

NOTES

Superacids and Their Derivatives XI. Cyclooligomerization of Ethylene Oxide Catalyzed by a Solid Superacid of Nafion-H

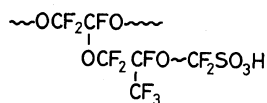
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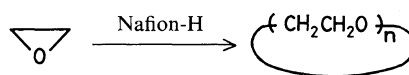
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Crown ethers can be considered as cyclic oligomers of ethylene oxide (EO). Cyclooligomerization of EO, therefore, is an attractive method to prepare crown ethers^{1,2} in a practically large scale for commercial uses, because the method is a single-step reaction and because EO is an industrially important monomer. The extension of our studies on polymerizations of cyclic ethers³ and on the cyclodimerization of EO⁴ catalyzed by superacids and their derivatives, led to a resin of perfluorinated sulfonic acid (Nafion-H, a solid superacid) which was employed as a catalyst for the reaction of EO. It has been found that the reaction underwent the oligomerization of EO to produce cyclic oligomers of EO selectively. The amount of these cyclic oligomers



Nafion-H

was quantitatively determined as crown ethers being produced in a significant amount. As to a solid superacid catalyst, Nafion-H has been used extensively for Friedel–Crafts type reactions in organic synthesis⁵ and for oligomerization of styrene.⁶



EXPERIMENTAL

Materials

EO was supplied from Meisei Kagaku Co. (Kyoto) and distilled before use. Nafion-H (the protonic acid form) was prepared from potassium salt of powdery Nafion-501 resin which was given from du Pont Co. Nafion-501 was treated with 4*N*-HNO₃ followed by FSO₃H and dried at 120—140°C for 2 days *in vacuo* with aspirator to give a white powdery resin of Nafion-H.⁵ The back-titration of Nafion-H gave proton concentrations of 0.16 mmol g⁻¹-resin. CF₃SO₃H was obtained from 3M Chemical Co. and used without further purification. All solvents were purified by distillation before use. 12-Crown-4, 15-crown-5, and 18-crown-6 (Aldrich Co.) were commercially obtained.

Cyclooligomerization

All reactions were carried out in a sealed tube under nitrogen. The reaction procedure of No. 1 (Table I) is given as a typical example. In a test tube Nafion-H (50 mg, 0.16 mmol

Table I. Cyclooligomerization of ethylene oxide (EO) catalyzed by Nafion-H^a

No.	Solvent	Reaction temp,	Reaction time	Conversion of EO	Fraction of cyclic oligomers/wt%					
					h	%	n=2	3	4	5
1	CHCl ₃	r.t.	45	100	80.5	0.2	2.6	9.1	4.3	3.3
2 ^b	CHCl ₃	0°C	190	41	86.2	0.5	1.8	5.8	4.1	1.8
3	—	0°C	190	48	87.2	0.1	2.1	6.4	2.7	1.5
4	CH ₂ Cl ₂	r.t.	168	100	92.6	0.1	1.8	2.8	1.4	1.2
5	C ₆ H ₆	0°C	270	62	89.4	0.4	1.6	5.2	1.8	1.4
6	C ₆ H ₆	r.t.	66	80	87.6	0.2	1.2	5.8	2.9	2.3
7	CH ₃ CN	r.t.	230	22	83.8	0.2	2.6	9.8	2.5	1.1
8	CH ₃ CN	0°C	270	15	70.1	0.5	4.6	16.9	5.0	2.9
9 ^c	CHCl ₃	0°C	20	100	93.1	0.2	0.9	2.5	1.8	1.5

^a EO (5.0 mmol) + Nafion-H catalyst (50 mg = 0.16 mmol of H⁺) in 0.2 ml of solvent in a sealed tube unless otherwise indicated.

^b The Nafion-H catalyst recovered from No. 1 was reused after keeping it for 60 days in air at room temperature.

^c CF₃SO₃H (0.2 mmol) was used as catalyst instead of Nafion-H.

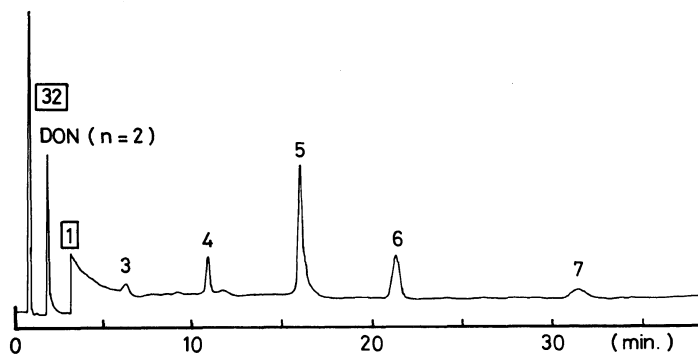


Figure 1. Gas chromatographic (GC) chart of the cyclooligomerization products of EO catalyzed by Nafion-H. Peak numbers indicate the number of EO unit of cyclic oligomers. 32 and 1 show the sensitivity of the GC detector. Column temperature was raised from 50°C to 220°C at the rate of 10°C min⁻¹.

equivalent of the acid) was placed under nitrogen and 0.2 ml of CHCl₃ was added to it. Into the tube kept at -78°C EO (5 mmol) was introduced by distillation. Then, the tube was sealed and kept standing with occasional shaking at room temperature for 45 h. The tube was cooled to 0°C and opened. The supernatant reaction mixture was transferred by using a syringe into an NMR sample tube at 0°C which was sealed and subjected to ¹H NMR measurement. The ¹H NMR analysis of the mixture revealed that the peak of EO (δ 2.5) disappeared and new signals due to open-chain oxy-ethylene units appeared at δ 3.5 (100%

conversion of EO).

Products were analyzed by gas chromatography (GC) (Shimadzu GC 6A gas chromatograph with a column packed with Silicon DC550 using hydrogen gas carrier at 1.5 kg cm⁻²) with raising the column temperature at the rate of 10°C min⁻¹ from the starting temperature of 50°C. After 17 min later, the column temperature reached 220°C and this temperature was kept thereafter. Under these GC conditions the retention times of cyclic oligomers were 1.8 min (dimer), 6.0 min (trimer), 11.0 min (tetramer), 16.0 min (pentamer), 21.0 min (hexamer), and 31.0 min

(heptamer) (Figure 1), respectively. Authentic cyclic oligomers of tetramer, pentamer, and hexamer were used to assign the GC retention times of each products. Cyclic oligomers higher than octamer were not detected.

RESULTS AND DISCUSSION

Heterogeneous Cyclooligomerization by Nafion-H

Cyclooligomerization of EO catalyzed by a powdery resin of Nafion-H was performed in a sealed tube with occasional shaking at 0°C or at room temperature (No. 1—8, Table I). For example, ¹H NMR analysis of the reaction No. 1 carried out in CHCl₃ solvent showed the complete consumption of EO after 45 h at room temperature. The GC analysis of the reaction mixture revealed that cyclic oligomers of EO (crown ethers) were produced in a fairly large amount although 1,4-dioxane (DON) was the largest in amount among these cyclic products (Figure 1). In addition to these, unidentified peaks were observed in the GC chart, which might be probably due to linear oligomers. The amount of cyclic oligomers exceeded at least 80% of the consumed EO in every run. Solvent effects on the cyclooligomerization were not clear. In CH₃CN, the consumption of EO was slow and the selectivity of crown ethers, however, was remarkably enhanced, *e.g.*, the production of 15-crown-5 reached 16.9% yield (No. 8). Without solvent the reaction (No. 3) proceeded almost the same as the CHCl₃ system. It is to be noted that Nafion-H could be used again without decreasing the catalyst activity (No. 2). In addition, the treatment of 18-crown-6 (8.0 mmol equivalent to EO unit) with 0.90 mmol of Nafion-H in 2.0 ml of CHCl₃ did not cause any change of 18-crown-6 after 58 h at 25°C. This result suggests that the produced crown ethers are not isomerized during the reaction by Nafion-H catalyst, which shows a sharp contrast to results² that the produced oligomers from EO changed by a Lewis acid catalyst to a

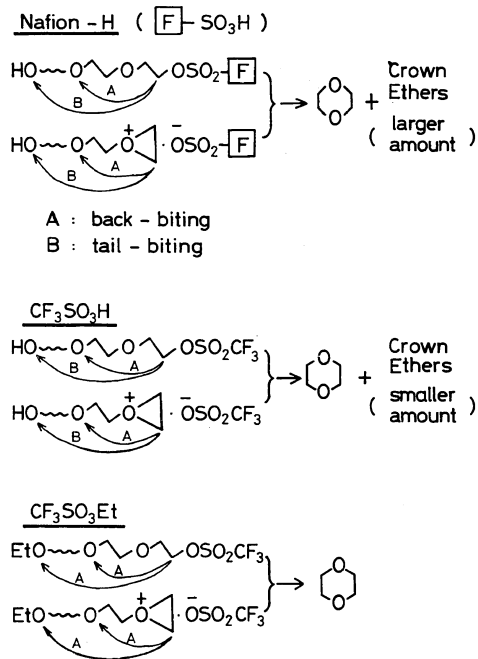
more thermodynamically stable DON.

Homogeneous Cyclooligomerization by CF₃SO₃H

A homogeneous catalyst corresponding to Nafion-H is a liquid superacid of CF₃SO₃H. The reaction of EO catalyzed by CF₃SO₃H, therefore, was examined in comparison with the catalytic behavior of Nafion-H. As seen in reaction No. 9 (Table I) the catalytic activity of CF₃SO₃H was much higher than that of Nafion-H. However, the production of crown ethers was much less and the total amount of cyclic oligomers was also less; at most 70% of EO. In addition, a separate experiment showed that CF₃SO₃H did not induce any isomerization of 18-crown-6 in CH₂Cl₂ at 25°C for 20 h; crown ethers such as DON being resistant to isomerization by a protonic acid catalyst like CF₃SO₃H. This is in contrast to an oxonium catalyst² or a Lewis acid catalyst^{1d} which caused an isomerization of crown ethers.

Reaction Mechanism

A heterogeneous catalysis by Nafion-H is characterized by a higher selectivity of the production of crown ethers. This characteristic may be explained according to Scheme 1. Oligomerization of EO by a superacid catalyst proceeds *via* ester species and/or cyclic oxonium species.^{3,4} With Nafion-H or CF₃SO₃H catalyst, a linear oligomer having an OH group at the end is first to be formed. Then, two intramolecular reactions will take place; back-biting reaction (course A) and tail-biting reaction (course B). These two courses are intramolecular competitive reactions. The tail-biting is probably more readily to occur than the back-biting if the same cyclic product is formed because proton is a better leaving group than an oxyethylene chain. It is likely that crown ethers are mainly produced *via* course B rather than course A. With Nafion-H catalyst, course A becomes less probable due to the steric hindrance in the polymer matrix



Scheme 1

of Nafion resin. Therefore the Nafion-H system possesses a higher probability to proceed to linear oligomers of several EO units whose tail-biting reaction gives rise to crown ethers. With a homogeneous catalyst of $\text{CF}_3\text{SO}_3\text{H}$, on the other hand, such a steric situation is not present. Thus, the formation of crown ethers is more preferable with Nafion-H than with $\text{CF}_3\text{SO}_3\text{H}$. Finally, the superacid ester ($\text{CF}_3\text{SO}_3\text{Et}$) system does not involve the tail-biting course since no OH group (tail) is present at the end. This situation will rationalize the predominant formation of DON with the ester catalyst *via* the back-biting (course

A), as the production of crown ethers is negligible in very small amount.⁴

CONCLUSION

Nafion-H is an effective catalyst for the cyclooligomerization of EO to give crown ethers with higher selectivity. It is a powdery resin and hence, is easy to handle; the catalyst is able to separate from the reaction mixture by a simple filtration. The catalyst can be used repeatedly without a decrease in the catalyst activities.

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