[Contribution from the Division of Applied Chemistry, National Research Council]

# The Cationic Polymerization of Ethylene Oxide. III. Depolymerization of Polyglycols by Oxonium Fluoroborates

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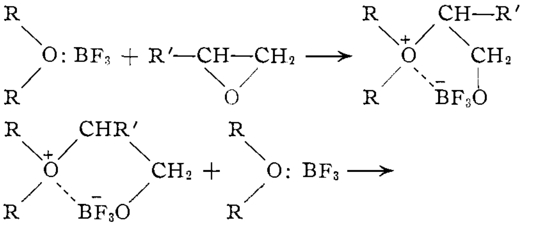
The apparent equilibrium molecular weight of polymers obtained from ethylene oxide with boron fluoride is considered to result from an equilibrium between two distinct reactions, one a polymerization and the other a depolymerization. The present paper discusses the depolymerization process and suggests a mechanism based on oxonium ion intermediates to account for the results.

When ethylene oxide is polymerized by boron fluoride in an ethylene dichloride solution containing a small amount of hydroxylic compound as chain initiator, the polymerization proceeds only to a molecular weight of about 700, although monomer continues to disappear more or less indefinitely.[1] The number of polymer molecules, initially equal to the number of hydroxyl groups, may increase appreciably during prolonged reaction but the continued disappearance of oxide is due almost entirely to the formation, not of new polymer, but of dioxane. If high molecular weight polyglycols are introduced into the reaction mixture, their molecular weight is reduced until, given sufficient ethylene oxide, the average molecular weight is once again about 700. This reduction in molecular weight is accomplished by elimination of dioxane from the polymer chain as shown by the fact that deuterated oxide produces undeuterated dioxane in the early stages of the depolymerization. Apparently the oxide and boron fluoride initiate a chain reaction which yields up to three or four molecules of dioxane for each molecule of reacted oxide.

The approach of the system to a fairly definite molecular weight from either higher or lower polymer suggests at first sight an equilibrium between polymer and monomer and/or dioxane. Such equilibria are known in polymer chemistry[2] and are characterized by strong dependence of the molecular weight upon reactant concentrations and upon reaction temperature. In the present case, however, the molecular weight is not greatly influenced by the concentrations of oxide or of dioxane, or by the temperature. It is, however, markedly dependent upon the catalyst, for stannic chloride and antimony pentachloride both yield relatively high molecular weight polymers (5000–10,000) along with some dioxane, without apparent "equilibrium." Furthermore we may note that Rose[3] observed the formation of large amounts of cyclic tetramer in the polymerization of trimethylene oxide with boron fluoride, a surprising result because the energy gained in going from polymer to these 16-membered rings must be small. There thus seems to be a fair amount of evidence to suggest that the rather constant molecular weight obtained in the boron fluoride–ethylene oxide reaction is not due directly to a polymer–monomer or polymer–dimer equilibrium. If there is no such equilibrium, then it seems necessary to conclude that the polymerization and depolymerization reactions are essentially independent of each other but have approximately equal rates in the presence of a polyglycol of molecular weight ~700. At first sight such a conclusion seems unacceptable since it requires either or both of the rates to vary with molecular weight in order to achieve equilibrium at a finite molecular weight. However, the bifunctional nature of the polyglycols suggests a way around this difficulty because if polymerization were to occur at the terminal hydroxyl groups while depolymerization took place at centers along the chain then, provided that the number of chains remained relatively constant, the number of centers for initiation of depolymerization would increase steadily with respect to those for polymerization as the chain length increased. It follows that molecular weight equilibrium could result if the two reactions were suitably dependent upon the concentrations of monomer, catalyst, hydroxyls, etc. As there is now good reason to believe that the ethylene oxide polymerization is, in fact, controlled in some such manner, the purpose of the present paper is to examine the nature of the depolymerization process.

It is evident that if a reaction scheme such as that outlined is to apply to the polyglycols, then the ether groups must undergo some rather vigorous and specific reaction. Such reactions are not common, but fortunately much of the pertinent chemistry for this discussion was described some years ago by Meerwein and his co-workers[4] when they reported the preparation of tertiary alkyloxonium fluoroborates from boron fluoride, epoxides and simple aliphatic ethers according to the reaction scheme



(1)

$$R_3\overset{+}{O}\,\overset{-}{BF_4} + ROCHR'CH_2OBF_2 \quad (2)$$

$$3ROCHR'CH_2OBF_2 \longrightarrow (ROCHR'CH_2O)_3B + 2BF_3 \quad (3)$$

The first product is the rather unstable and insoluble "inner" oxonium salt which slowly reacts with further boron fluoride etherate to form the much more soluble tertiary alkyloxonium fluoroborate. The reactions are vigorous and, because

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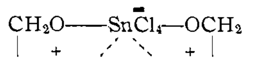
[1] D. J. Worsfold and A. M. Eastham, This Journal, **79**, 900 (1957).

[2] F. S. Dainton and K. J. Ivin, *Quart. Revs.*, **12**, No. 1 (1958).

[3] J. B. Rose, *J. Chem. Soc.*, 542 (1956).

[4] H. Meerwein, E. Battenburg, H. Gold, E. Pfeill and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

of the regeneration of boron fluoride from the alkoxy boron fluoride, essentially quantitative. Tertiary oxonium salts were obtained in this way from boron fluoride, antimony pentachloride, ferric chloride and aluminum chloride, but stannic chloride formed only the double inner oxonium salt



which then decomposed either to $(EtOCH_2CH_2O)_2$-$SnCl_2$ and ethyl chloride or to $EtOCH_2CH_2OEt$ and stannic chloride etherate. This difference is interesting because according to our earlier observations[5] stannic chloride produces two molecules of polymer per molecule of catalyst and the polymer grows until terminated, apparently by chlorine transfer. Some dioxane is produced, but the molecular weight of the final polymer seems to be controlled by the monomer/catalyst ratio. The essential difference between boron fluoride and stannic chloride as catalysts may therefore be related to the ability of these compounds to form tertiary oxonium salts which do not readily lose halogen to the growing chain.

## Experimental

Triethyloxonium fluoborate was prepared from diethyl ether, boron fluoride and epichlorohydrin by the method of Meerwein, *et al.*[4] The entire preparation was carried out in a vacuum system in such a manner that the product was obtained as a weighed sample in a sealed ampoule which could be transferred to the reaction flask without exposure to the atmosphere.

Polyglycols were purified by precipitating from acetone with petroleum ether, filtering, and pumping off residual solvent. In a few cases they were also passed, in benzene solution, through silica gel columns, but the additional treatment had no effect upon the results. They were stored over phosphorus pentoxide and pumped under high vacuum for several hours just before use.

Reactions were carried out at 20° in the solvent ethylene dichloride prepared as described previously. All manipulations were carried out within the vacuum system to minimize contamination by moisture. The extent of depolymerization was determined by weighing the residue obtained at the end of the reactions after distilling off volatile materials under vacuum, first at room temperature, finally at 50°.

Absorption spectra were obtained with a Beckman DK spectrophotometer and 1-cm. rectangular silica cells. The cells had been fused to render them vacuum tight, then sealed to the reaction flask so that they could be filled without exposure to the atmosphere. After filling, the contents were frozen and the flask and cell cut off the vacuum line with the torch.

Other materials and methods were essentially as described previously.

## Discussion

Figure 1 shows the results obtained on allowing samples of triethyloxonium fluoroborate to react to completion with a series of polyglycols in ethylene dichloride solution. Equal weights (0.86 g.) of polymer were taken for all experiments, so the essential difference between runs with polymers of molecular weight 1540, 4000, 6000 and 20,000 lies in the hydroxyl content of the solutions. With sufficient oxonium salt the polymers were completely decomposed and the product was found, by gas chromatography, to consist almost exclusively of dioxane. We have never observed in these experiments with oxonium salts the significant amounts of 2-methyl-1,3-dioxolane found in the earlier experiments with boron fluoride and oxide. The effectiveness of the oxonium salt in decomposing the polymer increases with increasing molecular weight of the polymer (decreasing hydroxyl content) until an apparent maximum is reached at a molecular weight of 6000. The results suggest that the oxonium salt initiates a dioxane-forming chain reaction which is terminated by hydroxyl groups and which has a maximum chain length of about forty moles of dioxane per mole of catalyst.

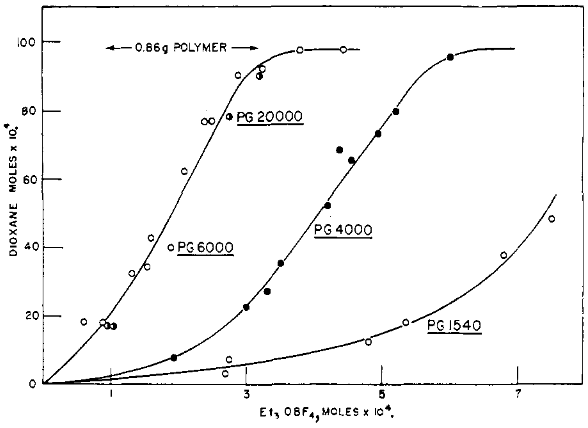
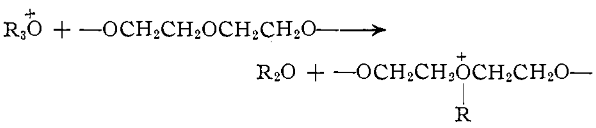


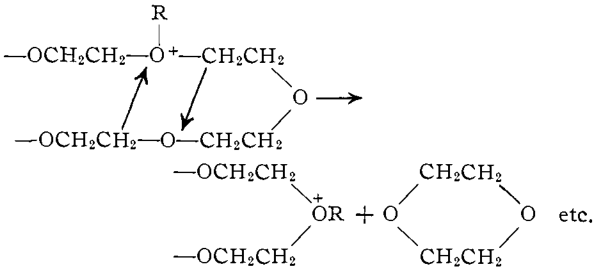
Fig. 1.—Depolymerization of polyglycols by triethyloxonium fluoroborate.

We must suppose, in keeping with the known chemistry of the oxonium ions, that the first step in the decomposition process is an ether exchange reaction which transfers the oxonium ion to the polyglycol chain

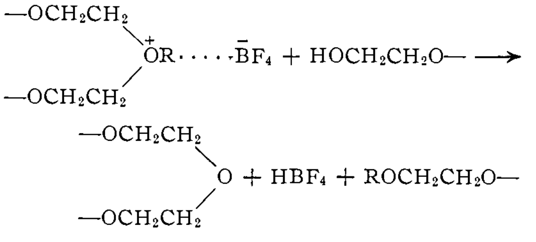


$$R_3\overset{+}{O} + \text{—OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O—} \longrightarrow R_2O + \text{—OCH}_2\text{CH}_2\underset{\displaystyle R}{\overset{+}{O}}\text{CH}_2\text{CH}_2\text{O—}$$

Internal ether exchange reactions could then eliminate dioxane



until the oxonium ion is destroyed in the termination step



(4)

In agreement with this view it is found that if the quantity of polyglycol 1540 is reduced to make the

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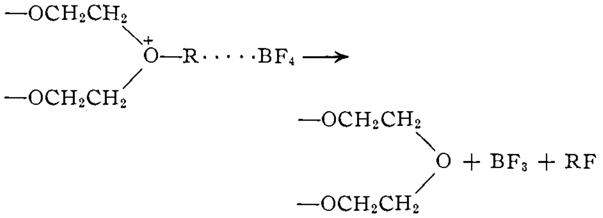
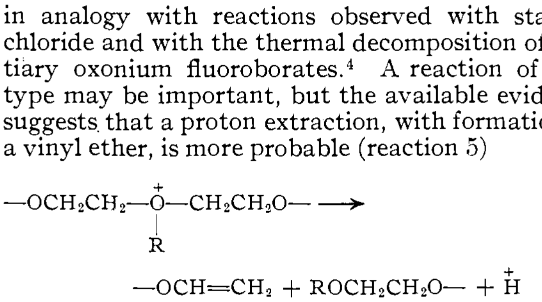
[5] D. J. Worsfold and A. M. Eastham, THIS JOURNAL, **79**, 897 (1957).

hydroxyl concentration equal to that in the experiments with polyglycol 4000, then the two polymers yield equal amounts of dioxane from equal catalyst. Small amounts of water markedly reduce the extent of depolymerization but addition of dioxane appears to have little effect upon the reaction. The above mechanism, together with inspection of models, suggests that larger rings than dioxane could be formed in the decomposition, but no evidence was found for them; the cyclic tetramer observed by Rose from trimethylene oxide was presumably formed because of strained rings in the 8- and 12-membered dimer and trimer.

There are two main points of interest in the depolymerization reaction: (a) the limiting of the reaction chain length to about forty dioxane units at molecular weights above 6000 and (b) the regeneration of oxonium ions by ethylene oxide. The limiting of the chain length could be due to traces of water in the polymer, but the results have been very consistent and independent of the method of sample preparation so a "spontaneous" termination reaction seems probable. One obvious possibility is the extraction of a fluorine ion

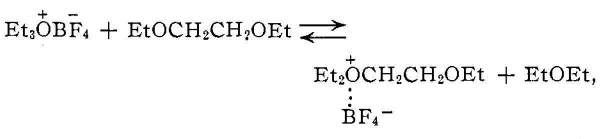


in analogy with reactions observed with stannic chloride and with the thermal decomposition of tertiary oxonium fluoroborates.[4] A reaction of this type may be important, but the available evidence suggests that a proton extraction, with formation of a vinyl ether, is more probable (reaction 5)



$$-OCH_2CH_2-\underset{R}{\overset{+}{O}}-CH_2CH_2O- \longrightarrow -OCH{=}CH_2 + ROCH_2CH_2O- + \overset{+}{H} \qquad (5)$$

The principal evidence for vinyl ether formation comes from the fact that reactions at low hydroxyl concentration, when carried nearly to completion, develop strong colors. These colors seem to be associated with the $\beta$-ether structure of the polyglycol chain since they can be reproduced very simply from 1,2-diethoxyethane and triethyloxonium fluoroborate. The reaction in this case is rather slow but is accelerated by distilling off some solvent, presumably to displace the equilibrium



$$Et_3\overset{+}{O}\overset{-}{B}F_4 + EtOCH_2CH_2OEt \rightleftharpoons \underset{BF_4^-}{Et_2\overset{+}{O}}CH_2CH_2OEt + EtOEt,$$

and the solution then undergoes the characteristic color changes.

Now, if boron fluoride is added to a series of compounds which includes vinyl ethers, phenyl ethers, allyl ethyl ether, $\beta$-fluoroethyl methyl ether, acetaldehyde, vinyl acetate, 2-methyl-1,3-dioxolane and acetal, only the vinyl ethers develop strong colors. The colors are similar to those observed in the depolymerizations (Fig. 2); they are intense, develop very rapidly, and change with time. The maximum at about 350 m$\mu$ appears to correspond to the 1 : 1 complex since it appears instantaneously at very low temperatures and then rapidly disappears, but the remaining peaks, at least seven in the range 350–800 m$\mu$, cannot be assigned. Their relative magnitudes vary sharply with the $BF_3$/vinyl ether ratio and no two of them seem to rise and fall together, so each apparently represents a different compound or complex. On the assumption that each chromophore contains boron fluoride, the molar extinction coefficients can be estimated at about $10^4$, but these absorptions seem to be intensified by the presence of hydroxyl groups. Because of the complex and rapidly changing nature of the spectra, the chromophore in the depolymerization cannot definitely be assigned the vinyl ether structure, but one can say that the unknown and the vinyl ether go through identical color changes in parts of their reaction cycles and hence are probably identical.

This direct evidence for a proton transfer reaction receives some support from the polymerization experiments. It would account, as we have seen, for the limit to the length of the depolymerization chain reaction and at the same time explain, through chain fission, the observed slow increase in the number of polymer molecules and the parallelism between chain increase and dioxane formation (Table I). It would also account for small but significant amounts of dioxane containing odd numbers of deuterium atoms which we have at times observed in the products from experiments employing *sym*-dideuterioethylene oxide.

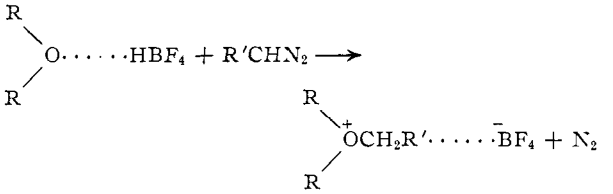
TABLE I

DEPOLYMERIZATION OF PG 4000 BY $BF_3$–ETHYLENE OXIDE[a]

| Initial concentrations | | Final concentrations | | Final molecular weight |
|---|---|---|---|---|
| Polymer | Oxide | Polymer | Dioxane | |
| 0.021 | 1.5 | 0.058 | 1.20 | 650 |
| .021 | 0.75 | .050 | 0.82 | 800 |
| .021 | .37 | .035 | .52 | 1410 |
| .021 | .275 | .028 | .41 | 1990 |
| .021 | .21 | .024 | .34 | 2390 |
| .015 | .21 | .023 | .35 | 1460 |
| .036 | .21 | .035 | .26 | 3570 |

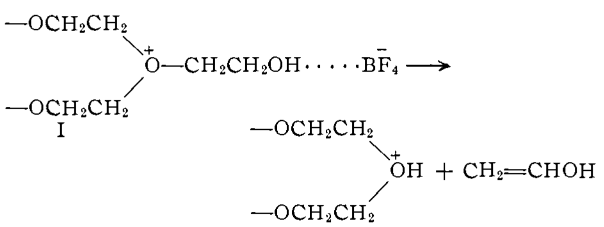
[a] All concentrations moles/liter; $BF_3$ = 0.017 mole/l.

The foregoing discussion has proposed two termination steps, reactions 4 and 5, which apply, respectively, to conditions of high and low hydroxyl (proton) concentration, but a mechanism must also provide for regeneration of the oxonium ion after termination since depolymerizations which are incomplete because of insufficient tertiary oxonium salt can be reactivated by addition of oxide. The yield of dioxane after reactivation, however, is only about two moles per mole of reacting oxide, a value far below the forty moles per mole of oxonium salt but about the same as was found in depolymerizations brought about entirely by boron fluoride–oxide.[1] This low yield suggests either that the regenerated oxonium ion is less effective than, and hence different from, the ion produced by the triethyl oxonium fluoroborate, or else that only a small part of the reacting ethylene oxide is involved in catalyst regeneration. For reasons discussed below, we believe that the latter view is incorrect and therefore that the low dioxane yield is due primarily to the structure of the new oxonium ion. This ion could be of the insoluble "inner" type (reaction 1), since the termination steps postulate the formation of boron trifluoride. Indeed, the "inner" salt does seem to be formed at very low hydroxyl concentrations since under these conditions one obtaines immediate precipitation and discoloration of the polymer. Under the usual reaction conditions however, with the concentration of boron fluoride no greater than that of hydroxyl, the solutions are clear and colorless so it seems quite probable, especially in view of the work of Klages and Meuresch,[6] that a true tertiary salt is formed. These workers showed that oxonium salts were rapidly and quantitatively produced from ethers and the acids $HBF_4$ and $HSbCl_6$ by reaction with a diazomethane as



$$R_2O\cdots\cdots HBF_4 + R'CHN_2 \longrightarrow R_2\overset{+}{O}CH_2R'\cdots\cdots\overset{-}{B}F_4 + N_2$$

If ethylene oxide could replace the diazomethane in this reaction then, since $HBF_4$ is the postulated product of the termination steps, direct regeneration of a tertiary oxonium salt would occur. The ion in this case, however, would have the structure I



$$(\text{—OCH}_2\text{CH}_2)_2\overset{+}{O}\text{—CH}_2\text{CH}_2\text{OH}\cdots\cdots\overset{-}{B}F_4 \longrightarrow (\text{—OCH}_2\text{CH}_2)_2\overset{+}{O}H + CH_2{=}CHOH$$

I

which could yield dioxane but also acetaldehyde as shown. This point is interesting because methyldioxolane, which is the product obtained from the reaction of acetaldehyde and ethylene oxide in the presence of Friedel–Crafts catalysts,[7] is observed in depolymerizations brought about by boron fluoride-oxide but not in those by oxonium salts. Furthermore the dioxolane obtained with deuterated oxide is deuterated as would be expected from the above mechanism. (Methyldioxolane could also arise according to Shostakovsky, *et al.*,[8] by rearrangement of the vinyl ether $HOCH_2CH_2OCH{=}CH_2$, but in this case need not be fully deuterated and would be expected along with other cyclic acetals in the products from tertiary oxonium ion decomposition.) Actually the acid $HBF_4$ may not itself be essential in this regeneration process because boron fluoride, in a solution containing both ether and alcohol groups, is normally present as the ternary complex $R'OBF_3 \cdots HOR_2$ which might serve equally well. The evidence for this view is, in fact, fairly strong and will be discussed in a later paper dealing with the polymerization process. For the present we can only suggest that the low efficiency of the depolymerization process after regeneration of the oxonium ion may be due to the substitution of a 2-hydroxyethyl group for the ethyl group of the original ion.

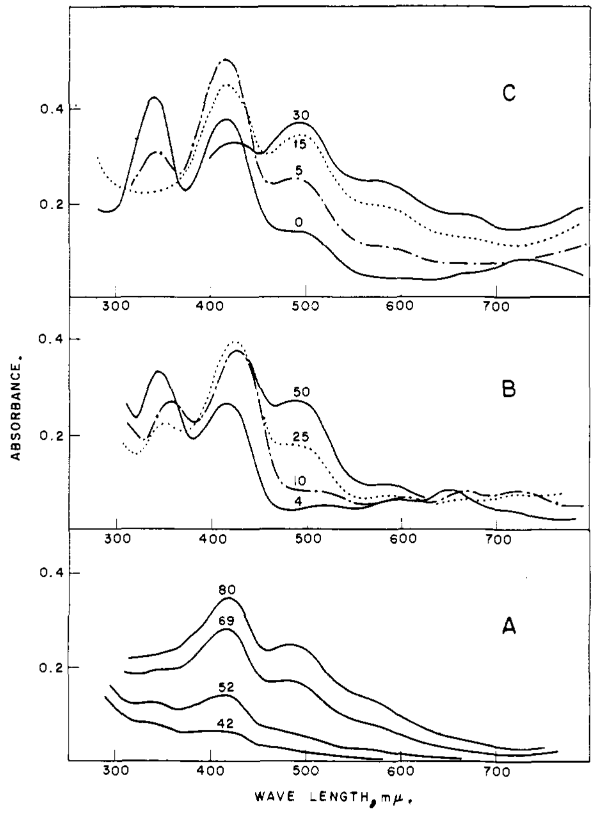


Fig. 2.—Absorption spectra in ethylene chloride: A, $EtOBF_4$, 1.5 × $10^{-2}$ m.; PG 4000, 1.6 × $10^{-2}$ m.; B, $BF_3$, 3.1 × $10^{-3}$ m.; ethyl vinyl ether, 3.1 × $10^{-3}$ m.; C, $BF_3$, 8.2 × $10^{-4}$ m.; ethyl vinyl ether, 5.6 × $10^{-4}$ m.; PG 6000, 6.7 × $10^{-4}$ m. Figures on the curves are times (in minutes) after mixing.

In this attempt to describe the depolymerization process an important point remains rather obscure, namely, the extent to which monomer undergoes direct reaction with oxonium ions along the polymer chain. In the previous paper it was reported that the rate of disappearance of oxide throughout polymerizations was dependent upon a fractional (about 0.5) power of the oxide concentration. Further experiments have now shown, however, that under conditions where depolymerization is the dominant reaction, the order in oxide is very nearly zero and furthermore that if deuterated oxide is used in these experiments, then the initial dioxane formed contains no detectable deuterium at all. These results would be consistent with the above mechanism for depolymerization if oxide were consumed only in a relatively fast regeneration of oxonium ions and not by direct reaction with those ions. On the other hand, however, Meerwein[9] has shown that trialkyloxonium ions bring about polymeriza-

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(6) F. Klages and H. Meuresch, *Chem. Ber.*, **85**, 863 (1952).

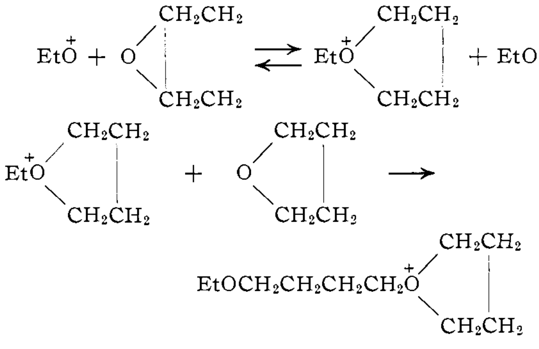
(7) T. Bersin and G. Willfang, *Ber.*, **70**, 2167 (1937).

(8) M. F. Shostakovsky and I. A. Chekulaeva, *Bull. Acad. Sci. U.S.S.R.*, 1103 (1954).

(9) H Meerwein, German Patent 741,478.

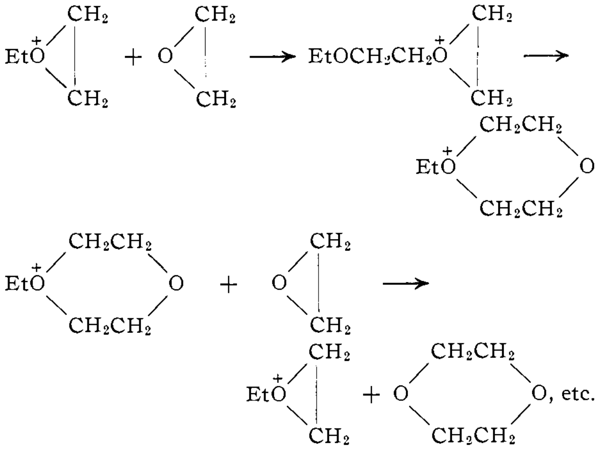
tion of tetrahydrofuran and we have now found that triethyloxonium fluoroborate, in the absence of hydroxylic compounds, brings about nearly quantitative conversion of ethylene oxide to dioxane. These reactions seem to indicate that a direct reaction between oxonium ions and ethylene oxide is at least a possibility.

The polymerization of tetrahydrofuran probably proceeds through an oxonium ion propagation



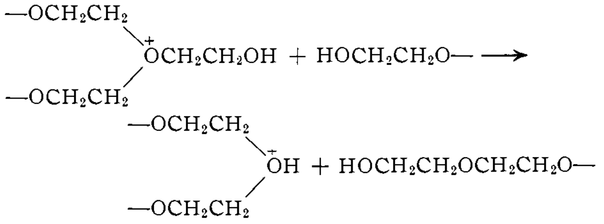
(6)

in which the propagation step (reaction 6) conceivably could be reversible. Rose[3] proposed a similar mechanism for the polymerization of trimethylene oxide by boron fluoride and in our previous paper we subscribed to this view for the case of ethylene oxide. The new results seem to indicate, however, that a propagation of this type does not occur with ethylene oxide presumably because the reverse reaction, dioxane formation, is highly favored. The corresponding reactions could therefore be, in the simplest form



Examination of the kinetics of this reaction failed to clarify the problem. Preliminary studies of the simple ether exchange between dimethyl ether and triethyloxonium fluoroborate had shown, as expected, first-order dependence on both reactants so similar kinetics might be expected for the oxide–triethyloxonium reaction. In fact, however, it was found that the kinetics were complex; at the higher ratios of salt/oxide the first-order dependence on oxide fell off with time while at low ratios the plots rose sharply. Initial rate measurements were equally complex. It is not particularly difficult to rationalize these results for, if one supposes that the initial ether exchange between the salt and the oxide is more rapid than the subsequent ones, then the decreasing rate at higher catalyst ratios is quite reasonable. At low catalyst concentration, oxonium ion destruction may become important since these reactions all show the vinyl ether colors. Catalyst regeneration is then necessary and if, as we have suggested above, this regeneration is a zero-order process, the rise in the plots at low catalyst/oxide ratio is to be attributed to a decrease in order rather than to an increase in rate. Interpreted in this way the results become consistent with the proposed mechanism for depolymerization but contribute very little to the problem of the importance of the reaction of oxide with oxonium ions during polymerization. The best evidence on this point remains the absence of deuterium in the initially formed dioxane which seems to indicate little reaction in this manner.

On the whole, this description of the depolymerization seems to account fairly well for most of our observations on the system. In a later paper the reactions leading to polymerization and their relationship to those of depolymerization will be considered in order to show how the molecular weight is limited by competition between the two processes. For the present it is perhaps sufficient to point out that if an oxonium ion of structure I were to react with hydroxyl groups (reaction 4), then a termination step in the depolymerization process would become a propagation step in polymerization, *i.e.*



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