacetate, was first produced on a commercial scale by Carbide and Carbon Chemicals Co. in 1931 via the chlorhydrin process. Curme and Johnston(*3*) state that the production of propylene glycol has become increasingly important, and in 1950 85,000,000 lb. was produced. In 1951 propylene glycol was being produced in five plants located in three states(*3*). Although the major portion of propylene glycol is manufactured by the chlorhydrin process, there is increasing interest in its production by the hydration of propylene oxide.

This investigation, made because of the lack of information on this reaction in the literature, was set up for study of the kinetics of this reaction. Some data on the distri-

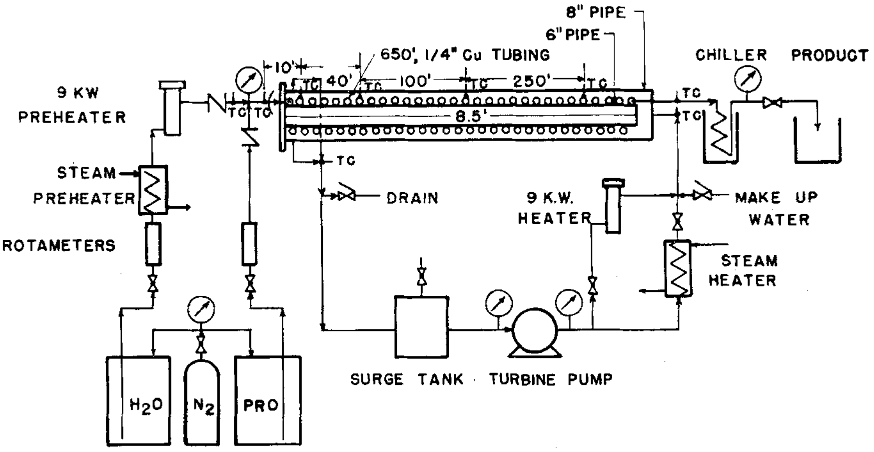

FIG. 1. FLOW DIAGRAM OF REACTOR.

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bution of products when propylene and dipropylene glycols are formed were also desired. The study was limited to a liquid-phase, homogeneous reaction, and both the uncatalyzed reaction and the reaction catalyzed with sulfuric acid were included in the study. The reaction was studied over a temperature range of 100° to 300° F.; the feed ratio was varied from 2.5 to 10 lb. water/lb. propylene oxide; and the catalyst concentration ranged up to 0.25 wt. % of the feed.

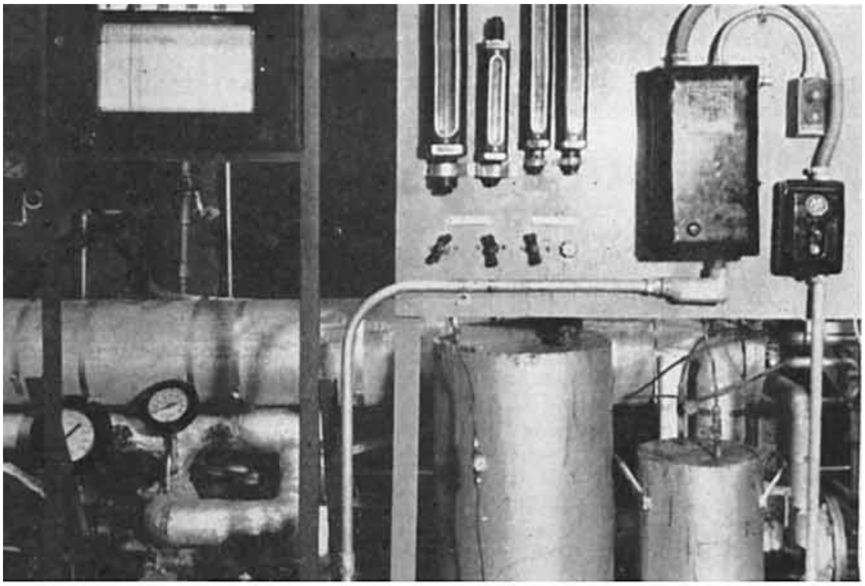

FIG. 2. REACTOR CONTROL PANEL.→

APPARATUS AND PROCEDURE

Apparatus. The reactor may be described with reference to the flow diagram shown in Figure 1 and the photographs in Figures 2, 3, and 4. In general the reactor consisted of a 650-ft. section of 1/4-in. copper tubing wound on the inside pipe of two concentric pipes with water circulating in the annulus to maintain the desired temperature. The coil was wound so that the water could circulate on both sides of the coil. The reactants mixed immediately before entering the reactor, and the reacted mass was quenched in an ice bath immediately after leaving the constant-temperature reactor.

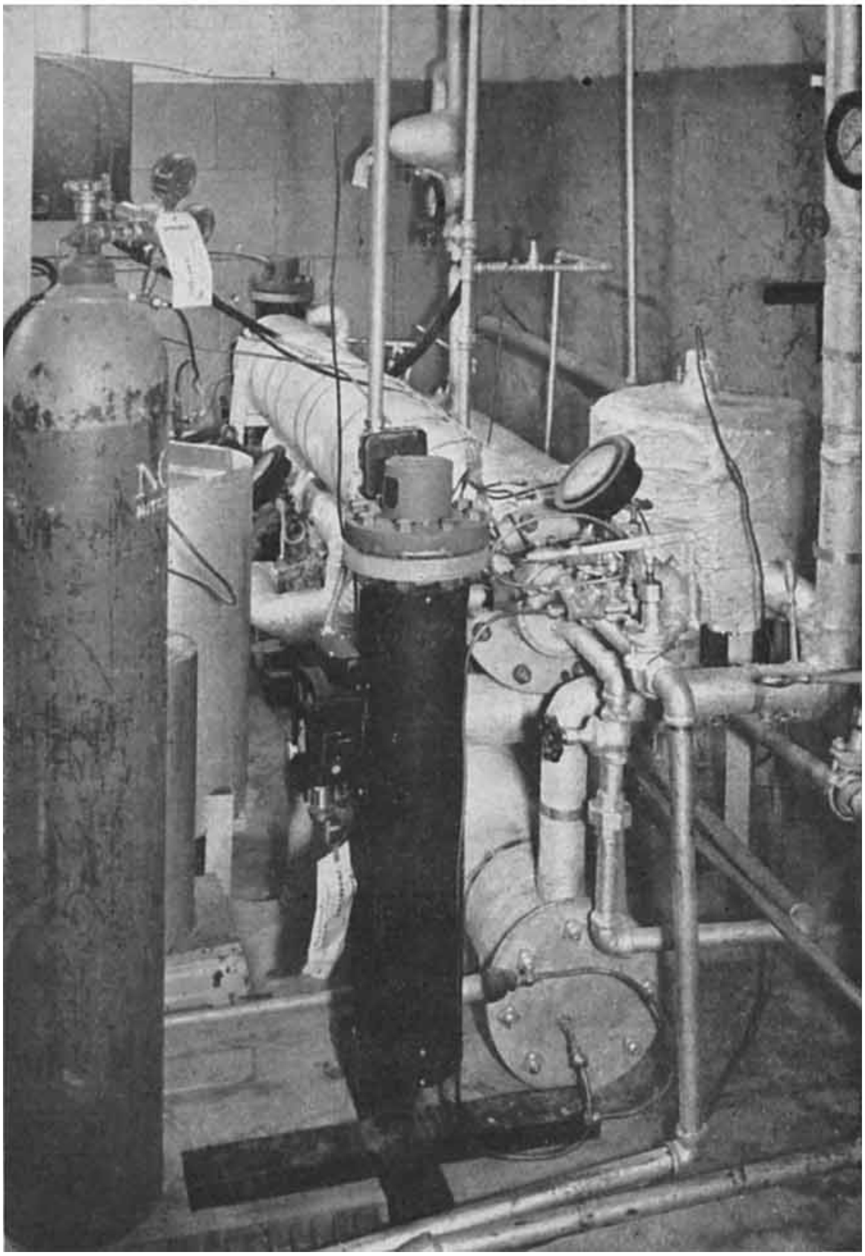

FIG. 4. OVERHEAD VIEW OF REACTOR.→

FIG. 3. SAMPLING THE REACTOR PRODUCT.

The two reactants were water and propylene oxide. The water was contained in a 20-gal. steel tank and the propylene oxide in a 5-gal. steel container. When catalytic runs were made, the sulfuric acid was mixed with the feed water. For these runs the steel feed-water tank was replaced by two 9-gal. stainless steel tanks. A nitrogen cylinder was connected to both the water and the propylene oxide containers and a pressure regulator maintained a constant pressure on them. The feed water left the tank through 1/4-in. copper tubing which led to a needle valve, then to a rotameter, a preheater consisting of a steam heat exchanger, a 9-kw. electric immersion preheater, and a check valve to the point where it mixed with propylene oxide. The propylene oxide was caused to flow through a needle valve, a rotameter, and a check valve to the point where it mixed with the feed water. The reactant solution then passed into the reactor proper. As a safety precaution, a rupture disk was placed in the mixing section. The reactor proper was made of 650 ft. of 1/4-in. copper tubing which was wound on an 8.5-ft. section of 6-in. pipe, which was then inserted coaxially in an 8-in. pipe. Water flowed in the annular space between two pipes in order to maintain the reaction mass at a constant temperature. This water was kept at a constant temperature by circulating it through an outside circuit where it flowed first into a surge tank, then through a turbine pump, through a heater, and back into the bath. Pressure was maintained in the bath circuit to keep the water in the liquid phase.

After the reactant mass had passed through the 650 ft. of tubing, it was immediately passed through an ice bath, where it was chilled in order effectively to stop the reaction. The solution was then passed through a pressure relief valve and was collected in a sample container.

A pressure gauge was placed in the line preceding the reactor section and one was placed following the quenching section. Nine thermocouples were included in the system in order to measure temperatures. Their locations were as follows:

1. Ten feet from the inlet in the reactor tubing
2. Fifty feet from the inlet in the reactor tubing
3. One hundred and fifty feet from the inlet in the reactor tubing
4. Four hundred feet from the inlet in the reactor tubing
5. Exit of circulating water from reactor
6. Inlet of circulating water to reactor
7. Six hundred and fifty feet from inlet in the reactor tubing just outside reactor
8. After preheater in feed water line
9. In the mixing section

Thermocouples 1 through 4 were soldered onto the outside of the reactor tube wall. Calculations showed that for the conditions chosen for this study, these thermocouples would indicate essentially the temperature of the fluid in the tube. The other thermocouples were placed in wells in the fluid stream. The temperatures in the various sections of the reactor never varied more than 1°F. from one point to another.

The reactants for this project were distilled water and propylene oxide, which was obtained from Carbide and Carbon Chemical Corp. The specifications for the propylene oxide (*2*) follow:

Acidity	0.05 wt. % max. as acetic acid
Water	1.0 wt. % max.
Residue	0.005 g./ml. max.
Color	15 pt-Co APHA units, max.
Suspended matter	Substantially free
Distillation at 760 mm.	I.b.p. 30.0°C. min. 95 ml. 40.0°C. max.

Procedure. The circulating pump was started first and the reactor was heated to the desired temperature by controlling the heater in the circulation system. The reaction temperature was easily controlled within ± 1° F. for any given run. Feed water was then fed into the reactor system at a specified rate and the feed preheater was used to heat it a few degrees above the desired reaction temperature. Then cold propylene oxide was metered into the system and the water preheater was regulated to bring the temperature of the reactants, after mixing, to the desired reaction temperature. The individual flow rates were indicated by rotameters and controlled by needle valves. Pressure was maintained in the reactor by a pressure-relief valve downstream from the quenching zone so that the reactants were

TABLE 1.—UNCATALYZED REACTION-RATE CONSTANTS

Run	Reaction temp., °F.	Feed ratio, R_i $\frac{\text{lb. H}_2\text{O}}{\text{lb. PrO}}$	V_R/F $\frac{\text{(cu. ft.) (sec.)}}{\text{(lb. mole)}}$	Fractional conversion of PrO, X	Reaction-rate constant, k_1, $\frac{\text{lb. mole}}{\text{(cu. ft.) (sec.)}}$
1	200	10.0	55.9	0.0357	0.000649
2	200	10.0	111.7	0.0572	0.000526
3	200	10.0	227.7	0.111	0.000511
17	200	10.0	219.2	0.120	0.000645
7	200	10.0	319.2	0.187	0.000593
18	200	10.0	312.7	0.173	0.000580
8	200	10.0	446.9	0.234	0.000604
				Representative	0.000625
14	200	5.0	217.0	0.081	0.000405
15	200	5.0	310.0	0.102	0.000331
16	200	5.0	867.7	0.232	0.000303
				Representative	0.00037
27	200	2.5	102.5	0.0454	0.000535
28	200	2.5	205.0	0.0550	0.000275
23	200	2.5	356.5	0.0760	0.000244
24	200	2.5	510.5	0.111	0.000242
				Representative	0.00024
4	250	10.0	55.9	0.154	0.00298
5	250	10.0	111.7	0.242	0.00247
6	250	10.0	223.5	0.460	0.00275
9	250	10.0	319.2	0.536	0.00239
19	250	10.0	319.2	0.502	0.00264
10	250	10.0	447.0	0.697	0.00216
				Representative	0.0025
20	250	5.0	215.9	0.280	0.00151
21	250	5.0	309.9	0.372	0.00148
22	250	5.0	867.3	0.724	0.00147
				Representative	0.00148
29	250	2.5	102.5	0.104	0.00060
30	250	2.5	205.0	0.139	0.00107
25	250	2.5	356.0	0.194	0.00073
				Representative	0.00087
11	300	10.0	55.9	0.392	0.00888
31	300	10.0	219.2	0.802	0.00728
32	300	10.0	319.2	0.916	0.00765
				Representative	0.0080
12	300	15.0	63.6	0.548	0.01242

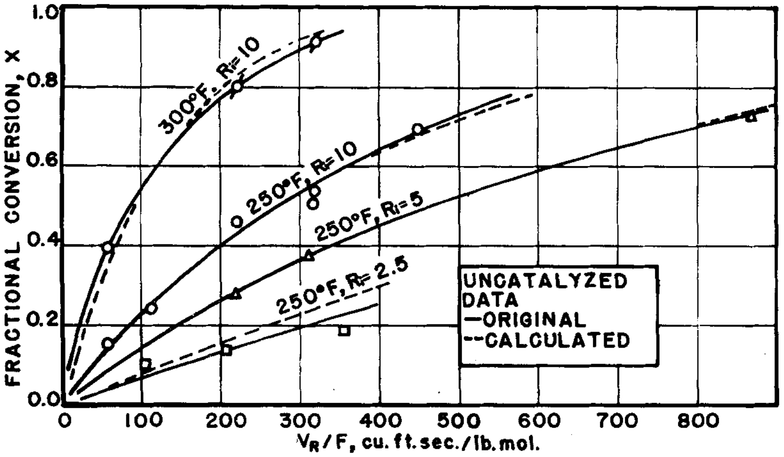

FIG. 5. UNCATALYZED DATA, CONVERSION OF PROPYLENE OXIDE TO GLYCOL, 250° AND 300°F.

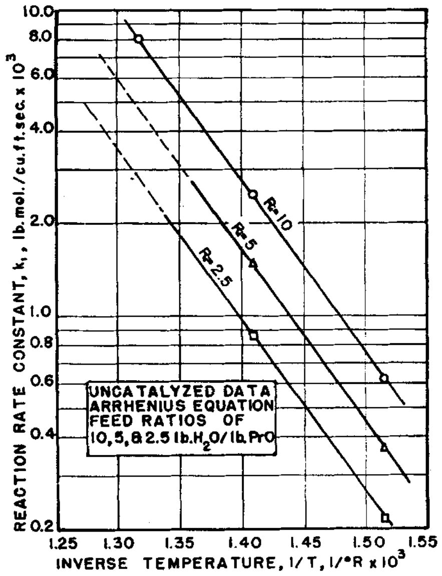

FIG. 6. ARRHENIUS EQUATION FOR UNCATALYZED REACTION.

TABLE 2.—CONSTANTS CHARACTERISTIC OF UNCATALYZED REACTION

Arrhenius constants

$$k_1 = Ae \frac{-E}{RT}$$

Feed ratio, R_i lb. H_2O	A, lb. mole	Energy of activation, E, B.t.u.
lb. PrO	(cu. ft.) (sec.)	lb. mole
10.0	1.868×10^5	25.6×10^3
5.0	1.125×10^5	25.6×10^3
2.5	0.668×10^5	25.6×10^3

Concentration function

$$k_1 = a\,R_i^b$$

Reaction temperature, °F.	a, lb. mole	b, unitless
	(cu. ft.) (sec.)	
200	1.41×10^{-3}	¾
250	4.40×10^{-4}	¾
300	1.11×10^{-4}	¾

maintained in the liquid phase. The reactor product was chilled after leaving the constant temperature zone and was collected in a sample bottle. A sample was not taken until after the flow rates and temperature had been maintained over a period of time which would allow the reactants to pass through the reactor. The sample was analyzed by the method used by Davis, Von Waaden, and Kurata(4).

When catalytic runs were made, the sulfuric acid catalyst was mixed with the feed water. In order to stop the reaction effectively, the product sample was immediately neutralized with sodium hydroxide.

Under certain conditions two liquid phases are possible for this system. The solubility data of Wickert, Tamplin, and Shank(9) were extended for use at higher temperatures. Conditions for study were then chosen which would ensure the reactant mass being in the single liquid phase.

RESULTS

Noncatalytic Reaction. The results of thirty noncatalytic runs are summarized in Table 1. The uncatalyzed reaction was found to be pseudo first order with respect to the propylene oxide concentration. The reaction-rate constants were calculated from the integrated equation below, which was derived from the basic assumption that the rate of reaction is proportional to the mole fraction of propylene oxide. The relationship between the measurable quantities (V_R, F, X, A') was further developed starting with the material balance over a differential section of the flow reactor, as suggested by Hougen and Watson(5).

$$CH_3 - C_2H_3O + H_2O \longrightarrow$$
$$CH_3 - CHOH - CH_2OH$$

$$A + B \longrightarrow C$$

or

$$\frac{V_R}{F} = \frac{1}{k_1}\left[(1-A')\ln\frac{1}{1-X} + A'X\right]$$

where

A' = initial concentration of propylene oxide, mole fraction

F = total feed rate, lb. moles/sec.
k_1 = first-order reaction-rate constant, lb. mole/(cu. ft.)(sec.)
V_R = reactor volume, cu. ft.
X = fractional conversion of propylene oxide

A representative reaction constant was found for each series of runs at a given temperature and feed ratio but with varying feed rates. The representative rate constant was found by fitting a calculated curve to the experimental points as shown in Figure 5. Similar procedures were carried out at other temperatures and feed ratios. The effect of temperature on the reaction-rate constant at three different feed ratios is shown in Figure 6.

The value of the reaction-rate constant was found to change with the initial propylene oxide concentration. This effect is correlated for three different reaction temperatures, as shown in Figure 7. The equation of the line is of the form

$$k_1 = aR_i^b$$

where

a = constant for a given temperature, lb. moles/(cu. ft.)(sec.)
b = constant for uncatalyzed reaction, unitless
k_1 = reaction-rate constant, lb. mole/(cu.ft.)(sec.)
R_i = feed ratio of reactants, lb. water/lb. propylene oxide

The values of the constants for the Arrhenius equation as obtained from Figure 6 and the constants obtained for the curves in Figure 7 are given in Table 2.

Catalytic Reaction. The summarized results of the reaction catalyzed with sulfuric acid are available elsewhere.* This reaction was found to be pseudo second order with respect to the mole fraction of propylene oxide. The rate constants were computed by use of the integrated form of the second-order rate expression for the reaction:

$$\frac{V_R}{F} = \frac{1}{k_2}\left[\frac{(1-A')^2}{A'}\left(\frac{\wedge}{1-X}\right) + A'X + (A'-1)\ln(1-X)^2\right]$$

where

A' = initial concentration of propylene oxide, mole fraction
F = total feed rate, lb. moles/sec.
k_2 = second-order reaction-rate constant, lb. mole/(cu.ft.)(sec.)
N_A = concentration of propylene oxide at any time, mole fraction
V_R = reactor volume, cu.ft.
X = fraction conversion of propylene oxide

This expression was derived on the assumption that the rate of reaction is proportional to the square of the mole fraction of propylene oxide and that there is no competing reaction for propylene oxide. This latter asumption is true except for twelve of the catalytic runs in which detectable amounts of dipropylene glycol were formed. The results of these twelve runs are given in Table 3. It is seen from this table that the conversion of propylene oxide to di-propylene glycol did not exceed 2% and that the conversion to propylene glycol varied from 23 to 90%. The effect of the competing reaction upon the calculation of the rate constant was therefore negligible.

A representative reaction-rate constant was found for each series of runs at a given temperature, feed ratio, and catalyst concentration but at different throughput rates. The rate constant was found in the same manner as for the uncatalyzed reaction. Figure 8 shows the computed and the experimental curves of fractional conversion vs. V_R/F at 100°, 125°, and 150°F. for a feed ratio of 10 lb. water/lb. propylene oxide when the catalyst concentration is 0.05 wt. %. Similar curves were drawn for other catalyst concentrations and feed ratios.

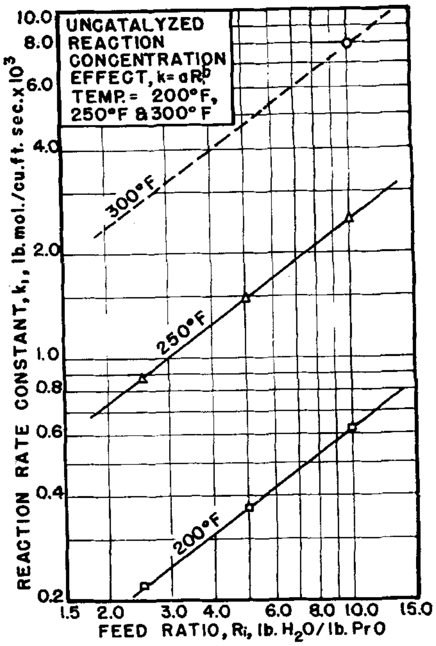

FIG. 7. CONCENTRATION EFFECT FOR UNCATALYZED REACTION.

The effect of temperature on the reaction-rate constant is shown in Figure 9 for different catalyst concentrations and feed ratios.

For conditions of constant temperature and acid concentration, the effect of the initial feed ratio on the rate constant was correlated as shown in Figure 10. The curve is of the form $k_2 = aR_i^b$.

The effect of the catalyst concentration on the rate constant at reaction temperatures of 100°, 125°, and 150°F. and with feed ratios of 5 and 10 is shown in Figures 11 and 12.

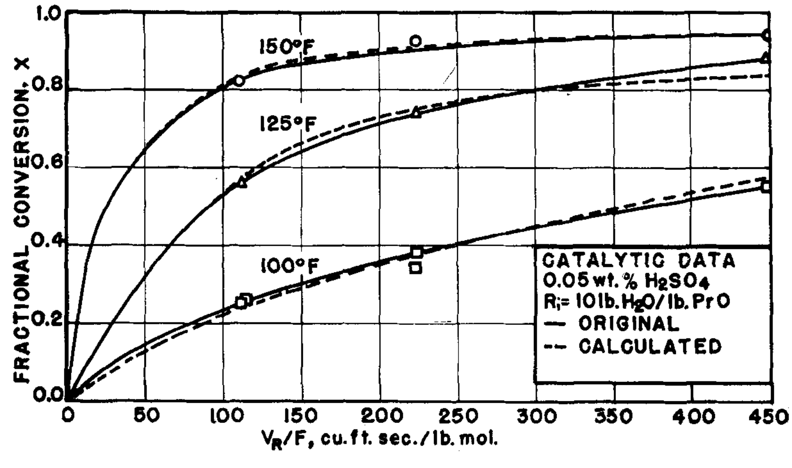

FIG. 8. CATALYTIC DATA, CONVERSION OF PROPYLENE OXIDE TO GLYCOL, 0.05 WT. % H_2SO_4, 10 LB. H_2O/LB. PrO.

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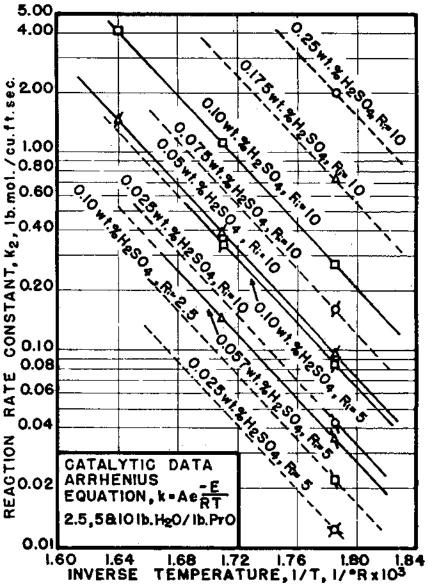

FIG. 9. ARRHENIUS RELATIONSHIP FOR CATALYZED REACTION.

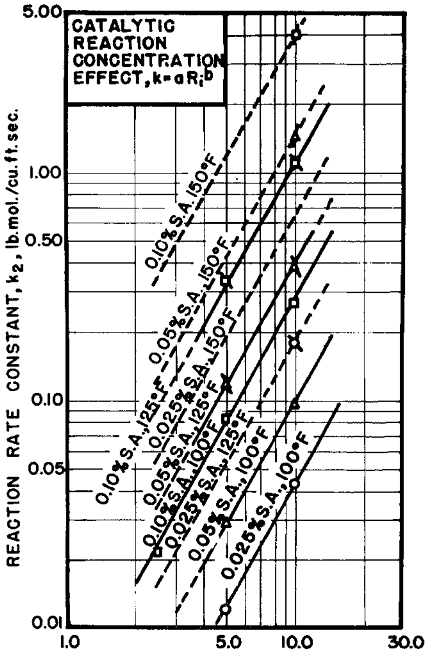

FIG. 10. CONCENTRATION EFFECT FOR CATALYZED REACTION.

The constants for the Arrhenius equation as obtained from Figure 9 and for the effect of the feed ratio as taken from Figure 10 are given in Table 4.

DISCUSSION OF RESULTS

A comparison of the correlation with the experimental data points has been made in order to estimate the accuracy of the correlation, which was used to calculate the experimental data points as shown by dashed lines in Figures 5 and 8. For the uncatalyzed reaction the average percentage of deviation of the correlation from the experimental points was found to be 9.6, and the standard deviation was 0.024. The average percentage of deviation for the catalyzed reaction was 3.8 and the standard deviation was 0.026.

Since other experimental data for this reaction are not available in the literature, a direct comparison of this study cannot be made; however, data are available for a few other epoxide reactions.

Brönsted et al.(*1*) and Lichtenstein and Twigg(*6*) studied the liquid-phase hydration of ethylene oxide. Both groups found that the uncatalyzed reaction was first order with respect to ethylene oxide. This may be compared with the pseudo first-order rate found for the uncatalyzed reaction of this study. Brönsted et al.(*1*) studied the perchloric acid catalyzed hydration of ethylene oxide and found this reaction to be first order with respect to ethylene oxide and the rate to be proportional to the hydrogen ion concentration. In the present study such a simple dependence on the hydrogen ion was not found, and the catalytic reaction was found to be second order with respect to propylene oxide.

Lichtenstein and Twigg(*6*) studied the sodium hydroxide catalyzed reaction and found that the reaction-velocity constant could be expressed as follows: $k = a\,[\mathrm{OH^-}] + b\,[\mathrm{OH^-}]^2$. Smith, Wode, and Widhe(*8*) caried out kinetic studies on the liquid-phase hydration of ethylene oxide with perchloric and nitric acids as a catalyst. They found that the rate of this reaction was independent of the kind of acid used. Percorini(*7*), studying the reaction of propylene oxide with methanol to form 1-methoxy-2-propanol by use of a sodium hydroxide catalyst, found the effect of the sodium hydroxide to be one of direct proportionality.

CONCLUSIONS

The kinetics of the catalyzed and uncatalyzed homogeneous liquid-phase hydration of propylene oxide to form propylene glycol have been studied and the results correlated in a form convenient for the design of reactors.

The uncatalyzed reaction was found to be pseudo first order with respect to the concentration of propylene oxide. From the results of the uncatalyzed study, the reaction-rate constants for different initial propylene oxide concentrations have been expressed as a function of the feed ratio of water to propylene oxide.

The reaction catalyzed with sulfuric acid was found to be pseudo second order with respect to the concentration of propylene oxide. The rate constant for this reaction has been expressed as a function of the acid concentration, feed ratio, and temperature.

In order to check the accuracy of the correlations obtained from this

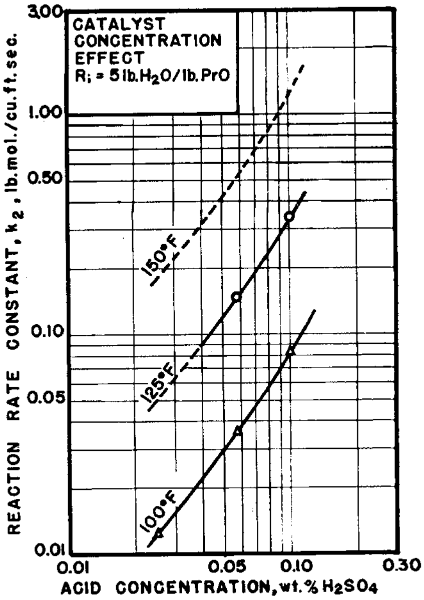

FIG. 11. EFFECT OF CATALYST CONCENTRATION UPON REACTION RATE.

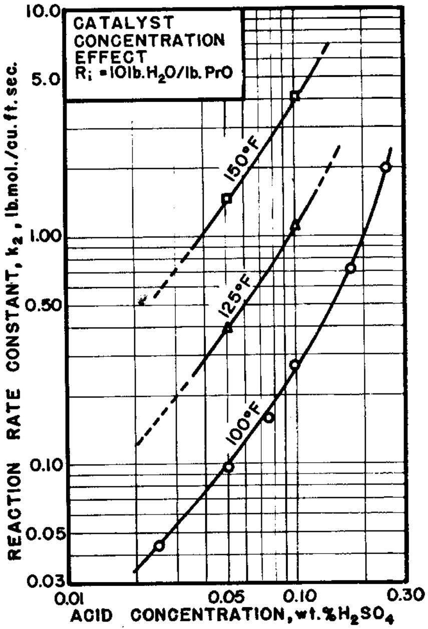

FIG. 12. EFFECT OF CATALYST CONCENTRATION UPON REACTION RATE.

TABLE. 3.—DISTRIBUTION OF PRODUCTS FOR RUNS WHERE DIPROPYLENE GLYCOL WAS FORMED

Run	Reaction temp., °F.	Catalyst conc. H_2SO_4, wt. %	Feed ratio R_i, $\frac{\text{lb. } H_2O}{\text{lb. PrO}}$	V_R/F, cu. ft./(sec.)(lb. mole)	Propylene oxide conversion, fraction: to glycol X_1	to diglycol X_2	Total X_T
72	125	0.10	5.0	108.5	0.633	0.012	0.645
70	125	0.10	5.0	216.9	0.829	0.007	0.836
71	125	0.10	5.0	309.9	0.887	0.017	0.904
78	100	0.10	5.0	108.5	0.326	0.007	0.333
76	100	0.10	5.0	216.9	0.512	0.007	0.519
77	100	0.10	5.0	309.9	0.625	0.009	0.634
79	125	0.05	5.0	108.5	0.497	0.008	0.505
80	125	0.05	5.0	216.9	0.634	0.009	0.643
81	125	0.05	5.0	309.9	0.722	0.010	0.732
82	100	0.10	2.5	102.5	0.228	0.004	0.232
83	100	0.10	2.5	205.0	0.321	0.006	0.327
84	100	0.10	2.5	356.5	0.451	0.007	0.458

study, they were used to compute the conversion of propylene oxide. These calculated conversions were compared with the experimental conversions, and standard deviations and percentage errors were computed. The standard deviation for the uncatalyzed runs was 0.024 and the average percentage deviation was found to be 9.6. The catalytic data show a standard deviation of 0.026 and an average percentage deviation of 3.8.

ACKNOWLEDGMENT

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TABLE 4.—CONSTANTS CHARACTERISTIC OF CATALYZED REACTION

Arrhenius constants

$$k_2 = Ae\frac{-E}{RT}$$

Feed ratio, R_i, $\frac{\text{lb. } H_2O}{\text{lb. PrO}}$	Catalyst concentration, H_2SO_4, wt. %	A, $\frac{\text{lb. mole}}{\text{(cu. ft.) (sec.)}}$	Energy of activation E, $\frac{\text{B. t. u.}}{\text{lb. mole}}$
10.0	0.025	1.09×10^{13}	36.9×10^3
10.0	0.050	2.42×10^{13}	36.9×10^3
10.0	0.075	4.04×10^{13}	36.9×10^3
10.0	0.100	6.82×10^{13}	36.9×10^3
10.0	0.175	18.2×10^{13}	36.9×10^3
10.0	0.250	50.5×10^{13}	36.9×10^3
5.0	0.025	0.318×10^{13}	36.9×10^3
5.0	0.057	0.909×10^{13}	36.9×10^3
5.0	0.100	2.10×10^{13}	36.9×10^3
2.5	0.100	0.555×10^{13}	36.9×10^3

Concentration function

$$k_2 = a R_i^b$$

Reaction temperature. °F.	Catalyst concentration, H_2SO_4, wt. %	a, $\frac{\text{lb. mole}}{\text{(cu. ft.) (sec.)}}$	b, unitless
100	0.10	0.00428	1.8
100	0.05	0.00155	1.8
100	0.025	0.000682	1.8
125	0.10	0.0174	1.8
125	0.050	0.00634	1.8
125	0.025	0.00285	1.8
150	0.10	0.0650	1.8
150	0.050	0.0230	1.8
150	0.025	0.0106	1.8

NOTATION

A = proportionality factor defined by the Arrhenius equation, lb. mole/(cu.ft.) (sec.)
A' = initial concentration of propylene oxide, mole fraction
a = constant for a given temperature and catalyst concentration, units of k
b = constant for reaction, value depending only on whether a reaction is catalyzed, unitless
E = molal energy of activation, B.t.u./lb. mole
F = feed rate, lb. mole/sec.
k_1 = specific reaction-rate constant for first-order reaction, lb. mole/(cu.ft.) (sec.)
k_2 = specific reaction-rate constant for second-order reaction, lb. mole/(cu.ft.) (sec.)
N_A = propylene oxide concentration, mole fraction
R = gas-law constant, B.t.u./(lb. mole) (°R.)
R_i = initial feed ratio of water to propylene oxide, lb./lb.
T = absolute temperature, °R.
V_R = volume of reactor, cu.ft.
X = fractional conversion of propylene oxide, lb. mole converted/lb. mole fed
PrO = propylene oxide

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