$$Ph_3P^+CH_2CH_2CO_2\sim\sim\sim CH_2CH_2O^-$$

7

$$CH_2{=}CHCO_2\sim\sim\sim CH_2CH_2O^-\cdot Ph_3P^+X$$

8

(X = H or alkyl derivative)

ion[1] **8** species. By washing with H_2O the gegencation of **8** must be washed out,[1] whereas that of **7** is not. Coupled with this, an elemental analysis of the sample polymer showed a content in 0.52% of P. A molar ratio of **7** to **8** was calculated by NMR (15 H and 3 H, respectively) to be 1.0:2.9.

References and Notes

(1) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 256 (1974).

(2) D. S. Breslow, G. E. Hulse, and A. S. Matlack, *J. Am. Chem. Soc.*, **79**, 3760 (1957).

(3) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **8**, 374 (1975).

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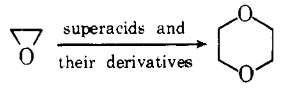
Superacids and Their Derivatives. IX.[1] Selective Cyclodimerization of Ethylene Oxide to 1,4-Dioxane Catalyzed by Superacids and Their Derivatives

Recently we have reported reactions of a series of cyclic ethers by means of superacids and their derivatives. In these works ring-opening polymerizations of seven-,[1] five-,[2-6] and four-membered cyclic ethers[7] and oxonium formation reactions of a six-membered cyclic ether[8] have been studied mainly from the kinetic and mechanistic viewpoints. Now we disclose, for the first time, that in the reaction of a three-membered cyclic ether, ethylene oxide (EO), catalyzed by superacids and their derivatives, selective cyclodimerization occurs to produce 1,4-dioxane (DON) in high yields (eq 1). Superacids are acids stronger



(1)

EO DON

than 100% sulfuric acid.[5,9] In the present study trifluoromethanesulfonic (CF_3SO_3H, TfOH), fluorosulfonic (FSO_3H), chlorosulfonic ($ClSO_3H$), and perchloric ($HClO_4$) acids were employed as the superacid components.

A typical run (No. 10 in Table I) was as follows. Into a reaction tube containing 0.088 mmol of MeOTf 8.0 mmol of EO was introduced at −78° under nitrogen. The reaction tube was sealed and kept at 35°. After 16.5 hr EO was completely consumed (examined by ^1H NMR spectroscopy), and the reaction mixture was poured into a methanol solution of sodium methoxide at −30° to stop the reaction. All the volatile material was trapped by vacuum distillation. The GLC analysis of the distillate (chlorobenzene as an internal standard) showed that 0.33 g of DON was produced (95% yield based on the charged EO). Besides DON, small amounts of 2-methyl-1,3-dioxolane (~3.0%) and of ethylene and diethylene glycol ethers were produced.

Similarly, four superacids (No. 1–5), four superacid esters[5] (No. 6–13), and a superacid anhydride (No. 14) were employed as catalysts for cyclodimerization of EO under various reaction conditions (Table I). It is shown that superacids and their derivatives are effective and selective catalysts for the production of DON from EO. In the systems catalyzed by superacid esters and by the anhydride the yield and selectivity of DON were always high (except for No. 13). Although the conversion of EO was quantitative in the superacid catalyzed systems (except for No. 3), the yield of DON was relatively low. The other part of EO was converted into poly-EO. The reactions by $ClSO_3H$ and $MeOSO_2Cl$ gave low conversion of EO (No. 3 and 13). Under the reaction conditions Cl–S bond cleavage probably took place readily due to the reduced stability of the $ClSO_3^-$ group,[6] which brought about the termination of reaction. An aprotic polar solvent, nitromethane, accelerated the reaction whereas a less polar one, CH_2Cl_2, rather retarded the reaction (No. 6–8 and vide infra). In the above reactions 2-methyl-1,3-dioxolane was detected as a main by-product. The amount of the by-product, however, was at most 4% for DON under the present reaction conditions. For the sake of comparison Table I includes the results of the reactions of EO catalyzed by H_2SO_4 and MeOTs (No. 15 and 16). Neither catalyst yielded DON under these conditions. This finding indicates the difference in catalyst activity between superacids and strong acids of H_2SO_4 and TsOH.

The cationic ring-opening polymerization of EO was first achieved in 1933 by Staudinger and Lehmann with the use

Table I
Cyclodimerization of Ethylene Oxide Catalyzed by Superacids and Their Derivatives under Various Reaction Conditions[a]

No.	Catalyst	Mol % for EO	Solvent	Reaction temp, °C	Reaction time, hr	Conversion of EO, %	Yield of DON,[b] %
1	TfOH	(2.0)		20	13.5	100	80
2	FSO_3H	(2.5)		20	17.5	100	65
3	$ClSO_3H$	(4.7)	CH_2Cl_2	20	4	20	3
4	$TfOH\cdot H_2O$	(2.0)		20	5	100	30
5	70% aq $HClO_4$	(2.1)		20	5	100	20
6	EtOTf	(5.0)	CH_3NO_2	35	1.3	100	90
7	EtOTf	(5.0)		35	10	100	92
8	EtOTf	(5.0)	CH_2Cl_2	35	28	100	89
9	MeOTf	(1.1)	CH_3NO_2	35	4	100	96
10	MeOTf	(1.1)		35	16.5	100	95
11	MeOTf	(5.0)	CH_3NO_2	10	14.5	100	88
12	$EtOSO_2F$	(5.1)		35	13	100	90
13	$MeOSO_2Cl$	(5.1)		40	4	30	6
14	Tf_2O	(4.6)	CH_2Cl_2	40	10	100	91
15	95% aq H_2SO_4	(2.0)		20	5	16	0
16	MeOTs[c]	(4.7)	$C_6H_5NO_2$	40	10	0	0

[a] The charged EO was 8.0 mmol when bulk and 4.0 mmol in 0.20 ml of solvent when in solution. [b] Based on the charged EO. [c] Methyl *p*-toluenesulfonate.

of $SnCl_4$ as catalyst.[10] Later, Eastham et al. extensively examined the mechanism of the polymerization of EO and depolymerization of poly-EO catalyzed by Lewis acids of $SnCl_4$[11] and BF_3.[12-14] They observed that these Lewis acid catalyzed polymerizations of EO resulted in all cases in the production of a mixture of poly-EO and DON. Furthermore, the fraction of 2-methyl-1,3-dioxolane, a by-product, was larger (e.g., 12% for DON[12]) than that of the present reactions. It has very recently been stated that the $HF–BF_3$ catalyzed reaction of EO produces oligocyclic ethers (crown ethers) in low yields.[15] Thus, we believe that the cyclodimerization of EO catalyzed by superacids and their derivatives provides a useful method to prepare DON directly from EO.

To examine the mechanism the reaction was monitored by ^1H and ^{19}F NMR spectroscopy. Since the reaction system becomes very complicated when "acidic" proton is involved,[5] a superacid ester of EtOTf was employed as catalyst for the NMR study. Figure 1 shows ^1H NMR spectra of the reaction system in CH_2Cl_2 at 35° after 37 min (a) and 9.5 hr (b). Sharp singlets B at δ 2.50 and C at δ 3.55 are due to EO monomer and DON, respectively. A triplet A_1 at δ 1.40 and a quartet D at δ 4.55 are ascribed to methyl and methylene signals of EtOTf. Two triplets A_2 at δ 1.10 and A_n at δ 1.06 are assigned to methyl signals of ethoxylethyl (E_1, $n = 1$) and ω-ethylpoly(β-oxyethyl) (E_n, $n \geq 2$) trifluoromethanesulfonates, respectively. Small multiplets at δ 3.3–4.1 are due to methylene protons adjacent to the ether oxygen in species of E_n. Finally, a triplet-like signal E at δ 4.60 is reasonably assigned to methylene protons of $\sim\!\sim CH_2OTf$ in E_n.[1-3]

$$\underset{E_n}{Et(OCH_2CH_2)_nOTf}$$

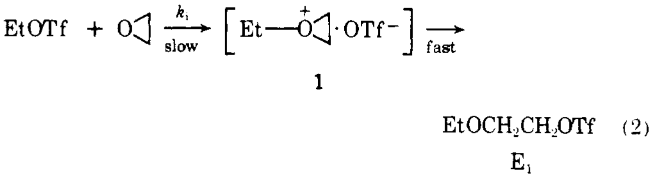
The above assignment was further confirmed by the GLC analysis of quenched products. A similar reaction system was quenched by sodium methoxide in methanol at −30°. The GLC analysis showed that the amount of DON, $EtOCH_2CH_2OMe$ produced from E_1, and $Et(OCH_2CH_2)_nOMe$ derived from E_n ($n \geq 2$) corresponded to the integrated values of the ^1H NMR peaks C, A_2, and A_n, respectively. E_1 was predominant among e_n species.

After 37 min at 35° 54% of EtOTf was reacted and the EO consumption was 3.9%. After 9.5 hr at the same temperature 37.0% of EO was reacted and the initiation stage (the EtOTf consumption) should have been completed. It should be noted, however, that a small quantity of EtOTf (~6%) was still detected.

The ^{19}F NMR spectroscopy of the same reaction system showed two sharp singlets at −2.62 ppm (relative to CF_3CO_2H external standard) due to EtOTf and at −2.98 ppm assignable to the ester species E_n,[1-3] indicating that the propagation proceeded through the ester type E_n. No oxonium species could be detected under the reaction conditions.

From the above findings the following will well explain the course of the cyclodimerization of EO catalyzed by EtOTf.

Initiation



$$EtOTf + O\triangleleft \xrightarrow[\text{slow}]{k_i} \underset{1}{\left[Et{-}\overset{+}{O}\triangleleft\cdot OTf^-\right]} \xrightarrow[\text{fast}]{} \underset{E_1}{EtOCH_2CH_2OTf} \qquad (2)$$

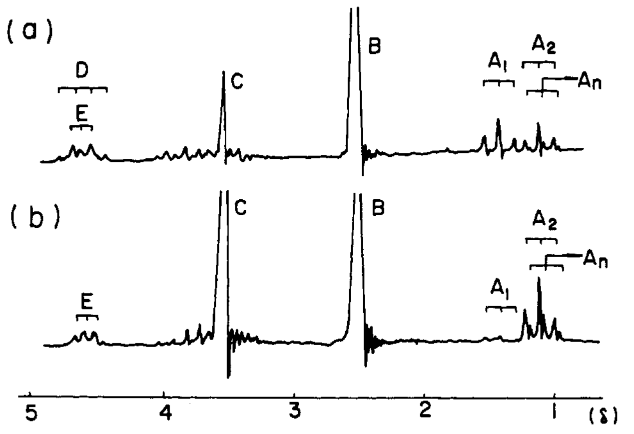
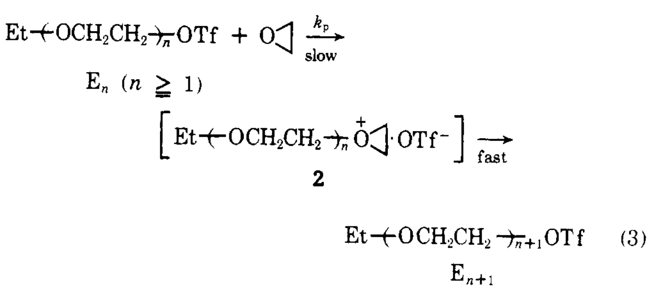


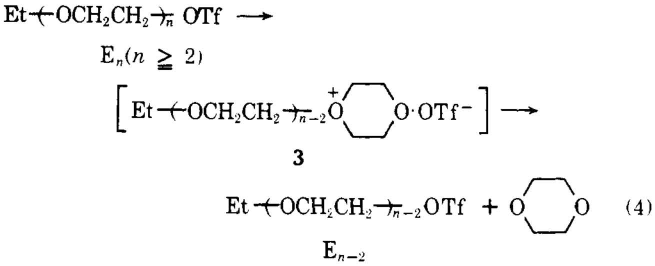
Figure 1. ^1H NMR spectra of the EO reaction system catalyzed by EtOTf in CH_2Cl_2 at 35° (a) after 37 min and (b) after 9.5 hr; $[EO]_0 = 9.2$ mol/l and $[EtOTf]_0 = 0.46$ mol/l.

Propagation



$$\underset{E_n\ (n \geq 1)}{Et(OCH_2CH_2)_nOTf} + O\triangleleft \xrightarrow[\text{slow}]{k_p} \underset{2}{\left[Et(OCH_2CH_2)_n\overset{+}{O}\triangleleft\cdot OTf^-\right]} \xrightarrow[\text{fast}]{} \underset{E_{n+1}}{Et(OCH_2CH_2)_{n+1}OTf} \qquad (3)$$

Cyclodimerization



$$\underset{E_n (n \geq 2)}{Et(OCH_2CH_2)_n OTf} \longrightarrow \underset{3}{\left[Et(OCH_2CH_2)_{n-2}\overset{+}{O}(CH_2CH_2)_2O\cdot OTf^-\right]} \longrightarrow \underset{E_{n-2}}{Et(OCH_2CH_2)_{n-2}OTf} + O(CH_2CH_2)_2O \qquad (4)$$

Reactions of eq 2 and 3 probably involve oxonium intermediates of EO 1 and 2 which are very unstable under reaction conditions[16,17] to rearrange quickly to ester species E_1 and E_{n+1}. EO is consumed according to the reactions of eq 2 and 3. The formation of DON is most reasonably explained by the so-called back-biting reaction of the ester species E_n ($n \geq 2$) to produce an oxonium species **3** which liberates DON (eq 4). It is very likely that EO is also consumed by the reaction of EO with **3** to form E_{n-1} and DON.

Based on the above scheme the following rate equations can be derived. At a very early stage of the initiation reaction the rate equation of initiation is given by

$$-d[I]/dt = k_i[I][EO] \qquad (5)$$

where k_i and [I] are the rate constant of initiation and the concentration of initiator. The rate of the EO consumption is generally given by

$$-d[EO]/dt = k_i[I][EO] + k_{p(ap)}[P^*][EO] \qquad (6)$$

where $k_{p(ap)}$ is the apparent rate constant of propagation and $[P^*]$ denotes the total concentration of propagating species. The integrated forms of eq 5 and 6 become respectively

Table II
Rate Constants in the Cyclodimerization of Ethylene Oxide Catalyzed by Superacid Esters at 35°[a]

Catalyst	Solvent	$k_i \times 10^5$, l./(mol sec)	$k_p(ap) \times 10^5$, l./(mol sec)
EtOTf	CCl_4	2.8	2.5
EtOTf	CH_2Cl_2	4.1	3.3
EtOTf		7.4	6.3
EtOTf	$C_6H_5NO_2$	22	15
MeOTf	CH_2Cl_2	5.6	2.9
$EtOSO_2F$		4.8	4.2

[a] $[EO]_0$ = 9.2 mol/l. in solution reaction and $[I]_0$ was 5.0 mol % for EO.

$$\ln [I]_0/[I]_t = k_i \int_0^t [EO] dt \qquad (7)$$

and

$$\ln [EO]_{t_1}/[EO]_{t_2} = k_i \int_{t_1}^{t_2} [I] dt + k_{p(ap)} \int_{t_1}^{t_2} [P^*] dt \qquad (8)$$

Since the k_i value and the relationship of [I] vs. time were obtained, the term of $k_i \int_{t_1}^{t_2} [I]dt$ in eq 8 became a known value. Thus, k_i and $k_{p(ap)}$ values were determined according to eq 7 and 8. In order to show the rate at what the reaction proceeded the preliminary results of several systems are given (Table II). Both the k_i and $k_{p(ap)}$ values increased in more polar media. It is interesting to note that in every case the value of $k_{p(ap)}$ is slightly smaller than that of k_i when $EtOSO_2X$ (X = CF_3 and F) is employed as a catalyst.

Further study is necessary to predict a definite mechanism of the present reaction, especially of the cyclodimerization process. As to the mechanism, however, it is important that the propagating end is an ester type species as observed in the superacid ester catalyzed polymerization of other cyclic ethers of oxepane,[1] tetrahydrofuran,[2-4,18] and 3,3-bis(chloromethyl)oxetane.[7] We are presently undertaking the kinetic and mechanistic studies on the cyclodimerization of EO in more detail, the reactions of substituted 1,2-epoxides, as well as the depolymerization of poly(ethylene oxides), all of which are catalyzed by superacids and their derivatives.

References and Notes

(1) Part VIII: S. Kobayashi, N. Tsuchida, K. Morikawa, and T. Saegusa *Macromolecules*, **8**, 942 (1975).
(2) S. Kobayashi, K. Morikawa, and T. Saegusa, *Macromolecules*, **8**, 386 (1975).
(3) S. Kobayashi, H. Danda, and T. Saegusa, *Macromolecules*, **7**, 415 (1974).
(4) S. Kobayashi, T. Nakagawa, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 2706 (1974).
(5) S. Kobayashi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **46**, 3214 (1973).
(6) S. Kobayashi, T. Saegusa, and Y. Tanaka, *Bull. Chem. Soc. Jpn.*, **46**, 3220 (1973).
(7) S. Kobayashi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 2699 (1974).
(8) S. Kobayashi, T. Ashida, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 1233 (1974).
(9) R. J. Gillespie, *Acc. Chem. Res.*, **1**, 202 (1968).
(10) H. Staudinger and H. Lehmann, *Justus Liebigs Ann. Chem.*, **505**, 41 (1933).
(11) D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 897 (1957).
(12) D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 900 (1957).
(13) G. A. Latremouille, G. T. Merrall, and A. M. Eastham, *J. Am. Chem. Soc.*, **82**, 120 (1959).
(14) G. T. Merrall, G. A. Latremouille, and A. M. Eastham, *Can. J. Chem.*, **38**, 1967 (1960).
(15) J. Dale et al., *Chem. Technol.*, 3 (1975).
(16) J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, **90**, 1349 (1968).
(17) G. A. Olah and P. J. Szilagyi, *J. Org. Chem.*, **36**, 1121 (1971).
(18) K. Matyjaszewski and S. Penczek, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1905 (1974).

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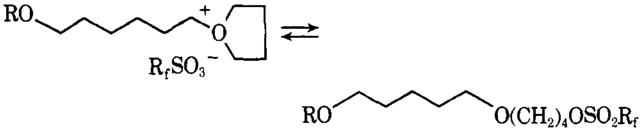
^{13}C Nuclear Magnetic Resonance Studies on the Polymerization of Cyclic Ethers

The polymerization of cyclic ethers has received considerable attention lately.[1-3] The polymerization kinetics have been established for many systems, based on the concentration of the propagating species, which were determined by phenoxy end capping,[4,5] and more recently by proton[2,6,8,9] and fluorine[3,7] NMR spectroscopy. In the polymerization of tetrahydrofuran (THF) a macroion ⇄ macroester equilibrium has been proposed,[9] and both end groups could be observed directly in high-resolution proton NMR spectra.[2]



The proton NMR signals are generally rather weak, unless large initiator concentrations are used, and due to strong solvent effects the assignments are not always unambiguous.[3,6,7] In polymerization systems where the initiator contains fluorine atoms, a clear distinction between covalent macroesters and ionic species can be made based on their different ^{19}F NMR signals.[3] However, the use of this technique is obviously restricted to polymerization systems with fluorine-containing initiators. Furthermore, it only allows a determination of the concentration of the counterion and does not permit monitoring of the actual propagating oxonium chain head during polymerization.

We have now utilized ^{13}C NMR spectroscopy to study these propagating chain heads and to monitor structural changes in the active species during the cationic polymerization of cyclic ethers. Not only can the presence of macroions or macroesters be clearly demonstrated in a noise-decoupled ^{13}C NMR spectrum, but a distinction can also be made between different types of ionic species formed in the course of the polymerization. This is generally not feasible by proton NMR spectroscopy. We wish to report preliminary results of these investigations.

The proton-noise decoupled spectra were obtained on a Bruker WH-90 Fourier transform NMR spectrometer, operating at 22.63 MHz. Typically, the spectra were recorded at 6024 Hz sweep width, and accumulation of 1000 pulses with phase alternating pulse sequence was found to give spectra with adequate signal-to-noise ratios. Field-frequency stabilization was maintained by deuterium lock on external perdeuterated benzene. The samples were prepared in 10 mm o.d. NMR sample tubes, with tetramethylsilane (TMS) as internal reference, and all chemical shifts are reported in ppm downfield from TMS. Spectral assignments were facilitated by spectra of model compounds and model polymers, which will be described in more detail at a later date.

Figure 1A shows the ^{13}C NMR spectrum of the polymerization mixture of tetrahydrofuran–methyl fluorosulfate (6:1) in nitromethane (64% by weight), after a reaction time of 20 min. Figure 1B shows a corresponding polymerization in carbon tetrachloride. The signal at lowest field in Figure