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A Study of the Polymerization of Propylene Oxide Catalyzed by Anhydrous Potassium Hydroxide

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The polymerization of propylene oxide catalyzed by solid anhydrous KOH is shown to have essentially the same mechanism as the well-known homogeneous base-catalyzed polymerizations. The reaction is not surface-catalyzed and the role of solid KOH is to convert hydroxylic groups almost quantitatively to alkoxide groups. Unsaturated end groups are shown to come from rearrangement of propylene oxide to allyl alcohol, which initiates new polymer chains. Allyl ethers thus formed are converted to *cis*-propenyl ethers at rates dependent upon their molecular weights. A kinetic analysis shows that the proposed reaction sequence accounts for all the characteristics of the polymerization including reaction rates, induction period, average molecular weight, and molecular weight distribution, and the amount and type of unsaturation in the polymer.

Alkylene oxides may be polymerized in a number of ways, the type of product obtained being dependent on the catalyst system used. Most commercial polymerizations are carried out by treating alkylene oxides with hydroxylic initiators (*e.g.*, propylene glycol) in the presence of small amounts of KOH at temperatures of 100° or higher. The products under these conditions are mostly telomers of the initiator and alkylene oxide and the average molecular weight is approximately determined by the ratio of alkylene oxide to initiator. When propylene oxide (PO) is polymerized under these conditions the product is always contaminated with a small amount of unsaturated, monohydroxy polymer. The unsaturation has been shown to be allyl and propenyl ether end groups.[1] This impurity is detrimental to the use of polyglycols for the preparation of polyurethans. Anhydrous KOH, in the absence of hydroxylic initiators, also causes propylene oxide to polymerize, but the reaction proceeds readily at room temperature and the product consists largely of unsaturated, monohydroxy polyethers whose average molecular weight is about 5000 regardless of the monomer-to-catalyst ratio.[2] Several other features of the polymerization in the presence of anhydrous KOH are different from the commercial process: (1) the polymerization rate is much higher; (2) the average molecular weight is relatively constant throughout the polymerization; (3) NaOH and LiOH are ineffective catalysts while KOH, RbOH, and CsOH are effective.[3] The marked changes in the characteristics of the polymerization caused by elimination of the hydroxylic initiator led St. Pierre and Price to suggest the possibility of a difference in reaction mechanism between the two polymerization systems. This paper deals with a study of the mechanism of the polymerization catalyzed by anhydrous KOH and will show that no basic change in mechanism is necessary to account for the change in characteristics of the two polymerization systems.

The generally accepted mechanism of polymerization in the commercial process is[4]

$$\mathrm{ROH} + \mathrm{HO}^- \overset{\text{fast}}{\rightleftharpoons} \mathrm{RO}^- + \mathrm{H_2O}$$

$$\mathrm{RO}^- + \mathrm{CH_2{-}CHCH_3}\,(\text{O}) \longrightarrow \mathrm{ROCH_2CH(CH_3)O}^- \xrightarrow{\text{PO}} \text{polymer}$$

$$\mathrm{HO}^- + \mathrm{CH_2{-}CHCH_3}\,(\text{O}) \longrightarrow \mathrm{HOCH_2CH(CH_3)O}^- \xrightarrow{\text{PO}} \text{polymer}$$

$$\mathrm{ROH} + \mathrm{RO}^- \overset{\text{fast}}{\rightleftharpoons} \mathrm{RO}^- + \mathrm{ROH}$$

where R = any of the possible organic moieties including the initiator.

The details of the mechanism are determined by the relative acidities of the various hydroxylic materials and the rate of nucleophilic attack of the different anionic species on propylene oxide. The source of unsaturation has been uncertain, but Price and Snyder[3,5] and Simons and Verbanc[6] suggested that it is produced by the reaction

$$\mathrm{RO}^- + \mathrm{H{-}CH_2CH{-}CH_2}\,(\text{O}) \longrightarrow \mathrm{ROH} + \mathrm{CH_2{=}CHCH_2O}^- \xrightarrow{\text{PO}} \mathrm{CH_2{=}CHCH_2(OC_3H_6)_nO}^-$$

They showed that allyl ethers will rearrange to propenyl ethers under basic conditions and thereby accounted for both types of unsaturation. Gee[7] had suggested earlier that isopropenyl ethers could be formed by an alternate rearrangement of propylene oxide

$$\mathrm{RO}^- + \mathrm{CH_2{-}CCH_3}\,(\text{O})\,(\mathrm{H}) \longrightarrow \mathrm{ROH} + \mathrm{CH_2{=}C(O^-)CH_3} \xrightarrow{\text{PO}} \mathrm{CH_2{=}C(CH_3){-}(OC_3H_6)_nO}^-$$

This reaction is not likely since there is no evidence for the presence of isopropenyl ethers in polyglycols.[1] However, the third analogous reaction has not been ruled out as a mode of formation of propenyl ethers

$$\mathrm{RO}^- + \mathrm{H{-}CH{-}CHCH_3}\,(\text{O}) \longrightarrow \mathrm{ROH} + \mathrm{CH_3CH{=}CHO}^- \xrightarrow{\text{PO}} \mathrm{CH_3CH{=}CH(OC_3H_6)_nO}^-$$

The mechanism of the polymerization catalyzed by anhydrous KOH is not as well understood. St. Pierre and Price[2] initially proposed that the reaction was catalyzed by the surface of the KOH and involved a chain-type reaction which yielded polymer of nearly constant molecular weight. It was suggested that the chain termination was an elimination reaction which amounted to a chain-transfer reaction.

(1) G. J. Dege, R. L. Harris, and H. S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 3374 (1959).

(2) L. E. St. Pierre and C. C. Price, *ibid.*, **78**, 2432 (1956).

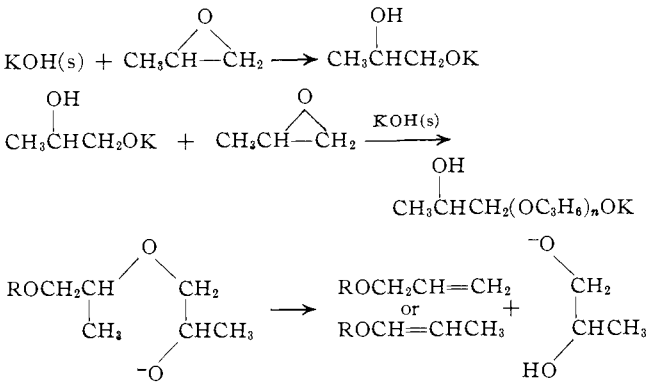
(3) W. H. Snyder, Jr., Ph.D. Thesis, University of Pennsylvania, 1961.

(4) G. Gee, W. C. E. Higginson, K. J. Taylor, and M. W. Trenholme, *J. Chem. Soc.*, 4298 (1961).

(5) C. C. Price, lecture delivered at Northwestern University, Dec. 8, 1959.

(6) D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

(7) G. Gee, *Chem. Ind.* (London), 678 (1959).



Price[5] later abandoned this mechanism on the basis of data obtained by Snyder[3] and now favors the rearrangement of propylene oxide to allyl alcohol. Simons and Verbanc[6] also disfavored the elimination reaction since heating an unneutralized polymerizate produced no increase in unsaturation. However, Snyder also reported a slight negative isotope effect for double bond formation when 1,2-epoxypropane-3,3,3-d_3 is polymerized over KOH. This appears to be strong evidence against the rearrangement. The question of surface catalysis has not been resolved in the literature, nor has a kinetic analysis of the polymerization been made.

Results and Discussion

The polymerizations reported here were all carried out at 30° using powdered, anhydrous KOH as the catalyst. It was established that the rate of polymerization and product characteristics are independent of the amount of solid catalyst present as long as there is an excess of catalyst. This is shown in Fig. 1 where

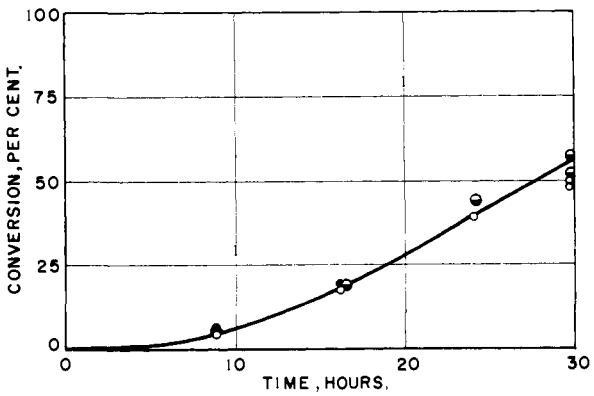


Fig. 1.—Effect of catalyst concentrations on rate of polymerization of propylene oxide by anhydrous KOH; mole ratio of KOH to propylene oxide: O, 0.022; ●, 0.044; ◒, 0.087.

a fourfold change in amount of catalyst was made. Even at a catalyst-to-propylene oxide mole ratio of one there was no significant change in reaction rate nor in product characteristics. These data rule out the possibility of any significant amount of surface catalysis.

The kinetic course of the polymerization is shown in Fig. 2. In these reactions, the mole ratio of KOH to propylene oxide was 0.044, which was enough to eliminate the complication reported by Snyder[3] that polymerization stops prematurely if insufficient catalyst is used. It was found that there is an induction period during which the amount of organic hydroxylic material increases to a significant level. The polymerization then accelerates markedly until the monomer

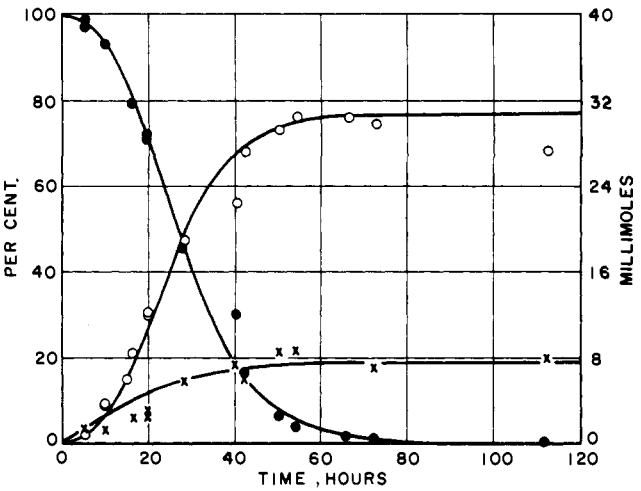


Fig. 2.—The polymerization of propylene oxide by anhydrous KOH: ●, propylene oxide remaining, percentage of starting material; O, mmoles unsaturated polyether chains formed from 200 g. of propylene oxide; X, mmoles of dihydroxy polyether chains formed from 200 g. of propylene oxide; ——, calculated curves.

is almost completely reacted. The total amounts of hydroxyl groups and of double bonds follow similar sigmoidal curves with the amount of hydroxyl always being greater than the amount of double bond. The average molecular weight of polymeric product, as determined by end group analysis, is high even at low conversion, and changes by a factor of only about two throughout the polymerization (see Fig. 3). This is in essential agreement with the results based on viscosity measurements reported by St. Pierre and Price.[2]

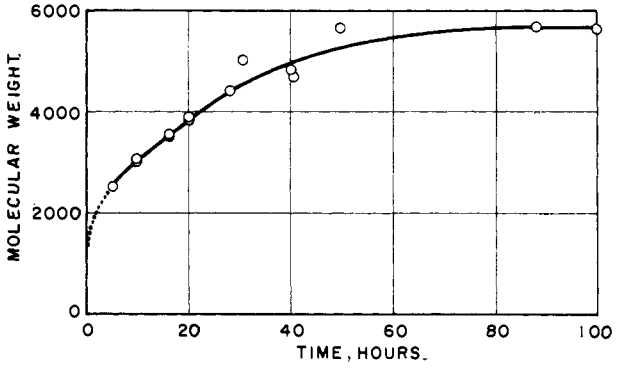


Fig. 3.—Molecular weight buildup during anhydrous KOH-catalyzed polymerization of propylene oxide.

The polymer obtained when reaction is complete is a viscous oil with an average molecular weight of 5000–6000. The molecular weight distribution is extremely broad as may be seen in Fig. 4. The lowest average molecular weight fraction obtained was about 1600 g./mole, whereas the highest was about 31,000 g./mole. This distribution is much broader than the "Flory" distribution (also included in Fig. 4) which is approximated in commercial polyglycols.[8] The Flory distribution[9] assumes that all of the initiator is present at the beginning of the polymerization, that there is no chain termination reaction, and that the propagation rate constant is independent of molecular weight.

(8) (a) L. C. Case, *J. Phys. Chem.*, **62**, 895 (1958); (b) R. J. Morris and H. E. Persinger, Paper No. 67, Div. of Polymer Chem., 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.

(9) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940).

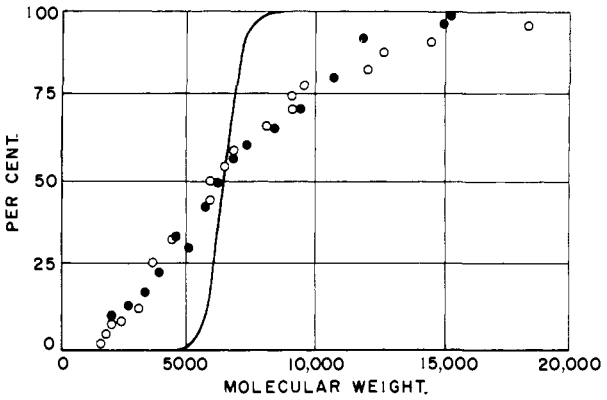


Fig. 4.—Cumulative molecular weight distribution of two polypropylene oxides prepared with anhydrous KOH catalysis. Solid line represents a "Flory" distribution for polymer of the same average molecular weight.

In order to explain the available data, the following reaction sequence, a modification of that suggested by Snyder[3] and Price, is proposed

$$\mathrm{KOH(solid)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{KOH(solution)} \qquad (1)$$

$$\mathrm{KOH(solution)} + \mathrm{CH_3\overset{O}{\overset{/\backslash}{CH}}{-}CH_2} \xrightarrow{k_d} \mathrm{CH_3\overset{OH}{\overset{|}{C}}HCH_2OK} \qquad (2)$$

$$\mathrm{ROK} + \mathrm{CH_3\overset{O}{\overset{/\backslash}{CH}}{-}CH_2} \xrightarrow{k_i} \mathrm{ROH} + \mathrm{CH_2{=}CHCH_2OK} \qquad (3)$$

$$\mathrm{ROK} + \mathrm{CH_3\overset{O}{\overset{/\backslash}{CH}}{-}CH_2} \xrightarrow{k_a} \mathrm{ROCH_2\underset{CH_3}{\underset{|}{C}}HOK} \qquad (4)$$

$$\mathrm{ROH} + \mathrm{KOH(solution)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{ROK} + \mathrm{H_2O} \qquad (5)$$

$$\mathrm{H_2O} + \mathrm{KOH(solid)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{KOH{\cdot}H_2O(solid)} \qquad (6)$$

$$\mathrm{CH_2{=}CHCH_2(OC_3H_6)_nOK} \xrightarrow{k_{rn}} \mathrm{CH_3CH{=}CH(OC_3H_6)_nOK} \qquad (7)$$

where R = any of the possible organic moieties.

A kinetic model derived from this sequence has been tested and found to fit the data in Fig. 2. Before discussing the kinetic analysis, however, the qualitative reasons for choosing this model should be mentioned. The reaction is not surface catalyzed; therefore there is no apparent reason why the well-known mechanism of commercial polymerizations should not apply. Hence, the homogeneous reactions 2 and 4 are included. If these two reactions apply, then the over-all rate of polymerization will depend on KOH concentration. For the rate to be independent of amount of solid KOH present, the KOH concentration must also be independent of it. Therefore, it is assumed that the dissolution process 1 is fast compared to the polymerization reactions and that KOH concentration is practically constant. Reactions 5 and 6 have been shown to be relatively fast and to go almost quantitatively to the right. Thus low molecular weight polypropylene glycols in tetrahydrofuran solution equilibrate with excess anhydrous KOH within 30 min. to give about 95% yield of the corresponding alkoxides. NaOH under the same conditions yields only 25% alkoxide. It is felt that the efficient dehydrating ability of KOH causes reaction 5 to shift to the right.

The rearrangement of substituted epoxides to α,β-unsaturated alcohols under basic conditions is a well-known reaction.[10] However, no definitive evidence has been reported for such a rearrangement under these reaction conditions. That the reaction does indeed go has now been shown in two ways. Attempts were made to copolymerize propylene oxide and *trans*-2,3-epoxybutane in the presence of anhydrous KOH. In these experiments varying mixtures of the two epoxides were allowed to react at 30° until no further change occurred and then the volatile and polymeric components were analyzed separately. The volatiles contained, along with unreacted butylene oxide, small amounts of 1-buten-2-ol, the product of a rearrangement corresponding to reaction 3. The alcohol was

$$\mathrm{RO^-} + \mathrm{H{-}CH_2\overset{O}{\overset{/\backslash}{CH}}{-}CH{-}CH_3} \longrightarrow \mathrm{ROH} + \mathrm{CH_2{=}CH\overset{O^-}{\overset{|}{C}}HCH_3}$$

isolated by gas–liquid chromatography and identified by comparing its infrared spectrum with that of an authentic sample. Essentially no propylene oxide remained at the end of the polymerizations. Added butylene oxide, also, has a marked effect on the properties of the polymeric product (Table I), whereas inert

TABLE I

EFFECT OF *trans*-2,3-EPOXYBUTANE (BO) ON POLYMERIZATION OF PROPYLENE OXIDE (PO)

Mole % BO in PO	Yield based on PO, %	Molecular weight	Unsaturation, mmole/g.
0	97.2	5650	0.141
10	97.5	3910	.218
20	95.8	2830	.291
30	100.5	2220	.393
50	99.5	1535	.616

solvents have only a small effect. These results are readily understandable on the basis of the proposed reaction scheme. Butylene oxide would not be expected to enter into the propagation reaction since Gee and his co-workers have shown that secondary alkoxides do not add at a significant rate to substituted oxirane ring carbon atoms.[4] However, it can rearrange to the unsaturated alkoxide and initiate new chains, and since its concentration remains high, new chains will continue to form even toward the end of the polymerization. Furthermore, its presence will slow the propagation reaction 4 by dilution of the propylene oxide. The net result is that the higher concentrations of butylene oxide lead to lower molecular weight products with higher double bond concentrations.

$$\mathrm{RO^-} + \mathrm{HCH_2\overset{O}{\overset{/\backslash}{CH}}{-}CH_2} \longrightarrow \left[\mathrm{RO{\cdots}H{\cdots}CH_2{\cdots}\overset{O}{\overset{/\backslash}{CH}}{-}CH_2}\right]^- \longrightarrow \mathrm{ROH} + \mathrm{CH_2{=}CHCH_2O^-}$$

$$\mathrm{RO^-} + \mathrm{HCH_2\overset{Br}{\overset{|}{C}}HCH_3} \longrightarrow \left[\mathrm{RO{\cdots}H{\cdots}CH_2{\cdots}\overset{Br}{\overset{|}{C}}HCH_3}\right]^- \longrightarrow \mathrm{ROH} + \mathrm{CH_2{=}CHCH_3} + \mathrm{Br^-}$$

(10) R. L. Letsinger, J. G. Traynham, and E. Bobko, *J. Am. Chem. Soc.*, **74**, 399 (1952); A. C. Cope, Robert A. Welch Foundation Conferences on Chemical Research, Houston, Texas, 1960; G. W. Fowler and J. T. Fitzpatrick, U. S. Patent 2,426,264 (1947).

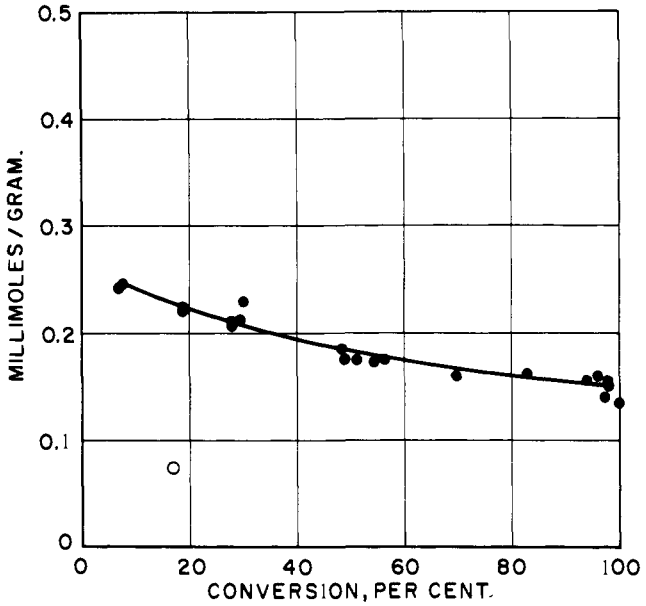


Fig. 5.—Unsaturation in polypropylene oxide as a function of conversion: ●, polymer from normal propylene oxide; O, polymer from deuterated propylene oxide.

The second way in which reaction 3 was shown to occur is based on isotope effects. The rearrangement reaction is very probably an E2 elimination reaction analogous to the dehydrohalogenation of 2-bromopropane. The latter reaction is known to exhibit a large positive isotope effect when the methyl groups are deuterated.[11] By analogy, 1,2-epoxypropane-3,3,3-d_3 should likewise show a positive isotope effect. If the postulated reaction scheme is right, the isotope effect should easily be detected by merely comparing the concentration of double bond in the deuterated and nondeuterated polymers. The over-all rate of polymerization should also be sensitive to the isotope effect. Snyder[3] studied this and reported a slight negative isotope effect. He rationalized the apparent anomaly by attempting to show why there should not be an isotope effect for the rearrangement reaction. It has been found in the present work that there actually is a positive isotope effect of 3.0 as determined from double bond concentrations in the two polymers. The rate of polymerization has also been found to be slower with the deuterated material. The data, shown in Table II, were obtained by allowing purified samples

TABLE II

ISOTOPE EFFECT IN KOH-CATALYZED POLYMERIZATION OF PROPYLENE OXIDE

	$CH_3CH(O)CH_2$	$CD_3CH(O)CH_2$
Conversion, %	30	17
Double bond, mmole/g.	0.224	0.074
k_H/k_D (corrected)	3.0	

of the two monomers to polymerize over anhydrous KOH at 30° for 21.3 hr. and analyzing the resultant polymers. The unsaturation data are shown in Fig. 5 in order to indicate the reproducibility of the values. The isotope effect was calculated from the double bond concentrations at 17% conversion in both cases and was corrected for the difference in molecular weight of the monomers. In order to check the

(11) V. J. Shriner, Jr., *J. Am. Chem. Soc.*, **74**, 5285 (1952).

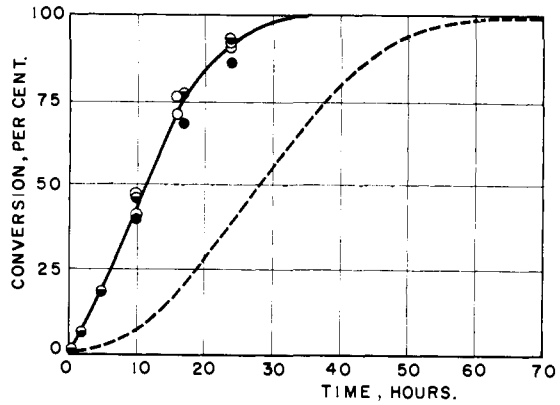


Fig. 6.—The effect of added alcohols on the rate of polymerization of propylene oxide catalyzed by anhydrous KOH: O, allyl alcohol; ●, 1-allyloxy-2-propanol; ◒, 1-(2-allyloxy-1-methylethoxy)-2-propanol; – – –, no added alcohol.

validity of these measurements, two pairs of homogeneous polymerizations were run with propylene oxide and deuterated propylene oxide using the potassium salt of the monomethyl ether of dipropylene glycol as the initiator. Isotope effects of 4.3 and 4.6 were obtained. This leaves little doubt that the mode of formation of double bond is the rearrangement of propylene oxide and that it is the same in homogeneous polymerizations and in those catalyzed by anhydrous KOH.

The induction period in the polymerization is readily explained by the proposed reaction sequence. At the beginning of the reaction there is a slow build-up of diol molecules attributed to reaction 2. These are converted to their potassium salts by KOH. As alkoxide ion is formed, reaction 3 becomes significant and is autocatalytic in the presence of anhydrous KOH. Hence, the over-all rate of formation of growing polymer chains is increasing and gives the typical induction period. If this situation obtains, addition of hydroxylic materials should eliminate the induction period and increase the over-all rate of polymerization. This is so, as is shown in Fig. 6. In these reactions allyl alcohol, 1-allyloxy-2-propanol, and 1-(2-allyloxy-1-methylethoxy)-2-propanol were added as initiators in amounts approximately equivalent to the total hydroxylic material produced in "uninitiated" polymerizations. If too much alcohol is added, however, the reaction is slowed markedly as was reported by Snyder.[3]

The wide molecular weight distribution of the polymeric product is predicted from the reaction scheme. Since there is no termination step, the growing chains initiated early in the reaction will have a long time to grow to high molecular weight, whereas those initiated near the end of the reaction will remain as low molecular weight adducts. The presence of both mono- and difunctional chains will have an effect on distribution, but the effect will be small compared to that of the initiation pattern. Likewise, small differences in the rates of reaction of the various alkoxides with propylene oxide will have a relatively small effect.

A kinetic analysis of the polymerization has been made using the following simplifying assumptions: (1) that reactions 1, 5, and 6 are fast compared to the other reactions; (2) that the concentration of KOH remains constant throughout the polymerization;

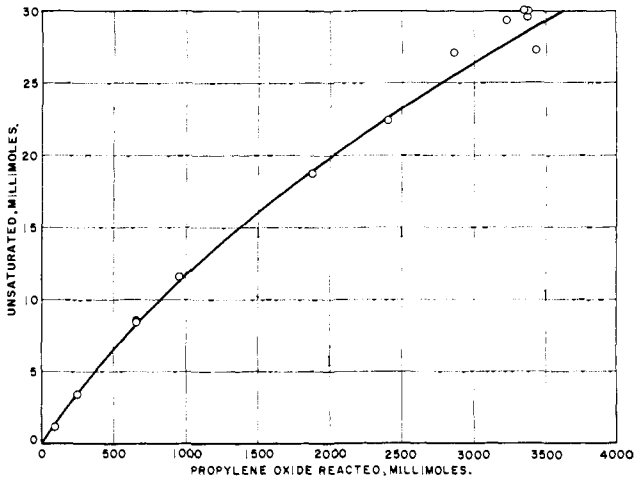


Fig. 7.—The relationship between amount of unsaturation formed and amount of propylene oxide consumed during the polymerization of propylene oxide.

(3) that essentially all of the organic hydroxylic compounds are in the form of their alkoxides; (4) that all the alkoxide species add to propylene oxide at approximately the same rate; (5) that the volumes of propylene oxide and polymer are additive; and (6) that the rate constant for reaction 3 is a linear function of propylene oxide concentration. The reasons for assumptions 1–3 have been discussed. Assumption 4 is not strictly true since it is known that rates of addition of low molecular weight alkoxides vary with structure. However, the polymeric alkoxides should add to propylene oxide at a rate essentially independent of molecular weight as may be judged from molecular weight distribution studies[7] and kinetic studies.[4] The contribution of the initial additions to the total rate of propylene oxide disappearance will be small. Data relating to assumption 5 are not available. However, small deviations from ideality will not have a significant effect on the kinetic model. Assumption 6 is arbitrary. The relative rates of double bond formation and of disappearance of propylene oxide vary by a factor of about 2.3 from beginning to end of the polymerization as may be seen in Fig. 7. This variation, which is probably due to changing medium, causes the change in average molecular weight during the reaction. It is not known what the absolute variation of each rate is nor is the exact function of the change known. Therefore, a simple linear function with respect to propylene oxide concentration has been assumed for the rearrangement rate constant and the parameter for the function was calculated from the initial and final slopes of Fig. 7. The kinetic model is

$$d(D)/dt = k_d[KOH](PO)$$

$$\frac{d(A_0)}{dt} = k_i\frac{(ROK)}{V}(PO)$$

$$\frac{d(ROK)}{dt} = 2k_d[KOH](PO) + k_i\frac{(ROK)}{V}(PO)$$

$$-\frac{d(PO)}{dt} = k_d[KOH](PO) + k_i\frac{(ROK)}{V}(PO) + k_a\frac{(ROK)}{V}(PO)$$

$$V = V_\infty\{1 + \alpha(PO)\}$$

$$k_i = k_{i\infty}\{1 + \beta[PO]\}$$

where

(D) = mmoles of diol
t = time, sec.
[KOH] = molar concentration of KOH, assumed constant
(PO) = mmoles of propylene oxide
(A_0) = mmoles of allyl alcohol formed (total double bond)
(ROK) = mequivalents of hydroxyl
V = volume, ml.
V_∞ = final volume
$k_{i\infty}$ = rate constant for reaction 3 at end of polymerization
α = empirical constant calculated from densities of propylene oxide and polyprpolyene glycol = 0.0119 mmole^{-1}
β = empirical constant = 0.093 M^{-1}

This kinetic model was fitted to the actual data with the aid of an analog computer and the following rate constants were found to give the best visual fit to the data

$$k_d[KOH] = 2.1 \times 10^{-8}\ \text{sec.}^{-1}$$
$$k_{i\infty} = 6.5 \times 10^{-7}\ M^{-1}\ \text{sec.}^{-1}$$
$$k_a = 1.2 \times 10^{-4}\ M^{-1}\ \text{sec.}^{-1}$$

The calculated curves using these constants are plotted in Fig. 2 where it may be seen that they fit the data satisfactorily.

It would be desirable to compare the calculated rate constants with ones determined directly. No truly comparable data have been measured. Gee[4] and his co-workers measured the rates of polymerization of propylene oxide in the presence of excess alcohol with sodium alkoxide as catalyst, and obtained the values listed in Table III. The value at 30°, extrapolated from their data, is about one-tenth the value reported here. This is to be expected since both the use of sodium as the cation and the presence of alcohols reduce the rate of polymerization.[3] Dudek[12] found that ethylene oxide in the presence of alcohol-free potassium alkoxide (0.003–0.012 M) at 29.2° polymerizes with a rate constant of 30–76 × 10^{-4} M^{-1} sec.$^{-1}$ in tetrahydrofuran. These high values are again compatible with the present ones since the reactive entities are primary alkoxides and an unsubstituted epoxide in contrast to the present system which involves a secondary alkoxide and a methyl-substituted epoxide. There are no rate data available for comparison with the constant calculated for rearrangement of propylene oxide. Even though the data which were obtained from the computer appear to be reasonable, it is apparent that further work on the rates of the various reactions would be desirable. In particular,

TABLE III

Temp., °C.	[RONa], M	[ROH], M	k_a, M^{-1} sec.$^{-1}$ × 10^4
30 (extrapolated)			*ca.* 0.14
70	0.019–0.065	0.5–1.4	1.1–1.4
80	.017– .035	.96–1.15	2.4–2.8
93	.017– .042	.61–1.18	6.1–6.9

(12) T. J. Dudek, Ph.D. Thesis, University of Akron, 1961.

a quantitative knowledge of the effect of hydroxylic materials, of different cations, and of temperature on rate constants would be very useful.

Although there is good evidence now that the predominant source of unsaturation in polyglycols is the rearrangement of propylene oxide to allyl alcohol, there are still some questions concerning the fate of the double bond once it is formed. Dege, *et al.*,[1] presented good evidence for both allyl and *cis*-propenyl ethers, but there is no evidence for isopropenyl ethers or for *trans*-propenyl ethers. Several workers have shown that allyl ethers rearrange to *cis*-propenyl ethers on treatment with strong bases,[6,13] thereby explaining the presence of both moieties. However, quantitative data concerning the amounts of each type of ether are lacking, and the alternate rearrangement of propylene oxide suggested above has not been eliminated as a source of unsaturation.

By the combination of infrared analysis for *cis*-propenyl ethers and mercuric acetate analysis for total unsaturation, some of the questions have been resolved. The ratio of propenyl ethers to total unsaturation was measured throughout the polymerizations. At very low conversion of propylene oxide (7%), the propenyl ethers account for about 12% of the unsaturation; at high conversion, they account for about 27% of the unsaturation (see Fig. 8). On long standing (1 year) the ratio increases to over 80%. If the unsaturation appears as allyl ethers and rearranges rapidly enough to give 12% propenyl ethers in the initial stages of polymerization, it would be expected that the ratio would increase to nearly 100% as polymerization goes to completion. Several explanations for the apparent anomaly have been examined.

Two competitive rearrangements of propylene oxide accompanied by slow bond migration in the allyl ethers would account for this. However, it was found that polymerizations initiated with allyl alcohol, or the monoallyl ethers of mono- and dipropylene glycol, exhibited the same behavior with regard to propenyl ether concentrations (see Table IV). Therefore this explanation is unsatisfactory.

TABLE IV

NATURE OF THE DOUBLE BOND IN INITIATED POLYMERS

Polymerization time, hr.	Propenyl ethers, % of total unsaturation		
	$CH_2{=}CHCH_2OH$[a]	$CH_2{=}CHCH_2(OC_3H_6)OH$[a]	$CH_2{=}CHCH_2(OC_3H_6)_2OH$[a]
0.5			8 (2)[b]
2			17 (7)
5			18 (19)
10	19, 20 (48, 41)	18 (40)	19 (47)
16	18, 18 (71, 76)	18 (68)	19 (77)
24	20, 19 (91, 91)	17 (86)	18 (93)

[a] Initiators. [b] Figures in parentheses are percentage conversions of propylene oxide to polymer.

A second possible explanation could be a large decrease in the rate constant for double bond migration with change in medium. This possibility became untenable when it was found that added 2-allyloxy-1-methoxypropane rearranged very slowly under reaction conditions and that there was no apparent change in rate constant with changing medium. These data, Table V, were obtained by analyzing separately the volatile and nonvolatile components as polymerization progressed.

(13) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961); C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

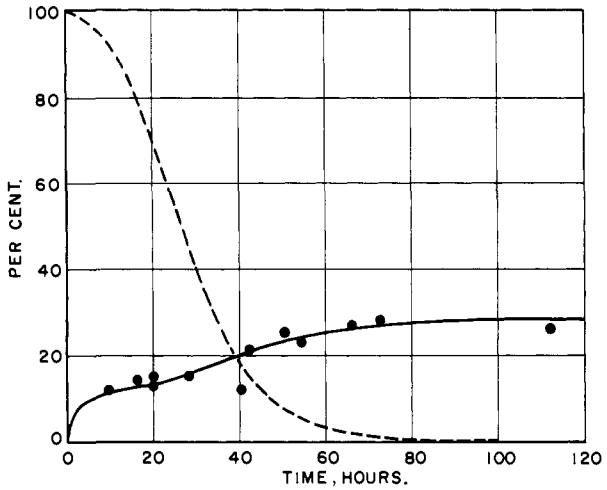


Fig. 8.—The ratio of propenyl ethers to total unsaturation during polymerization of propylene oxide catalyzed by anhydrous KOH: ———, calculated curve; – – –, calculated curve for propylene oxide remaining unreacted.

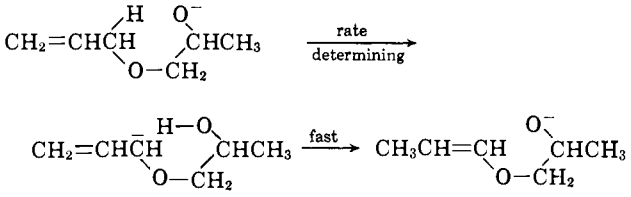
TABLE V

REARRANGEMENT OF ADDED ALLYL ETHER DURING POLYMERIZATION

Polymerization time, hr.	Conversion of PO, %	Propenyl ethers, % of total unsaturation	
		Volatiles	Residue
2	11		16
5	24	0.7	18
10	47	1.4	(?)
17	77	3.0	17
25	(?)	4.3	19

The possibility of an equilibrium between the two types of ethers was eliminated by initiating the reaction with 1-*cis*-propenoxy-2-propanol. The unsaturation remained almost completely as the propenyl ethers.

Finally, it was possible that the behavior of the propenyl ether concentration was caused by a marked dependence of rate of double bond migration upon the molecular weight of the allyl ethers. That this dependence is due to the six-membered transition state possible for allyloxypropanol was shown not to obtain by the data in Table IV. Here the polym-



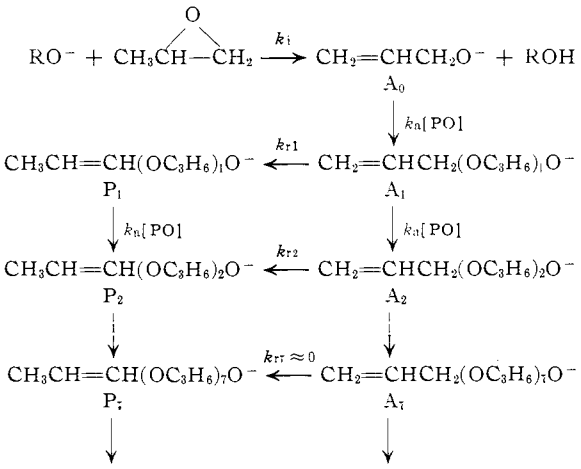
erization was initiated with the next higher adduct and yet the same pattern was obtained. However, an independent study of the rates of double bond migration in the potassium salts of monoallyl ethers of propylene oxide oligomers, $CH_2{=}CHCH_2(OC_3H_6)_nOK$, provided the data necessary to explain the observed behavior. In the study, which will be reported in detail later, it was found that the rate of migration when $n = 3$ is over 100 times as fast as when $n = 7$. The approximate rate constants are shown in Table VI. The effect of this pattern of rate constants upon the ratio of propenyl ethers to total unsaturation during

TABLE VI

RATE CONSTANTS FOR BOND MIGRATION IN $CH_2{=}CHCH_2(OC_3H_6)_nOK$

	Measured in THF, $\times 10^6$ sec.$^{-1}$	Programmed on computer	Calculated by computer, $\times 10^6$ sec.$^{-1}$
k_{r1}	1.6	k_{r1}	2.4
k_{r2}	11.0	$7k_{r1}$	16.0
k_{r3}	83.0	$50k_{r1}$	121.0
k_{r4}	45.0	$27k_{r1}$	66.0
k_{r5}	13.0	$8k_{r1}$	19.0
k_{r6}	1.6	k_{r1}	2.4
k_{r7}	0.6	0	0

the polymerization may be seen qualitatively in the reaction sequence



The probability of a newly generated allyl alcohol moiety's remaining as an allyl ether until more than seven propylene oxide units have been added is equal to

$$\prod_{n=1}^{6} \left\{ \frac{k_a[PO]}{k_{rn} + k_a[PO]} \right\}$$

At the beginning of the reaction when $k_a[PO]$ is large compared to k_{rn} the value is relatively insensitive to [PO] and the ratio of propenyl ethers to total unsaturation will be nearly constant. Toward the end of the reaction the probability decreases markedly and the relative amount of propenyl ethers in newly produced chains will be large. However, the effect on the overall ratio of propenyl ethers will be small because the total amount of unsaturation being formed becomes small.

The following kinetic model, based on the proposed reaction scheme, was studied with the computer in order to see if it could account quantitatively for the data

$$\frac{d(A_0)}{dt} = k_i \frac{(ROK)}{V}(PO) - k_a \frac{(PO)}{V}(A_0)$$

$$\frac{d(A_1)}{dt} = k_a \frac{(PO)}{V}(A_0) - k_a \frac{(PO)}{V}(A_1) - k_{r1}(A_1)$$

$$\frac{d(P_1)}{dt} = - k_a \frac{(PO)}{V}(P_1) + k_{r1}(A_1)$$

$$\frac{d(A_n)}{dt} = k_a \frac{(PO)}{V}(A_{n-1}) - k_a \frac{(PO)}{V}(A_n) - k_{rn}(A_n)$$

$n = 2$ to 6

$$\frac{d(P_n)}{dt} = k_a \frac{(PO)}{V}(P_{n-1}) - k_a \frac{(PO)}{V}(P_n) + k_{rn}(A_n)$$

$n = 2$ to 6

$$\frac{d(A_7)}{dt} = k_a \frac{(PO)}{V}(A_6)$$

$$\frac{d(P_7)}{dt} = k_a \frac{(PO)}{V}(P_6)$$

where A_7 and P_7 represent adducts with seven or more propylene oxide units and parentheses refer to millimolar quantities.

This kinetic model was programmed on the computer along with the previous model and the values of k_{rn} were programmed in such a way that their values relative to each other were the same as those measured independently. These values were varied as a group in the fitting process and the best ones are shown in Table VI. A plot of the ratio of propenyl ethers to total unsaturation *vs.* time was obtained from the computer using these constants and is shown in Fig. 8. The good fit to the data and the close agreement between measured and calculated constants (considering medium change) lends strong support to the validity of the proposed explanation of the polymerization data. It also adds to the evidence that no significant amount of rearrangement of propylene oxide to propenoxide ion occurs. That k_{rn}, when $n \geqslant 7$, is small but not actually equal to 0 is shown by the continued slow conversion of allyl ethers to propenyl ethers in the unneutralized polymerization mixture after all the propylene oxide is consumed.

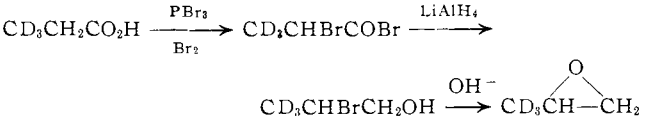
Experimental

Materials.—Commercial propylene oxide (Dow) was used for most of the polymerizations. In some cases, dried, refractionated material was used but no differences in any of the reaction characteristics were observed. The water content was insufficient to have any effect on the polymerizations.

Anhydrous KOH was prepared by heating 85% reagent grade KOH in a silver crucible on a flame until boiling ceased. It was allowed to cool under nitrogen and pulverized with a Mikro Pulverizer (Pulverizing Machinery Division, Metal Disintegrating Co., Inc.) keeping contact with air at a minimum. The resultant powder was found to be 96% KOH and about 4% K_2CO_3. It had a surface area of about 1 m.^{2}/g.

trans-2,3-Epoxybutane (Dow) was refractionated, b.p. 52.5° (750 mm.), and found by gas–liquid chromatography to be better than 99.9% pure.

1,2-Epoxypropane-3,3,3-d_3 was obtained from Merck Sharp and Dohme, Ltd., Canada, and was reported to contain the following isotopic constituents as indicated by mass spectroscopy: propylene oxide-d_3, 95.6%; propylene oxide-d_2, 4.4%; propylene oxide-d_4, 1–2%. It had been prepared by



It was repurified before use by preparative gas–liquid chromatography at room temperature on a 1 in. × 5 ft. column packed with 3,3′-oxydipropionitrile on Chromosorb P. It was then allowed to react with anhydrous KOH for 1 hr. at 30° and distilled. After this treatment it was found to be 99.6% pure. A nuclear magnetic resonance spectrum indicated that the methyl group was completely deuterated.

Normal Polymerizations.—Commercial propylene oxide (200 g., 3.45 moles) and powdered, anhydrous KOH (96%, 8.8 g., 0.150 mole) were placed in a nickel or stainless steel bomb. The bomb was flushed with nitrogen, capped, and weighed to deter-

mine the exact amount of propylene oxide remaining. The bomb was placed in a water bath maintained at 30 ± 0.5° and tumbled for the desired length of time. The bomb was opened and the base was neutralized by the reaction of Cretcher and Pittenger.[14] Chlorohydrin (13.3 g., 0.165 mole) was added as rapidly as possible without causing loss of material owing to boiling of the generated ethylene oxide. The reaction as described in the literature leads to low yields (in most cases 25–36%) of the hydroxyethyl ethers, and stops as soon as all the base is neutralized. In the present case, some hydroxyethyl ethers are undoubtedly formed. However, the reaction is carried out in such a way that minimal yields are obtained. This is verified by the lack of any polymer yields which are significantly greater than 100%. The small amounts which are formed will not affect the interpretation of the results. Reaction mixtures which were very viscous owing to high conversions were treated with the chlorohydrin dissolved in 100 ml. of hexane. The bomb was recapped and tumbled for about 30 min. to ensure complete neutralization and then the contents were transferred quantitatively to a tared flask. The volatile materials were removed by evaporation at 5 mm. on a steam bath using a rotating evaporator. The residue was weighed and the yield determined by subtracting the calculated weight of KCl. The polymer was dissolved in hexane (200 ml.) and centrifuged until the KCl settled, leaving a clear supernatant solution. The solution was decanted and evaporated as before to give the polymer. This procedure gave very reproducible yield data. It also eliminated the possibility of hydrolysis of propenyl ethers since the mixtures never became acidic and contact with water was minimal.

Small-Scale Polymerizations.—Vacuum techniques were used for the polymerizations involving deuterated propylene oxide. The desired amount of anhydrous KOH was weighed into a 5-ml. reaction vial equipped with O-ring joints at each end and a break-seal closure at one end. The vial was evacuated on a vacuum manifold. Propylene oxide was degassed by the freeze–thaw technique and distilled into the reaction vial which was subsequently sealed and weighed to obtain the exact amount of propylene oxide added. The vial was tumbled in a water bath at 30° for the desired time, replaced on the vacuum system using the break-seal end of the vial, and devolatilized without neutralization. This allowed the unreacted propylene oxide to be reused without further purification. After devolatilization, a solution of ethylene chlorohydrin in hexane was distilled into the vial to neutralize the base. The polymer was worked up and analyzed as usual. This procedure was tested with six polymerizations of normal propylene oxide and it was found that the yield could be reproduced within ±1% at an average conversion of 28%. With deuterated propylene oxide a yield of 17% was obtained under identical conditions.

Homogeneous polymerizations were initiated with essentially alcohol-free potassium salt of dipropylene glycol monomethyl ether. This was prepared by titrating the alcohol with a solution of triphenylmethylpotassium in tetrahydrofuran until a trace of triphenylmethide anion was visible. The desired amount of the resultant solution was transferred into a break-seal vial and placed on the vacuum system. The solvent was taken off and propylene oxide distilled into the vial. Polymerization was allowed to go to completion and the work-up was performed as usual. In one pair of experiments, conversion of monomer was 92 and 94% for normal and deuterated PO, respectively, while the unsaturation was 0.085 and 0.019 mmole/g. of PO reacted. In another set of experiments, conversion was quantitative and unsaturation values of 0.129 (average of 3) and 0.027 were obtained. Isotope effects of 4.3 and 4.6 are obtained after correction for molecular weight differences.

Analytical Procedures. Hydroxyl Analysis.—A slight modification of the ASTM standard phthalation method[15] was used in this work. A solution of 5 g. of polyglycol (1–4 mequiv. of hydroxyl) and 25.0 ml. of approximately 1 *M* phthalic anhydride in freshly distilled pyridine was heated on a steam bath for 1.5–2 hr. The solution was cooled in ice for 10 min. and a slight excess of water was added to hydrolyze residual anhydride. The solution was titrated with 1 *N* KOH in 50% aqueous pyridine to potentiometric or phenolphthalein end point. A similarly treated sample of anhydride reagent was used as a blank. The hydroxyl content is equivalent to the difference between acid content of sample and blank, corrected for residual basicity of the sample.

(14) L. H. Cretcher and W. H. Pittenger, *J. Am. Chem. Soc.*, **46**, 1503 (1924).

(15) ASTM designation: D1638-61T.

Unsaturation Analysis.—A slight modification of the ASTM method using mercuric acetate[15] was used. A sample of polyglycol containing 1–2 mmoles of double bond was allowed to react at room temperature for 2 hr. (the recommended 30 min. was not long enough) with 50 ml. of methanolic mercuric acetate (0.125 *M*) containing 10 drops of acetic acid per liter. Sodium bromide (about 5 g.) was added and the solution was swirled for at least 30 sec. before it was titrated with 0.1 *N* methanolic KOH to a phenolphthalein end point. A similarly treated sample of reagent was used as a blank. The double bond content of the sample is equivalent to the difference in acid content of the blank and sample, corrected for residual basicity of the sample. Coulometric bromination gave values which were in excellent agreement with those obtained with the mercuration method.

Residual Basicity.—The work-up procedure used in this work is such that there is less than 0.005 mequiv./g. of titratable base in the finished product. This was determined by titrating a methanolic solution of the polyether with 0.1 *N* methanolic KOH to a phenolphthalein end point.

Propenyl Ether Analysis.—A sample of polyglycol was scanned neat as a 0.5-mm. film on a Perkin–Elmer Model 137G grating infrared spectrophotometer using a 0.5-mm. film of hydrogenated polyglycol in the reference beam. The transmittance through such films in the 6-μ region is only about 15% and it was necessary to operate at slit widths of 500–750 μ and slow scan speeds in order to obtain sharp, quantitative peaks. Surprisingly good compensation was obtained under these conditions as may be seen in Fig. 9. Several solutions of known concentrations of

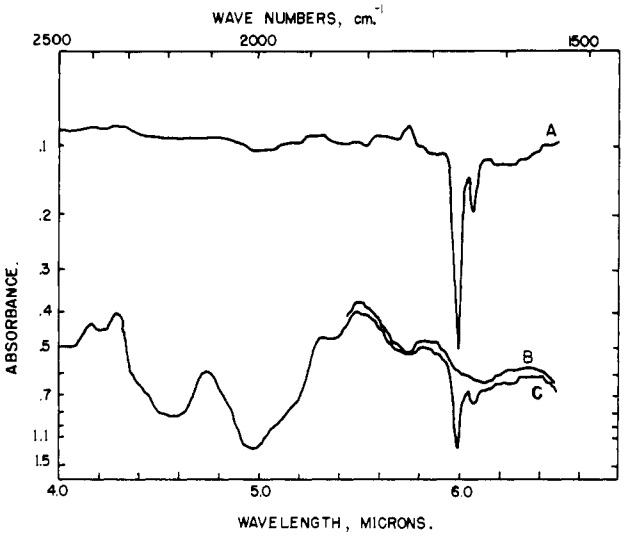


Fig. 9.—A typical infrared spectrum for propenyl ether analysis: A, compensated spectrum; B, reference spectrum; C, sample spectrum.

methyl *cis*-propenyl ether in hydrogenated commercial polyglycol of 1200 mol. wt. (Dow P1200) were used as standards. An absorbtivity of 24.1 g./mmole-mm. at 5.98 μ was obtained for the propenyl ether group. The polyglycols used in the reference beam were hydrogenated at room temperature and pressure in hexane solution using 5% platinum on carbon as the catalyst. After hydrogenation was complete (less than 30 min.) the solution was filtered and devolatilized at 5 mm. for 2 hr. on a steam bath in a rotating evaporator.

Molecular Weight Distribution.—A hexane solution of the polyglycol was extracted with water and then successively with aqueous methanol solutions of increasing methanol concentration. The aqueous solutions were evaporated to give the extracted polyglycol which was analyzed as usual for hydroxyl and double bond content. Details of the method will be published elsewhere.

Alkoxide Analysis.—The concentration of alkoxide ion in nonaqueous media in the presence of hydroxide ion was determined in the following way: A portion of the solution was titrated with aqueous acid to determine total base concentration. A second portion was added to excess, spent Karl Fischer reagent which had been titrated to its normal end point. The water produced by neutralization of hydroxide ion was then titrated in the usual

way.[16] The concentration of alkoxide was taken as the difference between the two values. Dissolved water causes a low value to be obtained, but the error is small in the systems described above.

(16) J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

Acknowledgment.—The authors are indebted to Mr. Merlin R. Kitchen for his guidance in the computer analysis of the kinetic data and to Dr. John W. Crump and Dr. David P. Sheetz for their helpful discussions throughout this study.

[CONTRIBUTION FROM SOCONY MOBIL OIL CO., INC., CENTRAL RESEARCH DIVISION LABORATORY, PRINCETON, NEW JERSEY]

Anodic Oxidation of Aliphatic Acids at Carbon Anodes

BY W. J. KOEHL, JR.

RECEIVED MAY 8, 1964

Electrolysis of simple aliphatic acids at carbon anodes produced high yields of products for which carbonium ion like species are intermediates: from acetic acid, methyl acetate was formed in 82% yield; from butyric acid, propene and cyclopropane in 1:2 ratio and *n*- and isopropyl butyrate also in 1:2 ratio. Pentanoic, 2-methylbutyric, and 3-methylbutyric acids yielded nearly all the possible butenes and butyl esters in addition to methylcyclopropane. These products are compared with the products of other carbonium ion reactions.

Introduction

Anodic oxidation—Kolbe electrolysis—of carboxylic acids produces hydrocarbons through a free radical sequence, $RCOO^- \rightarrow RCOO\cdot \rightarrow R\cdot + CO_2$, $2R\cdot \rightarrow R\text{-}R$.[1] In many cases, especially with α-substituted carboxylic acids, abnormal products such as olefins, alcohols, ethers, and esters are obtained which are more typical of carbonium ion reactions. Some specific examples are the formation of di- and triphenylmethyl ethers and acetates by electrolysis of di- and triphenylacetic acids in methanol or acetic acid,[2a] and of N-methoxymethyl amides by electrolysis of acylaminoacetic acids in methanol at platinum electrodes.[2b]

That cationic intermediates can be involved in such anodic oxidations was shown by Corey and co-workers[3] who compared the products of some solvolysis reactions and anodic oxidations. For example, anodic oxidation of *exo*- or *endo*-norbornane-2-carboxylic acid in methanol at platinum electrodes gave *exo*-norbornyl methyl ether, and *exo*- or *endo*-5-norbornene-2-carboxylic acid gave 3-methoxynortricyclene. Electrolysis of cyclobutanecarboxylic acid in water and deamination of cyclobutylamine both gave the same mixture of cyclobutanol, cyclopropylcarbinol, and allylcarbinol. The same anodic oxidation mechanism was invoked to explain the olefin and ether obtained by electrolysis in alcohols of 3β-acetoxybisnorallocholanic acid—an α-methyl-substituted acid.[4] In a system without α-substituents—3,3-diphenylpropanoic acid—Bonner and Mango have shown that electrolysis causes 1,2-phenyl migration *via* 2,2-diphenylethylcarbonium ion.[5]

In these and many other examples of the failure of the normal Kolbe electrolysis to occur the carbonium ion intermediates which might be generated from the initially formed alkyl radicals are relatively stable. With simple aliphatic carboxylic acids, particularly those with no α-substituents, the case for carbonium ion formation is less clear. Here, the abnormal (non-Kolbe) products are formed in minor amounts at platinum anodes while the radical-coupling reaction is the predominant reaction. We have found that at *carbon anodes* simple aliphatic acids yield the abnormal products almost exclusively. We have compared these products with those of the carbonium ion reactions, deamination[6] and deoxidation.[7]

(1) For a review of the Kolbe electrosynthesis see: (a) B. C. L. Weedon in R. A. Raphael, E. C. Taylor, and H. Wynberg, "Advances in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, Vol. 1, pp. 1–34; (b) G. E. Svadkovskaya and S. A. Voitkevich, *Russ. Chem. Rev. Eng. Trans.*, **29**, 161 (1960); (c) B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952).

(2) (a) R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 3641 (1952); (b) *ibid.*, 2854 (1951).

(3) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

(4) J. A. Waters, *J. Org. Chem.*, **29**, 428 (1964).

(5) W. A. Bonner and F. D. Mango, *ibid.*, **29**, 430 (1964).

Experimental

Apparatus.—**Cell A** consisted of a 1-l. resin kettle fitted with a stirrer, thermometer, reflux condenser, cooling bath, and an electrode assembly. The electrode assembly was made of four 1 × 32 × 115 mm. copper plates and three 6.5 × 32 × 115 mm. carbon plates which were stacked alternately and held together by two Teflon[8] rods which passed through all seven pieces. Teflon washers on the rods maintained 4 mm. spaces between the plates. This assembly was mounted vertically in the cell. The carbon plates were connected together as the anode and the copper plates were connected together as the cathode. The carbon plates were cut from the materials described in Table I.

TABLE I

ANODE CARBON

	Manufacturer	Apparent density, g./cc.	Real density, g./cc.	Pore volume, cc./g.
KC	Unknown	1.70	2.10	0.110
HPL	Great Lakes Carbon	1.68	2.24	.149
TPL	Great Lakes Carbon	1.78	2.24	.118
NC60	National Carbon	1.05	..	.457

Cell B was a 3.0-cm. diameter glass cylinder of about 100-ml. capacity fitted with a reflux condenser, thermometer, magnetic stirrer, and two 1.5 × 3.6 cm. platinum foil electrodes mounted parallel and 0.6 cm. apart.

The power supply was a variable transformer and rectifier capable of providing a direct current of 0 to 5 amp. at 0 to 120 v.

Analytical Methods.—**Gas analyses** were obtained by a combination of gas chromatographic and mass spectrometric methods. The relative amounts of propene, cyclopropane, and C_4H_8 and C_4H_{10} isomers were determined by gas chromatography on a 50 ft. column of di-*n*-propyl sulfone and dimethyl sulfolane on Chromosorb.[9] Absolute amounts of hydrogen, carbon dioxide, other light gases, and total C_4H_8 compounds were determined mass spectrometrically. Cyclopropane and propene from the

(6) (a) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957); (b) G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **84**, 2838 (1962).

(7) P. S. Skell and J. Starer, *ibid.*, **81**, 4117 (1959).

(8) Trademark of E. I. du Pont Co.

(9) M. G. Bloch in H. J. Nobles, R. F. Wall, and N. Brenner, "Gas Chromatography," Academic Press, Inc., New York, N. Y., 1961, pp. 133–161.