The Addition of Ethylene Oxide to Butanol in the Presence of HY Zeolite as Catalyst

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Studies concerning the catalytic activity of Zeolite HY in ethylene oxide addition to *n*-butanol at reactant molar ratio of 1:1 demonstrated the effects of catalyst amount and temperature upon alcohol conversion (max 64.2%) and product composition. The reaction produced butyl monoethers of mono-, di-, and triethylene glycol as the main products. Such a composition, different from the Poisson distribution usually observed in reactions catalyzed with acids, indicates the operation of sieve effect, due to the geometrical structure of catalyst, the distribution of active centers and the configuration of the oxyethylene chains being formed.

Minor reaction products, such as acetaldehyde, *p*-dioxane, 2-methyl-1,3-dioxolane and polyglycols, were the same as formed in reactions carried out in the presence of traditional acid catalysts. However, there was demonstrated also the formation of butanal-1, butanone-2, and 2-propyl-1,3-dioxolane, not reported previously.

The specificity of the HY catalyst and the reaction mechanism are discussed.
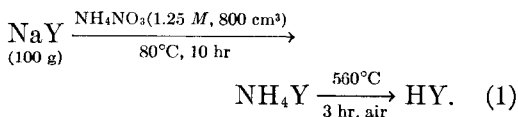
INTRODUCTION

Oxyethylenated alcohols belong to the most important groups of nonionic surface active substances. They are obtained by ethylene oxide addition to suitable alcohols in the presence of acid or basic catalysts (*1, 2*). Although the addition of ethylene oxide to alcohols has been known for a long time the effects of catalysts in this reaction are open to continuous study because catalysts have profound effects on the composition of the addition products, and therefore affect their surface active and other useful properties.

We turned our attention to synthetic zeolites which have recently found wide application as catalysts for many organic

reactions, including isomerizations (*3–5*) and addition reactions (*6, 7*) of alkylene oxides. In this paper we report the results of our studies on ethylene oxide addition to *n*-butanol in the presence of active forms of zeolite H-Y.

EXPERIMENTAL METHODS

Preparation of catalyst. The starting material for the catalyst was Na-Y powder (obtained from the Institute of Industrial Chemistry, Warsaw, Poland). Its composition was as follows: $0.98 \ Na_2O \cdot Al_2O_3 \cdot 5.21 \ SiO_2 \cdot H_2O$. The active forms were prepared by ion-exchange with aqueous NH_4NO_3 solutions:

$$NaY \underset{(100 \ g)}{} \xrightarrow[80°C, \ 10 \ hr]{NH_4NO_3(1.25 \ M, \ 800 \ cm^3)} $$

$$NH_4Y \xrightarrow[3 \ hr, \ air]{560°C} HY. \quad (1)$$

The degree of ion exchange in the hydrogen forms thus obtained, as measured by flame

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photometry, was within 78–82%. The catalyst was used as powder; prior to the reaction it was dried at 120°C.

Materials. n-Butanol, analytical grade, was distilled and stored over 13 X Zeolite. Ethylene oxide (Fluka, Switzerland) had a purity better than 99.8%. It was used without further purification.

Apparatus and procedure. The reactions of ethylene oxide addition to n-butanol as reactant were carried out periodically in a standard glass apparatus (round-bottom flask equipped with a mechanical stirrer, thermometer, inlet tube and condenser) under normal pressure by passing gaseous ethylene oxide into a suspension of a varying amount of catalyst in 0.5 mole alcohol. The rate of flow of ethylene oxide was regulated with a valve. The reactions were carried out at temperatures maintained within ±1°C. When the desired reactant conversion was achieved, as given by the amount of consumed ethylene oxide (determined by weighing) the reaction was discontinued, the product cooled, weighed and samples were taken for analysis.

Analysis. The qualitative and quantitative composition of reaction products was determined by gas–liquid chromatography using a Perkin–Elmer F11 apparatus with a flame-ionization detector. Glass columns (1 m) packed with 20% Carbowax M20 on Chromosorb G 60/80 mesh or with 8% Apiezon L Gas Chrom P 80/100 mesh, were used. The temperatures were held in the range of 80–200°C with nitrogen as a carrier gas (20–50 ml/min). The content of polyglycols in the reaction products was determined by the extraction method described by Blomeyer (8). Infrared spectra were recorded by means of a UR-20 Zeiss spectrophotometer, using liquid films in a NaCl cell.

RESULTS AND DISCUSSION

All studies were performed at a reactant molar ratio of 1:1 with catalyst amount and temperature as variable parameters.
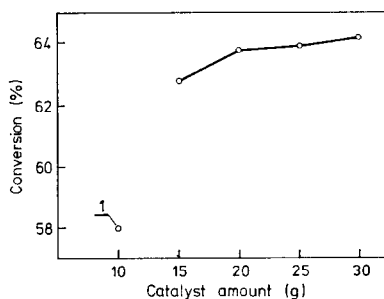

FIG. 1. Effect of catalyst amount on conversion of butanol. Reaction temperature: 80°C; (1) $C_2H_4O/C_4H_9OH = 0.9$.

Effect of Reaction Conditions on Conversion

The effect of catalyst amount on butanol conversion is shown in Fig. 1. With amounts of over 20 g of catalyst/mole of alcohol the conversion of alcohol does not increase very much over 64% and smaller amounts significantly prolong the period necessary for ethylene oxide conversion, as shown in Fig. 2.

The effect of temperature in the range of 70–110°C at the optimum catalyst amount (20 g/mole of butanol) upon alcohol conversion is shown in Fig. 3. A distinct maximum of alcohol conversion is seen at temperatures of 80–90°C.

Composition of Reaction Products

The reaction products are multicomponent mixtures containing, in addition to unreacted material, the butyl monoethers of ethylene glycols and side products. In Table 1 there is shown the composition of oxyethylenation products of butanol at 80°C with variable amounts of catalyst. The results indicate that the catalyst amount does not significantly affect the qualitative and quantitative composition of the fraction containing the butyl ethers of ethylene glycols. Also the reaction temperature is without any significant effect on the product composition. These results are in accord with data reported by Tischbirek (9) in his studies on the oxyethylen-

ation of alcohols in the presence of catalysts of Lewis acid type.

As the main products of ethylene oxide reaction with butanol there are formed the butyl monoethers of ethylene, diethylene and triethylene glycols. In all cases chromatographic analysis failed to indicate the presence of any monoethers of higher ethylene glycols. Thus, our results are different from those obtained so far in studies involving acid catalysts, whether protonic or Lewis acids. In the presence of homogeneous acid catalysts there are usually obtained mixtures of homologous alkyl ethers of ethylene glycols and the compositions of these mixtures correspond approximately to the distribution curve calculated from the Poisson equation (9, 10). Figure 4 shows distribution curves for an average oxyethylenation degree equal to 1.02 (i.e., 1.02 moles of ethylene oxide reacted with 1 mole of alcohol). The shapes of the curves indicate that the composition of the product obtained with $BF_3 \cdot Et_2O$ (curve 2) does not differ very much from the composition curve calculated from the Poisson equation at the same oxyethylenation degree (curve 1). On the other hand, the composition of the product obtained with HY catalyst (curve 3) is much different from the calculated composition. The highest homologue contains
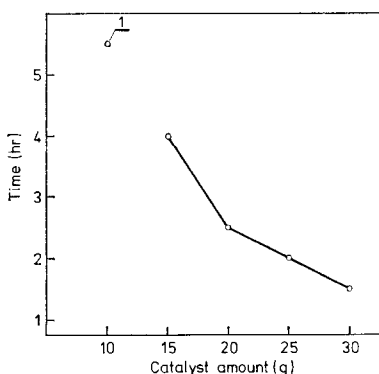

FIG. 3. Effect of temperature on conversion of butanol. Catalyst amount: 20 g/mole C_4H_9OH; (1) C_2H_4O/C_4H_9OH = 0.90.

only three oxyethylene groupings and the amount of lowest homologue ($n = 1$) is much larger than expected on the basis of the Poisson equation.

Apart from the products of ethylene oxide addition to butanol the reaction mixture was found to contain several side products, including polyglycols $HO(CH_2CH_2O)_nH$ and the following compounds identified by gas chromatography: acetaldehyde, p-dioxane, 2-methyl-1,3-dioxolane, 2-propyl-1,3-dioxolane, butanal-1, and butanone-2. The effect of catalyst amount on the formation of some of the side products is shown in Table 2. Butanal-1 and butanone are not included in Table 2 because their content in the reaction mixture is very small. Fractions enriched in these compounds were obtained by fractional distillation of combined products of several runs. The ir spectra of these fractions contained bands characteristic for carbonyl groups. Data in Table 2 present the sum of acetaldehyde and nonreacted ethylene oxide contained in the reaction products. These compounds had identical retention times on both column packings used in this study. The presence of acetaldehyde was demonstrated by chemical methods in gases escaping from the reactor.

Data in Table 2 indicate that the amount of catalyst has only a slight effect on the amount of polyglycols and is almost without any effect on the yields of other side

FIG. 2. Effect of catalyst amount on time of conversion of 1 mole of ethylene oxide. Reaction temperature: 80°C; (1) C_2H_4O/C_4H_9OH = 0.89.

TABLE 1

The Composition of Products of Ethylene Oxide Addition to Butanol[a]

No.	Mole ratio of reactants $C_2H_4O/$ C_4H_9OH (mole/ mole)	Amount of cata- lyst (g/mole)	Reac- tion time (hr)	Conver- sion of C_4H_9OH (%)	Composition of reaction mixture (wt%)						
					Unre- acted C_4H_9OH	Butyl ether of ethylene glycols				Poly- glycols	Other by- products (total)
						C_4E_1[b]	C_4E_2[c]	C_4E_3[d]	Total		
1	0.89	10	5.5	58.0	27.3	45.8	15.3	3.9	65.0	2.1	5.4
2	1.00	15	4.0	62.8	23.3	47.2	16.5	4.4	68.1	2.3	6.3
3	1.02	20	2.5	63.8	22.5	47.6	16.4	5.0	69.0	2.8	5.7
4	1.03	25	2.0	63.9	22.4	47.4	16.7	5.1	69.2	3.0	5.4
5	1.05	30	1.5	64.2	22.0	47.0	17.2	5.2	69.4	3.2	5.4

[a] Reaction temperature, 80°C.
[b] Ethylene glycol monobutyl ether.
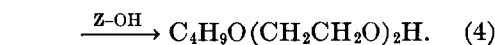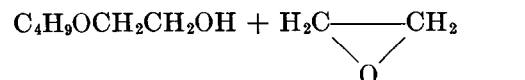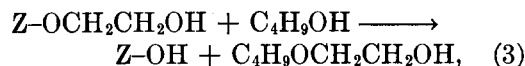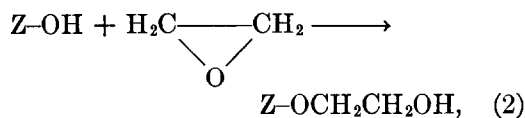[c] Diethylene glycol monobutyl ether.
[d] Triethylene glycol monobutyl ether.

products. Increasing temperature is without any effect on the yields of p-dioxane and 2-methyl-1,3-dioxolane but produces increasing amounts of polyglycols and 2-propyl-1,3-dioxolane. Quantitative relations at temperatures in the range of 70–110°C are presented in Fig. 5.
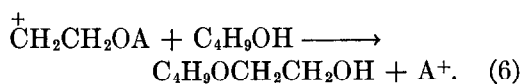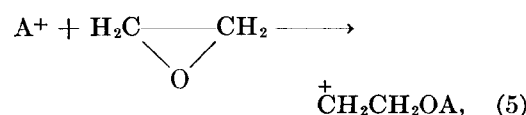
Reaction Mechanism

In the HY zeolites obtained in this study by decomposition of NH_4Y forms at 550°C there are present acid sites of both Brønsted and Lewis type (11). These sites can participate in ethylene oxide addition to butanol as shown by the following equations:

Brønsted acid sites (Z–OH):

$$Z-OH + H_2C\underset{O}{\overset{}{\diagdown\diagup}}CH_2 \longrightarrow$$

$$Z-OCH_2CH_2OH, \quad (2)$$

$$Z-OCH_2CH_2OH + C_4H_9OH \longrightarrow$$
$$Z-OH + C_4H_9OCH_2CH_2OH, \quad (3)$$

$$C_4H_9OCH_2CH_2OH + H_2C\underset{O}{\overset{}{\diagdown\diagup}}CH_2$$

$$\xrightarrow{Z-OH} C_4H_9O(CH_2CH_2O)_2H. \quad (4)$$

Lewis acid sites (A+):

$$A^+ + H_2C\underset{O}{\overset{}{\diagdown\diagup}}CH_2 \longrightarrow$$

$$\overset{+}{C}H_2CH_2OA, \quad (5)$$

$$\overset{+}{C}H_2CH_2OA + C_4H_9OH \longrightarrow$$
$$C_4H_9OCH_2CH_2OH + A^+. \quad (6)$$

In both cases the first stage includes ethylene oxide addition to acid followed by alcoholysis of the ester producing the monoether of ethylene glycol. Alcoholysis can be effected by the starting alcohol or by ether–alcohol. In the latter case the
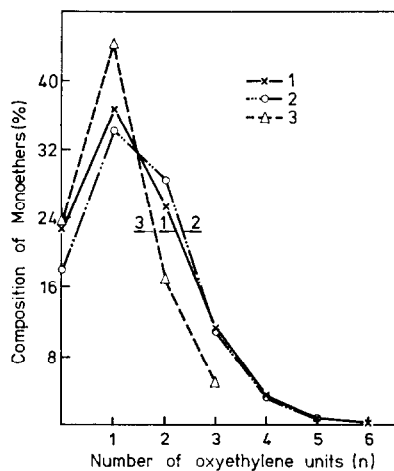

FIG. 4. Distribution curves of homologous ethers for oxyethylenation degree 1.02. (1) Poisson distribution; (2) Distribution of the product with $BF_3 \cdot Et_2O$ as catalyst (0.5% by weight; reaction temperature, 40°C); (3) Distribution of the product with HY as catalyst (20 g/mole; reaction temperature, 80°C)

TABLE 2

The Composition of By-products[a]

No.	Amount of catalyst (g/mole)	Content of by-products (wt%)				
		$CH_3CHO +$ C_2H_4O	2-Methyl-1,3-dioxolane	p-Dioxane	2-Propyl-1,3-dioxolane	Polyglycols
1	10	3.0	0.7	0.6	1.1	2.1
2	15	1.8	0.8	2.6	1.1	3.2
3	20	1.2	1.0	2.3	1.2	2.8
4	25	0.9	1.0	2.3	1.2	3.0
5	30	0.9	1.0	2.2	1.3	3.2

[a] Conditions: reaction temperature, 80°C; molar ratio $C_2H_4O/C_4H_9OH = 1$.

monoethers of higher ethylene glycols are formed.

It is necessary to explain why the reaction stops when the butyl ether of triethylene glycol is produced. This is probably due to steric factors involving the catalyst as well as reaction products. For example, the results of recent studies by Barrer and Oei (12) indicate that the polymerization of vinyl ethers takes place on active centers inside the pores (empty spaces) of HY zeolite. During reaction the polymer formed blocks the active intracrystalline sites. For this reason the stage of initiation predominates over the growth of polymer chain and products of low molecular weight are formed.

On the other hand Langbein (13) has observed that the terminal OH groups in monoethers of polyoxyethylene glycols form intramolecular hydrogen bonds with oxygen atoms in the polyoxyethylene chain. Because of this the chain ends are bent towards the oxyethylene chain and the hydrogen atom occupies a specific position in the space surrounding the second and/or more remote oxygen atoms. For this reason the molecule of the butyl ether of diethylene glycol occupies a large volume and has only a slight chance of entering the pores of HY zeolite and, consequently, the yield of triethylene glycol ether is small and no

tetraethylene glycol ether is formed at all. One has to consider also that the reaction takes place in butyl alcohol as solvent. The molecules of alcohol hydrogen-bonded to oxyethylene chain can make the penetration still more difficult.

The side products are formed in reactions involving the initial reactants. Acetaldehyde, p-dioxane, polyglycols and 2-methyl-1,3-dioxolane are always present in acid catalyzed addition products of ethylene oxide to alcohols (9, 14). The presence of butanal-1, butanone-2, and 2-propyl-1,3-dioxolane in products of alcohol oxyethylenation on zeolite HY as acid catalyst has not been observed previously. The first two compounds result probably from butanol oxidation on HY catalyst (15, 16). 2-Propyl-1,3-dioxolane is formed in a reaction
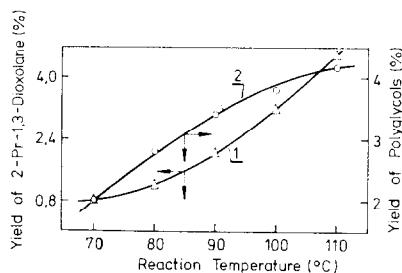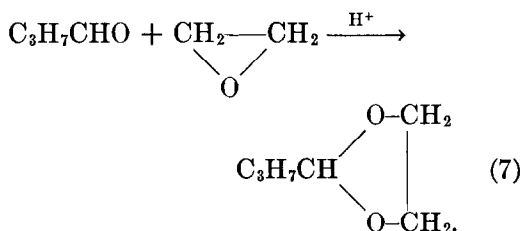

FIG. 5. Effect of temperature on yield of by-products: (1) 2-propyl-1,3-dioxolane; (2) polyglycols.

of butanal-1 with ethylene oxide:

$$C_3H_7CHO + CH_2{-}CH_2 \xrightarrow{H^+}$$

with the O bridging the two CH_2 groups

$$C_3H_7CH\begin{array}{c} O{-}CH_2 \\ | \\ O{-}CH_2. \end{array} \quad (7)$$

Increasing amounts of 2-propyl-1,3-dioxolane at higher temperatures (Fig. 5) appear to confirm this pathway of its formation, which requires that butanol is first oxidized to butanal.

Studies concerning the reaction of ethylene oxide with aliphatic alcohols in the presence of active forms of zeolites are being continued.

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