

Unexpected Cleavage of Crown Ether in the Reaction of Methyloxirane with $K^-, K^+(15\text{-crown-5})_2$

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Cleavage of oxirane and crown ether rings occurs when the supramolecular complex $K^-, K^+(15\text{-crown-5})_2$ reacts with methyloxirane in tetrahydrofuran solution. Potassium isopropoxide and potassium tetraethylene glycoxide vinyl ether are the main products of the reaction. The cleavage of 15-crown-5 is observed also in the reaction of the metal complex with methyl iodide. That means that the crown ether acts both as an activator and as a reagent in these processes. The solvent was inert in the studied systems.

Introduction

Supramolecular complexes of alkali metals containing metal anions and cations have previously been known as the reducing agents of many organic compounds,^{1–8} as well as the initiators of polymerization of vinyl monomers,^{9–11} dienes,^{12,13} lactones^{14,15} and oxiranes.^{16–18} In our earlier work¹⁸ on the use of such complexes to initiate polymerization of methyloxirane, we studied the mechanism of propagation and chain-transfer reactions. The rate constants for these reactions were determined. The initiation was observed to occur instantaneously. Therefore, it could be neglected when the kinetic equation which describes the polymerization process was derived.

The present work is a continuation of the study on polymerization of methyloxirane in the presence of supramolecular metal complexes. Its aim was to explain the course of the initiation reaction. $K^-, K^+(15\text{-crown-5})_2$

complex in tetrahydrofuran solution was selected for the study because of its particular stability at room temperature.¹⁹

Results and Discussion

The $K^-, K^+(15\text{-crown-5})_2$ solution in tetrahydrofuran has a characteristic dark blue color. The signals due to both metal ions were present in the ³⁹K NMR spectrum.²⁰ The addition of the supramolecular complex solution into the solution of methyloxirane caused an instantaneous discoloration due to the disappearance of potassium anions.^{9,21,22} After that only the signal of potassium cation was observed in the spectrum. That means that all metal anions present in the solution took part in the reaction. To identify the nonvolatile products, methyl iodide was added after mixing of the reagents. In the chromatogram of a sample separated from precipitated potassium iodide, the main product of the reaction was identified as tetraethylene glycol methyl vinyl ether, i.e., as a methyl derivative of potassium tetraethylene glycoxide vinyl ether, in 34% yield. No peak of 15-crown-5 was observed since the crown ether was displaced as a precipitate in the form of a complex with potassium iodide.

After solvent evaporation, in the ¹³C NMR spectrum of the sample, aside from the carbon signals of CH₂O groups in the range of 67–72 ppm, a signal at 59 ppm arising from the carbons of CH₃O and the signals due to the vinyl carbons of the CH₂=CH–O function at 86.6 and 151.7 ppm were found. These observations confirmed the result of analysis by the GC–MS method.

Further information was provided by the analysis of samples treated with benzyl bromide instead of methyl iodide. The signals of two main products of the reaction were found in the chromatogram. One of them was

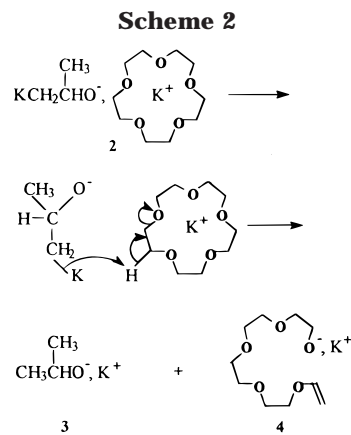
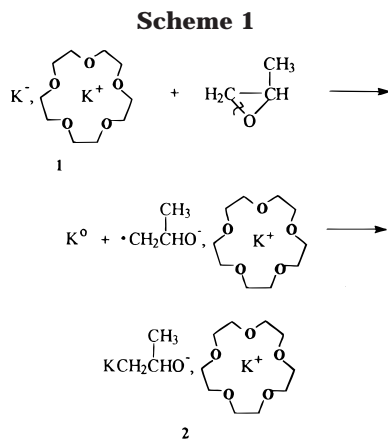
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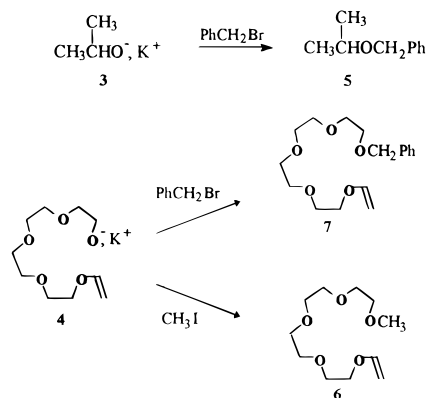


identified as benzyl isopropyl ether, i.e., the benzyl derivative of potassium isopropoxide, in 39% yield. The other product was found to be tetraethylene glycol benzyl vinyl ether, i.e., the benzyl derivative of potassium tetraethylene glycoxide vinyl ether, in 51% yield. The chromatogram also exhibited a signal due to 15-crown-5 present in the solution after decomplexation of potassium cations. In the ^{13}C NMR spectrum of the benzylated sample, both the signals due to vinyl carbons at 86.6 and 151.7 ppm, and the signals of CH_3 carbons of the isopropoxy group at 22.4 ppm were present.

As the potassium isopropoxide was found by benzylation to be one of the two main products of the examined reaction, the analysis of the samples subjected to methylation was repeated. It appeared that the expected peak of the methyl derivative of potassium isopropoxide, i.e., isopropyl methyl ether, could not be observed in the chromatogram due to its overlapping with the broad peak of the solvent. In turn, the carbon signals of isopropyl methyl ether could not be recorded in the ^{13}C NMR spectrum because prior to analysis the volatile ether (bp 32 °C) was removed from the methylated sample during evaporation of tetrahydrofuran.

We assume that the reaction of the supramolecular potassium complex **1** with methyloxirane starts by the opening of the oxirane ring in the β position (Scheme 1, the other 15-crown-5 molecule being omitted). There are two possible directions of the reaction, i.e., electron transfer or attack of K^- on the carbon atom from the CH_2 group of the oxirane ring. The mechanism of the reaction of metal anions with cyclic ethers was studied thoroughly by Jedliński et al.²³ Oxetane was taken as a model compound in that work. It was found that electron transfer occurred from potassium anion in that case. Radical anions were observed in the ESR spectra. This finding was confirmed in the reaction of K^- with 2-oxetanone.²⁴ Therefore, the electron-transfer mechanism was accepted in this work for Scheme 1. It is worth emphasizing that the regioselectivity observed in the reaction of methyloxirane with K^- is consistent with a mechanism involving cleavage of the oxirane ring to give the more substituted alkoxide, rather than the more substituted radical, as was discussed in ref 25. In that paper the key references can be found. In particular, the theoretical explanation for the apparently anomalous direction of opening is given.

Scheme 3



The proton exchange in the ion pair **2** results then in the formation of potassium isopropoxide **3** and potassium tetraethylene glycoxide vinyl ether **4** after the crown ring opening (Scheme 2). The proposed course of the reaction corresponds very well with the similar cleavage of dimethoxyethane by alkyllithium, yielding methyl vinyl ether and lithium methoxide.²⁶ Dimethoxyethane may be treated in this case as a model compound for the fragment of the crown ether molecule. It is also consistent with the mechanism for the reactions of organometallic compounds with simple cyclic ethers, such as 2-alkyl-substituted tetrahydrofuran or tetrahydropyran, and nonsubstituted oxepane.²⁷

The process described above is very fast. After mixing of the reagents, potassium anions diminish immediately, and upon the addition of methyl iodide or benzyl bromide, the respective methyl and benzyl derivatives of **3** and **4** are obtained (Scheme 3). No products were found in which methyl or benzyl groups are attached to the carbon atom associated with potassium in the ion pair **2**. Likewise, no product of the addition of methyloxirane to that carbon was observed to form. The corresponding methyl derivatives of byproducts of the reaction were also identified, i.e., triethylene glycol dimethyl ether and tetraethylene glycol dimethyl ether, in yields below 10%.

It is worthwhile to note that crown ethers, widely used in organic syntheses as activators, were until now considered to be stable. The exceptions were found earlier only for the self-decomposition of the alkali metal supramolecular complex occurring in tetrahydrofuran solu-

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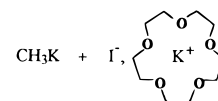
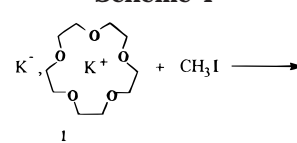
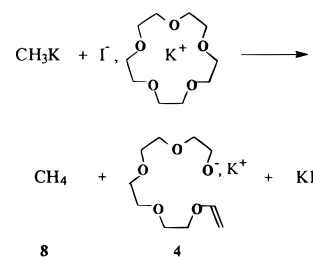
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tion^{28,29} as well as in the reaction of potassium with arenocrowns.³⁰ The reactions of metal anions with crown ethers were slow and led to a mixture of metal glycoxides and ethylene. The course of the process was described in detail for the $K^-, K^+(18\text{-crown-6})$ solution, which decomposes completely after 1.5 h at ambient temperature.²⁸ However, the $K^-, K^+(15\text{-crown-5})_2$ system used in this work is stable for 1 h after its preparation.¹⁹ The concentration of potassium anions does not change in this time. Therefore, our finding is the first example that the crown ether ring is opened when organometallic compound is present in the mixture. Unsaturated alkoxide is the product of the reaction. Cleavage of the latter by K^- affords dipotassium glycoxides, which lead, after addition of methyl iodide, to the above-mentioned dimethyl ethers of tetraethylene glycol and triethylene glycol. It means that the fast reactions observed in this work and the slow decomposition process of the potassium supramolecular complex have different natures. Another possible path to dipotassium glycoxides, namely, by elimination of acetylene from the unsaturated alkoxide **4**, was excluded, since no acetylene was found.

Moreover, it was considered whether the solvent takes part in the studied processes. It was known that, e.g., *n*-butylpotassium reacts rapidly with tetrahydrofuran already at -75°C to afford 2-tetrahydrofurylpotassium, which decomposed slowly at -75°C and rapidly at -50°C by fragmentation to ethylene and the potassium enolate of acetaldehyde.³¹ Tetrahydrofuran, used as the solvent, was found to be sufficiently acidic to allow rapid protonation of dianions at ambient temperature.³² It was also reported¹¹ that in the reaction of styrene with $K^-, K^+(18\text{-crown-6})$ in tetrahydrofuran there occurs a partial protonation of styrene dianion by the solvent. Therefore, an additional reaction of $K^-, K^+(15\text{-crown-5})_2$ with methyloxirane in deuterated tetrahydrofuran was performed. The reaction mixture was treated with benzyl bromide. After the precipitate was separated and the solvent was evaporated, the residue was analyzed by ¹³C NMR. No characteristic signals indicating the presence of deuterium in the structure of the compounds which could be formed in the reaction of **2** with THF-*d*₈ were found.

The higher reactivity of crown ether in comparison with tetrahydrofuran may originate from a specific activating effect of several oxygen atoms in the polydentate ligand as well as from the fact that crown ether takes part in the reaction in the form of the complex with potassium cation.³³ The complexation of the cation by the crown ether molecule would tend to make the C–H bond more acidic.³⁴

The possibility of the reaction of **2** with the CH_3 group of methyloxirane was also taken into account. In such a reaction potassium allyloxide was assumed to form.³⁵ However, in the reaction mixture treated with benzyl

Scheme 4**Scheme 5****Scheme 6**

bromide or methyl iodide, no corresponding derivatives were found.

Therefore, the organometallic product of oxirane ring opening reacts exclusively with crown ether. This process results in the formation of two metal alkoxides, which along with the products of side reactions compose a mixture of the real initiators when the methyloxirane polymerization is started in the presence of alkali metal supramolecular complexes.

It was interesting to determine whether the ring opening of crown ether occurs exclusively in the presence of methyloxirane. Therefore, a reaction of $K^-, K^+(15\text{-crown-5})_2$ with methyl iodide was conducted. In this case organometallic compound was also expected to form as an intermediate product, as in Scheme 1. A 1:2 mole ratio of reagents was used, and the products were analyzed by means of the GC–MS method. The intense peak of the methyl derivative of unsaturated potassium alkoxide **4** was observed in the chromatogram. The side reactions afford two glycoxides, as in the case of methyloxirane. The analysis of gaseous substances demonstrated methane **8** and ethane **9** to evolve. The liberated gases were determined quantitatively. In an experiment 10 cm³ of 0.1 M $K^-, K^+(15\text{-crown-5})_2$ solution was added dropwise to 10 cm³ of 0.2 M methyl iodide solution in tetrahydrofuran. In the reaction 8 cm³ of methane and 14.7 cm³ of ethane evolved; i.e., a total of 22.7 cm³ was found in the liquid and gas phases.

The supramolecular metal complex was concluded consequently to react with methyl iodide as shown in Scheme 4. Then, the crown ether molecule undergoes ring opening, leading to the formation of potassium tetraethylene glycoxide vinyl ether **4**. Liberation of methane occurs simultaneously (Scheme 5). It is accompanied by the formation of ethane (Scheme 6). According to Schemes 4–6 the theoretically calculated total volume of methane and ethane was 22.4 cm³. It was found to be in good agreement with the experimental results.

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Conclusions

Oxirane and crown ether rings are cleaved in the reaction of methyloxirane with $K^-, K^+(15\text{-crown-5})_2$ supramolecular complex in tetrahydrofuran solution. Metal alkoxides are the products of the reaction. The process is accompanied by side reactions, but no products of solvent decomposition were found. It was also shown that the crown ether ring opening reaction is not confined to the system containing methyloxirane.

Crown ethers, widely used in organic synthesis as activators, are considered, with some exceptions,^{28–30} to be stable. The reactions reported here demonstrate the possibility of their decomposition also in processes involving organometallic compounds.

Experimental Section

Analytical Methods. GC–MS analyses were run on a 30 m long DB 1701 fused silica capillary column, using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. The methylated or benzylated products were identified by comparing their mass spectra and retention times with those of authentic compounds. Diethylene glycol dimethyl ether was used as the internal standard for the yield measurement.

Gaseous products were identified by GC with a 2.4 m long stainless steel column packed with Al_2O_3 , 0.2–0.3 mm, deactivated with 5% K_2CO_3 , in an INCO 505 gas chromatograph equipped with a flame ionization detector.

1H , ^{13}C , and ^{39}K NMR spectra were recorded at 20 °C on a Varian VXR-300 multinuclear pulsed spectrometer operating at the 1H resonance frequency of 300 MHz, the ^{13}C resonance frequency of 75 MHz, and the ^{39}K resonance frequency of 14 MHz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard for 1H and ^{13}C measurements. To obtain a satisfactory signal-to-noise ratio, about 30 000 scans were accumulated for ^{13}C spectra. Deuterated acetone was used to dissolve the organic compounds, and D_2O for inorganic compounds.

Materials. Methyloxirane (Aldrich) was heated over CaH_2 for 6 h, and then distilled under a dry argon atmosphere; the fraction boiling at 35 °C was collected. Tetrahydrofuran (POCH) was boiled over $CuCl$ to decompose peroxides and then over CaH_2 for 10 h, and finally it was distilled at 66 °C. This fraction was dried over metallic potassium for 20 h and redistilled prior to use. 15-Crown-5 (Aldrich) was dried under vacuum at 50 °C for 8 h. Potassium (Fluka) was purified in boiling tetrahydrofuran. Potassium hydride (Aldrich) was purified from paraffin oil by repeated extraction with hexane. Triethylene glycol dimethyl ether and tetraethylene glycol dimethyl ether (both Aldrich) were used as model compounds.

General Procedure. Preparation of the solution of the supramolecular metal complex and its reaction with methyloxirane were accomplished in an apparatus equipped with Teflon valves enabling substrate delivery and sampling under an argon atmosphere (Figure 1). About 2 g of potassium was placed in a test tube (A) and degassed and distilled under high vacuum (ca. 10^{-5} bar) into the reactor (B). The distillate was again molten and heated under vacuum to remove the residual amounts of volatile impurities, giving rise to a metal layer at the bottom of the reactor.

The 0.1 M solution of $K^-, K^+(15\text{-crown-5})_2$ was obtained by ultrasonic dissolution of potassium in 10 cm^3 of 0.2 M 15-crown-5 solution in tetrahydrofuran, as in ref 19. The metal–solvent contact time, t_c , was 25 min. The obtained solution was filtered into a calibrated test tube (C).

The reaction was performed at 25 °C in a 50 cm^3 reactor (E) equipped with a magnetic stirrer and filled with dry argon. A 10 cm^3 sample of freshly prepared supramolecular complex solution was added to 10 cm^3 of 1.0 M methyloxirane solution in tetrahydrofuran. Then methyl iodide or benzyl bromide was introduced immediately to the reaction mixture. 15-Crown-5

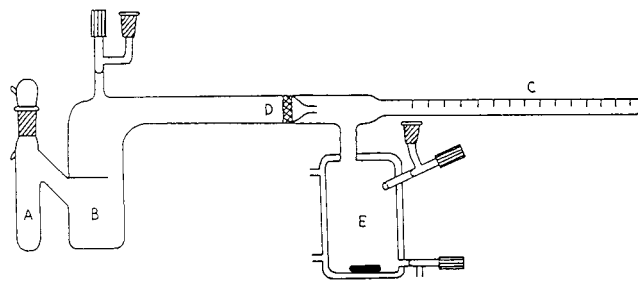


Figure 1. Apparatus for the preparation of the solution of the metal supramolecular complex and for its reaction with methyloxirane or with methyl iodide: (A) test tube; (B) reactor for preparing the metal solution; (C) calibrated test tube; (D) glass frit; (E) reactor for conducting the process.

after the addition of methyl iodide was found to be present in the precipitate along with potassium iodide. When benzyl bromide was used, potassium cation underwent decomplexation and crown ether remained in the solution. Other reactions were conducted in the same way.

Benzyl Isopropyl Ether (5). The method of its synthesis as well as its NMR and mass spectral data are given in refs 36–39, respectively.

Tetraethylene Glycol Methyl Vinyl Ether (6). A 0.10 g (2.5 mmol) sample of potassium hydride and 10 cm^3 of tetrahydrofuran were introduced into the reactor. Then, 0.33 g (2.5 mmol) of diethylene glycol vinyl ether was added dropwise. The course of the reaction was monitored by measuring the amount of hydrogen liberated. After 7 h of stirring, 0.46 g (2.5 mmol) of 1-bromo-2-(2-methoxyethoxy)ethane was added dropwise into the solution. After another 2 h of stirring, the potassium bromide precipitate was separated by decantation. The product present in the solution was distilled in a Kugelrohr apparatus; the fraction boiling at 100 °C, 0.15 mbar, consisted of tetraethylene glycol methyl vinyl ether. 1H NMR (acetone- d_6): δ 6.50 (dd, $J = 14.4$, 6.8 Hz, 1H, $OCH=$); 4.18 (dd, $J = 14.4$, 2.2 Hz, 1H, $CH_2=$); 4.01 (dd, $J = 6.8$, 2.2 Hz, 1H, $CH_2=$); 3.52–3.88 (m, 16H, OCH_2); 3.38 (s, 3H, OCH_3). ^{13}C NMR (acetone- d_6): δ 151.7 ($OCH=$); 86.5 ($CH_2=$); 67.1–71.9 (OCH_2 , 6 signals); 58.9 (CH_3). MS: m/e (rel intens) 189 (M – 45, 0.1); 175 (0.5); 159 (1); 133 (3); 117 (4); 103 (15), 87 (18), 73 (21), 59 (100), 45 (96), 43 (46); 29 (33).

Tetraethylene Glycol Monobenzyl Ether (HO[CH₂-CH₂O]₄CH₂Ph). An 80% dispersion of NaH (7.8 g containing 0.26 mol of NaH) in paraffin was washed twice with *tert*-butyl methyl ether and decanted; the NaH was suspended in 100 mL of tetrahydrofuran, and then a mixture of tetraethylene glycol (48.5 g, 0.25 mol) and 50 mL of tetrahydrofuran was added dropwise. After the evolution of hydrogen had stopped, benzyl bromide (25.6 g, 0.15 mol) was added and the reaction mixture stirred for 2 h. Water was added, the organic layer separated, and the aqueous phase extracted with *tert*-butyl methyl ether. The combined organic phases were dried and the solvents removed under reduced pressure. The crude product (37 g) was used in the next step without further purification.

Tetraethylene glycol benzyl vinyl ether (7) was prepared by the transesterification method.⁴⁰ A stirred solution of crude tetraethylene glycol monobenzyl ether (37 g, 0.13 mol), butyl vinyl ether (60 g, 0.60 mol), and mercury trifluoroacetate (1.2 g, 2.8 mmol) was heated for 1 h under reflux, then anhydrous potassium carbonate (2 g, 20 mmol) was added, and

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the excess of butyl vinyl ether was removed under reduced pressure. A sample of the residue was distilled in a Kugelrohr apparatus; the fraction boiling at 145 °C, 0.05 mbar, consisted of tetraethylene glycol benzyl vinyl ether in 66% yield. ¹H NMR (acetone-*d*₆): δ 7.34 (m, 5H, C₆H₅); 6.50 (dd, *J* = 14.4, 6.8 Hz, 1H, OCH=); 4.56 (s, 2H, Ph-CH₂); 4.23 (dd, *J* = 14.4, 2.2 Hz, 1H, CH₂=); 3.97 (dd, *J* = 6.8, 2.2 Hz, 1H, CH₂=); 3.63–3.86 (m, 16H, OCH₂). ¹³C NMR (acetone-*d*₆): δ 151.7 (OCH=); 138.2, 128.3, 127.7, 127.5 (C₆H₅); 86.5 (=CH₂); 73.2 (Ph-CH₂); 67.1–70.7 (OCH₂, 6 signals). MS: *m/e* (rel intens) 310 (M⁺, 2), 223 (1), 177 (5), 133 (15); 105 (17), 91 (100), 73 (19); 45 (62), 43 (30).

Triethylene Glycol Dimethyl Ether (CH₃O[CH₂CH₂O]₃-CH₃). ¹H NMR (acetone-*d*₆): δ 3.44–3.58 (m, 12H, OCH₂); 3.28 (s, 6H, OCH₃). ¹³C NMR (acetone-*d*₆): δ 72.6–71.0 (OCH₂, 3

signals); 58.8 (OCH₃). MS: *m/e* (rel intens) 179 (M⁺, 2), 133 (22), 103 (59), 89 (36), 73 (8), 58 (100), 45 (86), 43 (44).

Tetraethylene Glycol Dimethyl Ether (CH₃O[CH₂-CH₂O]₄CH₃). ¹H NMR (acetone-*d*₆): δ 3.44–3.59 (m, 16H, OCH₂); 3.28 (s, 6H, OCH₃). ¹³C NMR (acetone-*d*₆): δ 72.6–71.0 (OCH₂, 4 signals); 58.8 (OCH₃). MS: *m/e* (rel intens) 223 (M⁺, 1), 177 (2), 133 (6), 103 (31), 87 (14), 59 (100), 45 (8), 43 (44).

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