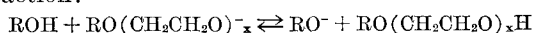


The Reactions of Alkylene Oxides with Various Butyl and Other Alcohols¹

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Abstract

Acid-catalyzed additions of ethylene oxide to various isomeric butyl alcohols were observed to agree with the Poisson equation and the products were relatively unaffected in composition by changes in the reactants or reaction conditions. Base-catalyzed reactions yielded products whose composition could be more closely approximated by Weibull and Nycander's equations. The product composition, although largely independent of reaction conditions, varied with the structure of the starting alcohol. Good correlation was found between the relative acidities of the starting alcohols and their reaction products and Weibull-Nycander distribution constants for base-catalyzed reactions of ethylene oxide and propylene oxide. It is believed that the relative acidities of the alcohol and its epoxide adduct influence the product composition through the equilibrium reaction:



Introduction

THE POLYMERIZATION of a cyclic monomer such as ethylene oxide can be initiated by substances, such as alcohols, which contain an active hydrogen group and are capable of cleaving the oxirane ring with the generation of a new hydroxyl group. Since the hydroxyl group which is thus formed may add additional monomer, the process can be continued until the desired degree of polymerization is achieved. Thus the polymerization is usually pictured as a series of successive competitive reactions of the epoxide with the alcohol and its products. Kinetically, the polymerization has some of the character of both a vinyl addition and a condensation polymerization. At intermediate stages of the reaction the product consists only of polymer and unreacted monomer similar to a vinyl addition reaction, and molecular growth occurs exclusively through addition of the monomer to the polymer. Similar to condensation polymerization, the various polymer molecules undergo more or less simultaneous growth and the average molecular weight increases as monomer is consumed.

Since the growth of all polymer molecules occurs at roughly the same rate, it is possible to modify the properties of the polymer by varying the mol ratio of epoxide to alcohol reacted. This principle is utilized industrially in the manufacture of nonionic surface-active agents from epoxides and high molecular weight fatty alcohols. Considerable variation in the properties of the surfactant can be obtained by varying the mol ratio of epoxide to alcohol, thus changing the hydrophylic-lipophylic balance in the molecule. At a given average epoxide chain length it is expected that the properties of the mixture as a whole will be determined by the product distribution. Consequently, a knowledge of the product distribution and of reaction conditions which result in a change in product distribution becomes of considerable practical importance.

Theoretically, it is possible to calculate the product distribution if certain assumptions concerning the relative reactivities of the starting alcohol and its epoxide adduct are accepted. Thus, if the relative reactivities of all of the competing alcohols are equal, Flory (1) has shown that the Poisson formula applies:

$$n_i/n_{oo} = e^{-V} V^{i-1}/(i-1)! \quad [\text{A}]$$

where:

V = mol ratio of epoxide to alcohol reacted

n_{oo} = no. of mols of starting alcohol

n_i = no. of mols of product containing i epoxide units

The Poisson distribution has been reported to describe the base-catalyzed reaction of ethylene oxide with ethylene glycol (2), and also the reaction of ethylene oxide with lauryl alcohol (3). Other theoretical distributions have been advanced in which the relative reactivities of either all (4) or some (2,7) of the alcohols formed are considered unequal. The simplest of these is that developed by Weibull and Nycander (2) resulting in equations [B] and [C] which are based on the assumption that the relative reactivity of the products are equal, but differ from the starting alcohol.

$$V = c \ln(n_{oo}/n_o) - (c-1)[1 - (n_o/n_{oo})] \quad [\text{B}]$$

$$n_i/n_{oo} = [c^{i-1}/(c-1)^{i-1}] \{ (n_o/n_{oo}) -$$

$$(n_o/n_{oo})^c \sum_{j=0}^{i-1} (1/j!) [(c-1) \ln(n_{oo}/n_o)]^j \} \quad [\text{C}]$$

where:

n_o = no. of mols of starting alcohol in product

c = distribution constant, a measure of the relative reactivities of the products to that of the starting alcohol.

This approach appears to be a reasonable compromise, since in all steps except the first the hydroxyl group is attached to an oxyethylene group. Several investigators have utilized the Weibull-Nycander equations to interpret the reactions of ethylene oxide with ethanol (2), tetradecanol (5), and lauryl alcohol (6).

The object of the present work was threefold. First, it was deemed important to determine how the product composition of epoxide reactions varied with reaction conditions, e.g., mol ratio of epoxide to alcohol reacted, catalyst, temperature, etc. Second, the validity of the Weibull-Nycander equation for the base-catalyzed reaction was tested against different alcohols and epoxides. Finally, a reaction mechanism for the base-catalyzed reaction was considered and several factors, such as the rate of the individual epoxide addition reaction and the relative acidity of the competing alcohols, were investigated.

Most of the work was done using isomeric butyl alcohols because of the ease with which their lower oxyethylene ethers could be separated by fractional distillation. Some experiments were conducted with higher molecular weight alcohols in order to determine the extent to which the results using butyl alcohol enable us to predict the composition of higher molecular weight alcohols reacted with many moles of ethylene oxide, where fractionation by distillation or solvent separation is not achievable.

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Experimental

Materials. Commercial ethylene oxide and the best available grade of alcohols were used in the epoxide addition reactions. Most of the alcohols were distilled before use. In selecting materials for use in the acidity measurements, more elaborate precautions were taken to be sure that they were free from trace impurities, such as acids or conducting salts. Whenever possible, gas-liquid chromatography (GLC) was used to establish purity. The electrical conductivity was also measured at a concentration greater than that used in the determination of the ionization constant and compared with that of water itself. Some of the alcohols containing several ether oxygens were unstable in the alkaline isopropanol solution used in the spectrophotometric study. These solutions become stable when treated to remove peroxides.

Compounds not commercially available were prepared as follows:

1-(2 hydroxyethoxy) propane-2-ol was fractionated from a base-catalyzed reaction product of propylene oxide and ethylene glycol

[bp110C (6mm) ; $n_D^{20} = 1.4435$.]

Ethylene glycol mono-sec-butyl ether [bp158C ; $n_D^{20} = 1.4170$] and diethylene glycol mono-sec-butyl ether [bp97C (8mm) ; $n_D^{20} = 1.4297$] were fractionated from the neutralized reaction product of ethylene oxide and the sodium salt of sec-butanol in toluene (8).

Alkylene Oxide Reactions. The reactions were conducted in a one-liter stainless steel, bottom-stirred autoclave provided with an internal cooling coil and automatic temperature and pressure recorders and inlet tubes for ethylene oxide and nitrogen additions. The commercially available epoxides were charged in increments to the starting alcohol at reaction temperature in a nitrogen atmosphere. The incremental additions were made from a calibrated cylinder maintained under a nitrogen pressure in excess of that in the autoclave.

By carefully monitoring the epoxide additions it was possible to follow the rate of epoxide consumption during the course of the reaction. At intermediate stages the epoxide consumption represents the rate of addition to a complex mixture of alcohols. However, at the start of the reaction the initial rate of consumption represents the rate of addition to the parent alcohol, as this is the only alcohol present. Initial reaction rate constants were calculated, based on the assumption that the epoxide was ideally soluble in the parent alcohols, thus providing an estimate of the amount of the added epoxide in the liquid phase. Most of this work was done before the generalized application of the technique of GLC, and fractional distillation was utilized to separate the products. The distillations were conducted in a vacuum jacketed, spinning-band column, 6mm I.D. x 16 cm long, under atmospheric and reduced pressures. Many distillation fractions were essentially pure compounds according to refractive index or hydroxyl number determination. The other fractions were considered two component mixtures and analyzed by linear interpolation between the refractive indices or hydroxyl numbers of the pure compounds.

The procedure used in a typical run was: 199 g n-butanol containing 0.14 g dissolved sodium metal was charged to the reactor, which was flushed with nitrogen and heated to 120C. The reactor was vented

TABLE I

Fractional Distillation of the Reaction Product of Ethylene Oxide with n-butanol.

Mol Ratio (Epoxide/Alcohol) = 1.30

Fraction no.	Wt % of fraction	n_D^{20}	Analysis based on n_D^{20} (Wt % of total charge)				
			n-butanol	Monobutyl ether of			
				EG ^c	Di-EG	Tri-EG	Tetra-EG
1	5.45	1.3991	5.45
2	4.43	1.3993	4.43
3	3.38	1.3992	3.38
4	4.52	1.4190	4.52
5	4.07	1.4191	4.07
6	0.62	1.4266	0.26	0.36
7	9.39	1.4314	0.51	8.88
8	6.87	1.4316	0.26	6.61
9	0.38	1.4311	0.05	0.33
10	4.08	1.4388	0.28	3.80
11	6.36	1.4390	0.27	6.09
12	2.84	1.4388	0.20	2.64
13	1.71	1.4433	0.44	1.27
14	5.12	1.4446	0.09	5.03
15	1.07	1.4444	0.06	1.01
Trap	23.2	1.4063	15.0	8.2
Residue	16.2	1.4535
Total	99.7	28.3	17.9	16.9	13.1	7.31

n_D^{20} (pure component)	Monobutyl ether of				
	n-butanol	EG	Di-EG	Tri-EG	Tetra-EG
1.3993 ^a	1.4191 ^b	1.4321 ^a	1.4393	1.4447

^a Obtained from reference (17).

^b Obtained from reference (18).

^c EG = ethylene glycol.

to 10 psi and ethylene oxide was introduced until a pressure of 24 psi was obtained. A 4 psi drop in pressure was permitted, after which ethylene oxide was added until 24 psi pressure was obtained. Ethylene oxide was thus introduced intermittently until a total of 154 g was added over a period of 310 min. The charge was reacted to a constant pressure, cooled and removed. The product recovered in a 98.6% yield was a light yellow liquid with a hydroxyl number of 418 (theory = 427). Distillation of a sample of the reaction product yielded the fractions given in Table I.

Acidity Measurements. Two methods were used to determine alcohol acidity. The relative acidity of an alcohol in isopropanol was determined spectrophotometrically as described by Hine and Hine (9). These measurements were made with a Beckman Quartz Spectrophotometer Model DU, Serial No. 1178, using 1 cm or 10 cm silica cells. The data reported are the average of at least three (usually more) determinations over a wide range of alcohol concentration. Some of the polyethylene glycols gave results which vary with the concentration of the alcohol. The data reported for these compounds (in parentheses) were obtained by extrapolation to zero concentration and are considered less reliable.

Acid ionization constants were determined from the change in conductance observed when an alcohol is added to a dilute aqueous alkaline solution, as was described by Ballinger and Long (10). The conductivity measurements were obtained at a frequency of 2000 cycle/sec on an LKB Precision Conductivity Bridge Type 3216B. A conductivity cell (cell constant = 0.4600cm⁻¹) of conventional design with platinum electrodes was suspended in a mineral oil bath at 25 ± 0.005C. The procedure was essentially that described by Ballinger and Long. A value of 30 was assumed for the ionic mobility of the alcoholate ion.

Results and Discussion

The base-catalyzed reaction of ethylene oxide with n-butanol was investigated most extensively. The vari-

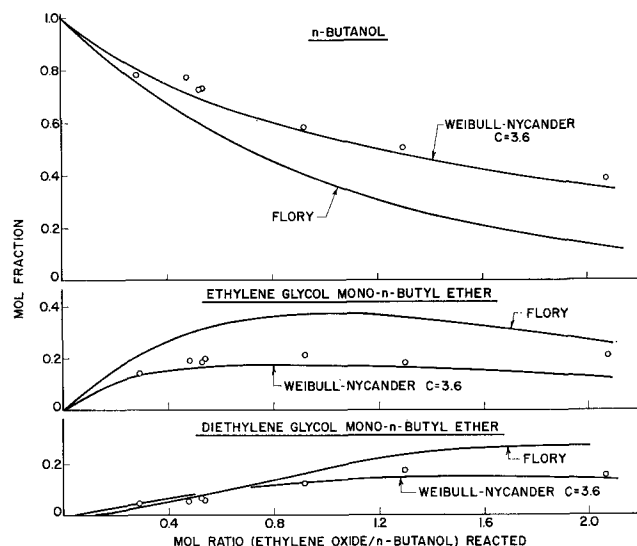


Fig. 1. The addition of ethylene oxide to n-butanol at 120°C in the presence of sodium n-butoxide. Variation of theoretical and experimental product composition with mol ratio of reactants.

ation of product composition with mol ratio of epoxide to alcohol reacted is shown in Figure 1.

Comparison of the experimental data with theory shows that the values predicted by the Flory equation deviate considerably from experiment, while those obtained with the Weibull-Nycander equations show better, though not perfect, agreement.

The theoretical Weibull and Nycander distributions were calculated from a distribution constant, $c = 3.6$. This is the average value of c calculated for each individual experiment shown in Figure 1. The c value for n-butanol is approximately the same as values reported by other workers; for ethanol, $c = 2.2$ (2); lauryl alcohol, $c = 2-3$ (6); and tetradecanol, $c = 3.0$ (5). The distribution constant, c , is a measure of the relative reactivity of the products versus that of the initial reactants. Since it is greater than unity, one can conclude that the n-butyl glycol ethers are more reactive towards ethylene oxide than is n-butanol itself.

Since the Weibull-Nycander equations approximate the experimental results, the distribution constant, c , can be used to compare product compositions obtained under varying reaction conditions with different reactants. Table II shows that the product composition of the base-catalyzed reaction of ethylene oxide with n-butanol is relatively unaffected by changes in reaction temperature, pressure, or catalyst concentration. Even variation in catalysts (as long as the catalyst is, or can be converted into, a base) has a minor effect upon the product composition, although the rate of ethylene oxide uptake may be varied considerably. Other workers (11,12) have also observed

TABLE II
The Reaction of Ethylene Oxide with n-Butanol

Catalyst	Temp C	EtO press psi	Cat. concn wt % of n-butanol charge	Weibull-Nycander c	k (l/mol min)
Sodium n-butoxide.....	55	8	1.1	3.2	0.11
Sodium n-butoxide.....	76	14	1.06	0.37
Sodium n-butoxide.....	110	14	0.30	3.0	2.6
Sodium n-butoxide.....	120	12	0.30	3.6	3.9
Sodium n-butoxide.....	130	11	0.30	3.4	7.5
Sodium n-butoxide.....	150	12	0.30	3.3	10
Benzyltrimethyl ammonium hydroxide....	100	16	1.0	2.7	5.7
N,N'-dimethylbenzyl amine.....	120	12	0.80	5.3	2.1
4-Methyl imidazole.....	120	11	0.44	2.7	4.2

TABLE III

The Base-Catalyzed Addition of Ethylene Oxide to Various Alcohols and Their Glycol Ethers

Catalyst = sodium alkoxide
Temp = 120°C

Alcohol	Weibull-Nycander c
n-Butanol.....	3.6
Isobutanol.....	6.1
sec-Butanol.....	29
tert-Butanol.....	ca. 300
Ethylene glycol mono-n-butyl ether.....	1.3
Diethylene glycol mono-n-butyl ether.....	1.1
Ethylene glycol mono-sec-butyl ether.....	1.3
n-Hexanol.....	3.1
n-Dodecanol.....	2.5
Tridecanol ^a	2.9

^a A mixture of highly branched alcohols having an average of 13 C atoms in the molecule.

that the product composition changes with the mol ratio of reactants, but is relatively independent of the reaction conditions.

Gee et al. (13) have shown that the base-catalyzed reactions of ethylene oxide with alcohols are first order with respect to the ethylene oxide and catalyst concentration, provided the catalyst (sodium alkoxide) is completely dissociated. In the present work a similar dependence of the initial rate of ethylene oxide consumption upon the epoxide and catalyst concentrations was observed and used to calculate rate constants for the addition of epoxide to the starting alcohol.

Initial rate constants for the sodium butoxide catalyzed addition of ethylene oxide to n-butanol are given for the temperature range 55–150°C. When these data were substituted in the Arrhenius equation an energy of activation of 14 kcal/g mol was obtained. This value agrees with that reported by Gee for the same reaction (13).

The base-catalyzed reaction is influenced by the structure of the alcohol. Table III shows that secondary and tertiary butyl alcohols are considerably less reactive than their ethylene oxide adducts, which are primary alcohols. Bases are considered poor catalysts for the reactions of secondary and tertiary alcohols, since the starting alcohol reacts with difficulty and the product contains a broad polymer distribution (14). On the other hand, the product composition is less affected by changes in the size of the alkyl group or the introduction of branch chains other than those on the α carbon. It is interesting to observe that the c values for the various mono- or diethylene glycol butyl ethers are slightly greater than one. Thus the basic assumption of Weibull and Nycander, that the products are equally reactive with epoxides, is not strictly true for polymers containing less than three epoxide units which, at least qualitatively, may account for the discrepancy between theory and experiment.

Acid catalysts (Table IV) result in products which approach the distribution predicted by Flory ($c = 1$). The product composition was similar for all of the catalysts investigated and was only slightly influenced by positioning the hydroxyl group upon a secondary or tertiary carbon atom. These results indicate that acid and base-catalyzed reactions proceed by different mechanisms. Acid-catalyzed reactions are believed to proceed with the formation of the conjugate acid of the epoxide (15).

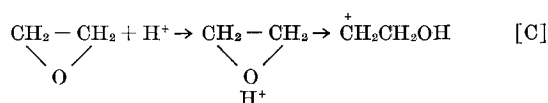


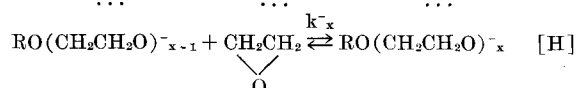
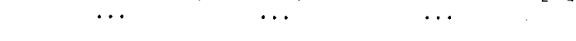
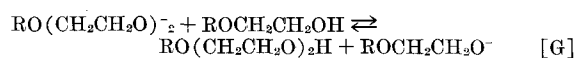
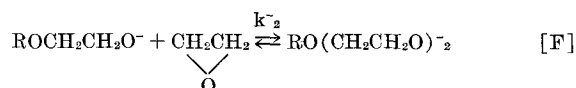
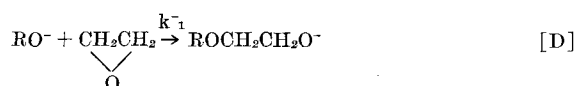
TABLE IV

The Acid-Catalyzed Addition of Ethylene Oxide to Several Butyl Alcohols

Alcohol	Catalyst	Temp C	Weibull- Nycander c
n-Butanol.....	BF ₃ · etherate	120	1.2
n-Butanol.....	BF ₃ · etherate	55	1.2
n-Butanol.....	p-Toluene sulfonic acid	148	1.2
n-Butanol.....	Fluosulfonic acid	120	1.2
n-Butanol.....	Aluminum butylate	150	1.2
n-Butanol.....	Perchloric acid	56	1.2
sec.-Butanol.....	BF ₃ · etherate	134	1.9
tert.-Butanol.....	BF ₃ · etherate	43	(2.6)

The use of the Weibull-Nycander equation for the base-catalyzed reaction implies that a difference exists in the reactivity of the epoxide with the product and the starting alcohol. This difference is represented by the distribution constant, *c*. Attempts have been made to correlate *c* with the observed velocity constants for the addition of epoxide to the starting alcohol and its glycol ether (2,4). The data presented in Table V show that the distribution constant cannot be estimated solely from the apparent second order rate constants.

It is apparent that a thorough analysis of *c* requires more detailed knowledge of the reaction mechanism. It is generally accepted that the base-catalyzed reaction of alkylene oxides with alcohols proceeds through the alkoxide ion (16) as shown below:



Equations [D] to [H] imply that the relative concentration of a component, *x*, depends not only upon the velocity constants of its formation and disappearance, but also upon the distribution of alkoxide ion among the competing alcohols. Under these circumstances Weibull and Nycander (2) have shown that equations similar to [B] and [C] can be derived, except that the distribution constant, *c*, is replaced by the product *c*′. Here *c*′ is a measure of the reactivities of the anions towards epoxide (k_2/k_1) and *c* is a measure of the acidity of the hydroxyl generated in comparison to the hydroxyl group of the starting material. *c*′ can be related directly to the ionization constants of the alcohol (K_x) and its epoxide

TABLE V

The Reaction of Ethylene Oxide with the Butyl Alcohols and Their Glycol Ethers

Temp = 120C

Catalyst = Sodium salt of alcohol listed

Alcohol	i	k (1/mol min)	k ₁ +1		Weibull- Nycander c
			k ₁		
n-Butanol.....	0	3.9	0.82		3.6
Ethylene glycol mono-n-butyl ether.....	1	3.2	1.2		1.3
Diethylene glycol mono-n-butyl ether.....	2	3.8		1.1
sec.-Butanol.....	0	1.7	1.3		29
Ethylene glycol mono-sec.-butyl ether.....	1	2.2

TABLE VI

Acid Ionization Constants and Relative Acidities of Some Hydroxyl Containing Compounds

Temp = 25C

Alcohol	Acid ioniza- tion constant in water (K × 10 ¹⁶) ^b	Relative acidity in isopropanol (K _r) ^c
sec.-Butanol.....	<0.8
n-Butanol.....	1.0 ^a	0.8
Water.....	1.8 ^b	1.2
1,2-Propylene glycol.....	4.9	28
Ethylene glycol mono-n-butyl ether.....	5.4	6.4
Ethylene glycol mono-sec.-butyl ether.....	6.3
1-(2 hydroxyethoxy) propane-2-ol.....	5.8	30
Ethylene glycol.....	14	44
Diethylene glycol.....	16	(66)
Tetraethylene glycol.....	18	(140)
Diethylene glycol mono-n-butyl ether.....	20	11
Diethylene glycol mono-sec.-butyl ether.....	10.5
Triethylene glycol.....	22	(120)

^a Estimated.^b See reference (10).^c See reference (9).

adduct (K_y) from the proton exchange equilibrium shown in equation [E].

$$K = \frac{[\text{ROCH}_2\text{CH}_2\text{OH}][\text{RO}^-]}{[\text{ROCH}_2\text{CH}_2\text{O}^-][\text{ROH}]} \cdot \frac{[\text{H}^+]}{[\text{H}^+]} = \frac{K_x}{K_y} = \frac{1}{c'}$$

The role of acidity in determining the product composition of the base-catalyzed reaction was suggested also by other workers. Recently Nagase and Sakaguchi (6) concluded that alcohol acidity was a principal factor in determining the product composition of oxyethylated nonyl phenol or lauryl alcohol. However, these workers did not compare distribution constants with the acidity of the corresponding alcohols, but based their conclusion on acidity data of simpler alcohols.

Data obtained in this laboratory on acid ionization constants in water and on relative acidities in isopropanol for water and several alcohols, glycols, and their alkylene oxide adducts are given in Table VI. The results obtained in the two solvents show a qualitative agreement even though the numerical values are quite different. This agreement becomes more obvious when the parent alcohol is compared with its epoxide adducts. Table VII shows a comparison of the experimental distribution constant, *c*, with that calculated from the ratio of ionization constants in water or relative acidity in isopropanol. The agreement between the experimental *c* and the calculated values is surprisingly good, considering that the acidity measurements were made at 25C while the epoxide reactions were conducted at elevated temperatures ca. 120C.

It should be noted that measurements for polyhydric alcohols pertain to the molecule as a whole. No attempt was made to distinguish between the acidity contributions of the various hydroxyl groups, nor were the various isomeric products isolated when de-

TABLE VII

Base-Catalyzed Reactions of Epoxides with Alcohols—Comparison of Experimental Weibull-Nycander Distribution Constant with that Predicted from the Acidity of the Components

Alcohol	c	K _{r(y)} ^a	
		K _{r(x)}	K _{r(x)}
A—Ethylene oxide			
Ethylene glycol.....	1.0	1.1	1.5
Diethylene glycol.....	1.0	1.4	1.8
Triethylene glycol.....	1.0	0.82	1.2
1,2-Propylene glycol.....	1.1	1.2	1.1
n-Butanol.....	3.6	5.4	8.0
Ethylene glycol n-butyl ether.....	1.3	3.7	1.6
sec.-Butanol.....	29	>7.9
Ethylene glycol sec.-butyl ether.....	1.3	1.7
B—Propylene oxide			
Ethylene glycol.....	0.5	0.42	0.68

^a *x* represent the starting alcohol and *y* the reaction product. Thus, for the reaction of ethylene oxide with ethylene glycol: $K_{r(y)}/K_{r(x)} = K_{r(\text{diethylene glycol})}/K_{r(\text{ethylene glycol})} = 16/14$ (Table VI).

termining the product composition. Undoubtedly the primary and secondary hydroxyl groups of an unsymmetrical glycol, such as propylene glycol, differ in acidity, which result in different isomeric products upon reaction.

One can conclude from these results that the specific rate constants for the base-catalyzed reactions of an epoxide with the various anions (Equations D,F, and H) have very little influence upon the product composition. The product composition is determined predominantly, if not solely, by the protonic acidity of the alcohol and its epoxide adducts, presumably competing in the proton exchange reaction of the type depicted in equations [E,G], etc. Additional support for this mechanism was obtained from the reaction of ethylene oxide with sodium *sec.*-butoxide. When this reaction was conducted at 120°C in toluene solution a product composition with *c* value of 1.3 (Flory *c* = 1.0) was obtained as compared to *c* value of 29 for the base-catalyzed reaction. The reaction with the sodium salt eliminates the proton transfer steps [E,G], etc., and the product composition will depend only upon the velocity constants of the epoxide addition reactions. The fact that the distribution constant *c* is close to unity shows that reactions [D,F], etc. proceed at equal rate.

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Methanesulfonic Acid Catalyzed Additions to Oleic Acid and Cyclohexene. III. Addition of Acids and Substituted Phenols¹

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Abstract

Benzoic acid adds to oleic acid in methanesulfonic acid as catalyst-solvent to form an addition product in 30% yield. Saponification studies on the product reveal that the addition is made via the carboxyl group and no rearrangement of the initial product takes place. A number of substituted benzoic acids were also tried but the yield of addition product was nil. Data are included for the experiments with a number of phenols not previously reported. These include: *o*-chlorophenol, 2,6-di-*tert.*-butylphenol, 2,4,6-trichlorophenol, resorcinol, 5-*n*-pentadecylresorcinol, hydroquinone, methyl salicylate, and 3-*n*-pentadecylphenol. Good yields of addition products of cyclohexene are obtained using methanesulfonic acid as catalyst-solvent and the same nucleophiles employed previously.

Introduction

IN PREVIOUS COMMUNICATIONS from this laboratory (1,2), data were presented showing improvement in yields of products when methanesulfonic acid was used in place of sulfuric acid (3,4) as catalyst-solvent for the addition of phenols and phenyl ethers to oleic acid. Infrared studies of the phenol addition reaction gave support to the theory that the addition proceeds via the formation of an intermediate which subsequently rearranges to give the substituted phenol instead of the phenoxy ether. It was also shown that arylthiols

could be added to oleic acid and good yields of product were obtained. The arylthiol addition, however, takes place without subsequent rearrangement of the initial addition product. Invariably, the end product of the reaction was a thioether.

Since diesters have been shown to have considerable utility, it seemed of interest to learn whether the addition reaction could be applied to the addition of aromatic carboxylic acids to oleic acid. If the reaction proceeded so that the addition resulted in the formation of a carbon-carbon bond, then the end product would be a dicarboxylic acid derivative. Some evidence in support of this hypothesis is found in a recent patent (5) and paper (6) describing the preparation and properties of benzoic acid modified alkyd resins. An interesting product was obtained in an attempt to add benzoic acid to oleic acid using methanesulfonic acid as catalyst. Infrared analyses of the product after esterification were inconclusive, in that it was not possible to differentiate between two possible products: methyl benzoxystearate or a carbomethoxyphenyl-stearic acid ester. The former, on saponification followed by esterification with methyl alcohol, would yield a mixture of methyl hydroxystearate and methyl benzoate. If the addition product was a carbomethoxyphenyl-stearic acid derivative, saponification followed by esterification would not alter the material. Saponification of the benzoic acid addition product yielded hydroxy-stearic acid demonstrating that the addition took place via the carboxyl group and no carbon-carbon bond was formed.

From the addition of benzoic acid to oleic acid

¹ Presented at the AOCs meeting in Toronto, Canada, 1962.

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