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Self-decomposition of K^-, $K^+(15\text{-crown-}5)_2$ tetrahydrofuran solution via organometallic intermediates

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Abstract

Self-decomposition of K^-, $K^+(15\text{-crown-}5)_2$ tetrahydrofuran solution results in dipotassium tetraethylene glycoxide and ethylene as the main reaction products. Dipotassium triethylene glycoxide, potassium tetraethylene glycoxide vinyl ether, potassium butoxide and potassium ethoxide are found as secondary products of the reaction. Organometallic intermediate compounds formed in the studied process are very reactive and their life-times are short. The mechanism of decomposition reactions is proposed. The course of the process is found to be different from that presented earlier in the literature for the K^-, $K^+(18\text{-crown-}6)$ system. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is known that alkali metals (except lithium) are soluble in some linear and cyclic ethers [1–4]. Their blue solutions contain metal anions and cations as well as a small amount of solvated electrons. Application of glymes, crown ethers or cryptands allow us to obtain high metal concentrations [2,4]. Such solutions are used in organic synthesis [5–11] and as initiators of the anionic polymerization [12–15].

The stability of these solutions depends on the temperature and on the kind of metal, solvent and ligand [16]. For example, K^-, $K^+(18\text{-crown-}6)$ solution in tetrahydrofuran starts to decompose already during its preparation at ambient temperature [17], whereas under the same conditions K^-, $K^+(15\text{-crown-}5)_2$ system is still stable during the one hour after the preparation [18]. However, in both cases the blue solution becomes colorless after some time. Potassium anions vanished at this moment [16].

A scheme of destruction reactions taking place during discoloration of K^-, $K^+(18\text{-crown-}6)$ in tetrahydrofuran solution was presented in Ref. [17]. It was assumed that the potassium anion attacked at first the crown ether molecule. The crown ring opening occurred in this case resulting in dipotassium pentaethylene glycoxide and ethylene or dipotassium tetraethylene glycoxide and tetrahydrofuran. The linear glycoxides formed were also cleaved by potassium anions. Further reactions, in which K^- and the next destruction products took part, led to a mixture of dipotassium glycoxides with the number of CH_2CH_2O repeating units equal from $n = 5$ to $n = 1$. However, dipotassium penta- and tetraethylene glycoxides ($n = 5$ and 4, respectively), i.e. the initial products of 18-crown-6 ring opening, as well as dipotassium triethylene glycoxide ($n = 3$) were formed in small amounts. Dipotassium diethylene glycoxide ($n = 2$) seemed to be the main decomposition product of the system. Quantitative data concerning the amount of dipotassium ethylene glycoxide ($n = 1$) were not reported. Potassium glycoxides are non-volatile, therefore, the reaction mixture was treated with methanol for gas chromatography–mass spectrometry (GC–MS) analysis. Appropriate glycols were observed in this case in the chromatogram. Butanol was also found in the protonated mixture. It was concluded that the tetrahydrofuran ring was opened by potassium anions giving butanol after protonation. However, a

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mechanism of decomposition reactions taking place in this metal solution was not proposed.

Some years later Dye [19] suggested that an important step of decomposition may be deprotonation of CH_2 groups in crown ethers and cryptands by electrons or metal anions. It would lead to the formation of hydrogen atoms and carbanions, a process that would readily lead to radical chain decomposition. Cauliez et al. [20] investigated the decomposition of crystalline salts M^+C_n, M'^- free of solvent (where M and M′ are alkali metals, C is a crown ether and n is 1 or 2), called by Dye [21] as alkalides. Their samples were decomposed at room temperature under inert atmosphere. The process took place from a few minutes for the more sensitive compounds to several days for the more stable species. Several gaseous products were identified in the reaction mixture, e.g. ethylene, ethane and butane. Glymes were obtained when methyl iodide was used as a quenching agent. No other methylated products were observed. This ruled out the presence of carbanions in the reaction mixture. The authors proposed that the main pathway is a ‘chemical’ reduction of the crown ether molecule by electrons, analogous to the reduction of vicinal dihalides [22].

Various systems containing alkali metal anions were studied till now. However, to our best knowledge for the first time in the present work an attempt was made to explain the decomposition mechanism of K^-, K^+(15-crown-5)$_2$ tetrahydrofuran solution. The selected system is the most stable one from the midst of known alkalide solutions [16].

It is worth noting that alkalides prepared with the use of the fully methylated aza-analogue of cryptand [2.2.2], i.e. without oxygen atoms in the molecule, were found to be stable for weeks at ambient temperature [23]. However, those sodide and potasside were crystals free of the solvent.

2. Results and discussion

Colorless mixtures obtained from K^-, K^+(15-crown-5)$_2$ blue tetrahydrofuran solutions were analyzed by the GC–MS technique after treating with methyl iodide or benzyl bromide. This allowed the transformation of non-volatile decomposition products to their volatile methyl or benzyl derivatives.

Tetraethylene glycol dimethyl ether (in 64% yield) was identified as the compound giving the main signal in the chromatogram of methylated sample. Two other signals of a weaker intensity were found as belonging to triethylene glycol dimethyl ether (15%) and tetraethylene glycol methyl vinyl ether (2%). On the other hand, signals of some analogous products, i.e. tetraethylene glycol dibenzyl ether, triethylene glycol dibenzyl ether and tetraethylene glycol benzyl vinyl ether (2%) as well as benzyl butyl ether (10%) and benzyl ethyl ether (4%) were present in the chromatogram of the benzylated sample. Tetra- and triethylene glycol dibenzyl ethers were found to be rather unstable at elevated temperature [24]. Therefore, their real yields could not be estimated by GC. Di- and monoethylene glycol dibenzyl or dimethyl ethers were not observed in the chromatograms of benzylated and methylated samples.

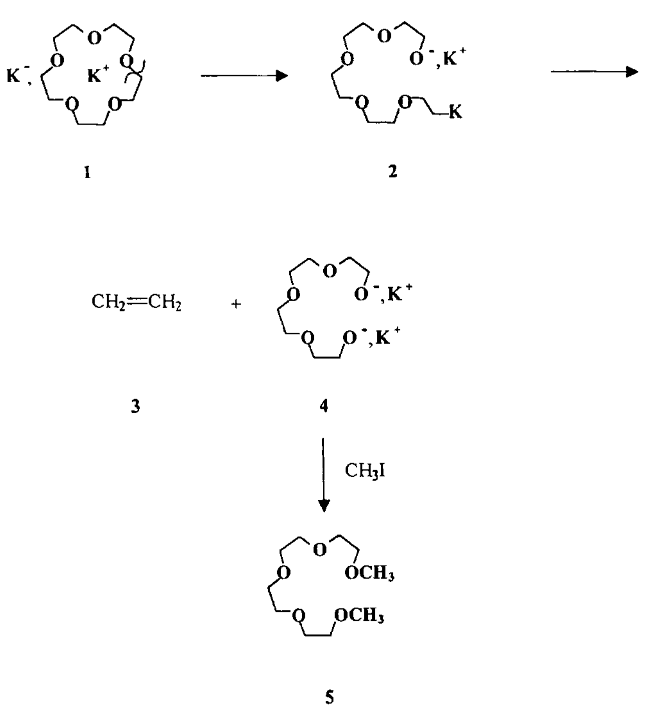
As benzyl butyl ether and benzyl ethyl ether were identified after benzylation, the analysis of samples subjected to methylation was repeated. It appeared that the expected peaks of the methyl derivative of potassium butoxide and potassium ethoxide, i.e. butyl methyl ether and ethyl methyl ether, could not be observed in the chromatogram due to their overlapping with the broad peak of the solvent.

Ethylene (10 cm^3) as well as traces of ethane and hydrogen were found in gaseous and liquid phases before and after benzylation or methylation. No higher hydrocarbons were observed.

In separate experiments water was added to the methylated or benzylated samples, causing the formation of two layers. One of them was the water solution of potassium iodide or potassium bromide and the second a tetrahydrofuran solution of the organic compounds. The pH value of both the layers was found to be equal to 7 indicating that such inorganic compounds as K_2O or KOH had not been formed in the reaction mixture.

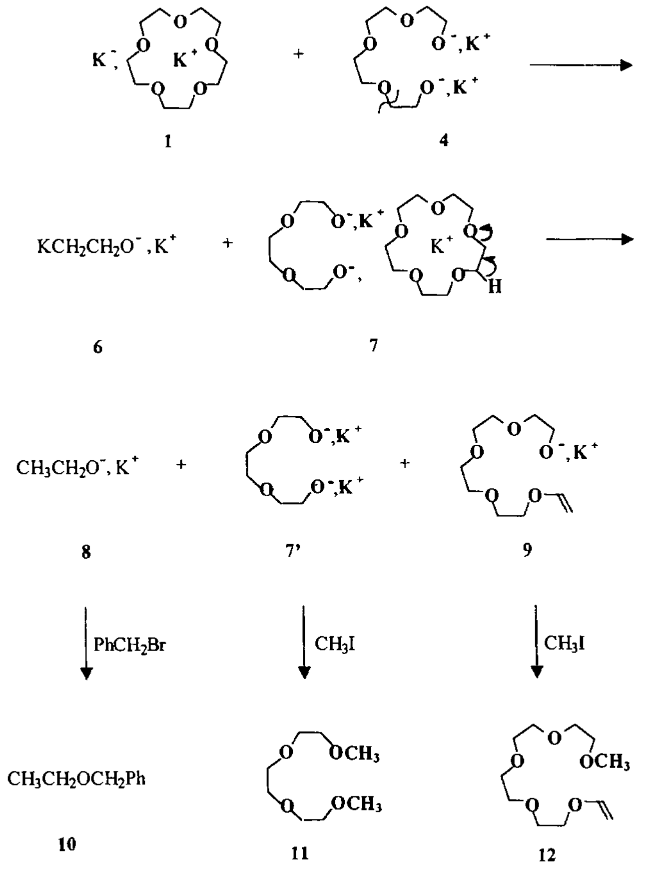
The results allowed us to assume that dipotassium tetraethylene glycoxide, i.e. the initial product of 15-crown-5 ring opening, and ethylene were the main reaction products in the studied system. Dipotassium triethylene glycoxide, potassium tetraethylene glycoxide vinyl ether, potassium butoxide and potassium ethoxide should be treated as the secondary decomposition products.

It means that this system differs qualitatively and quantitatively from K^-, K^+(18-crown-6) described in the literature [17]. In that work, as mentioned before, the original crown ring opening products, i.e. dipotassium pentaethylene glycoxide and dipotassium tetraethylene glycoxide, were found only in small amounts in the decomposed reaction mixture. On the other hand, in the present work potassium tetraethylene glycoxide vinyl ether, potassium butoxide and potassium ethoxide were found for the first time in the discolored potassium solution. Moreover, the presence of hydrogen in only trace amounts in the reaction mixture showed that the earlier hypothesis about the deprotonation of CH_2 groups in crown ether by electrons or potassium anions, suggested for several alkali metal complexes [19], cannot be accepted in the case of potassium system with 15-crown-5. Therefore, the kind of crown ether influences not only the stability of



(the second 15-crown-5 molecule was omitted)

Scheme 1.



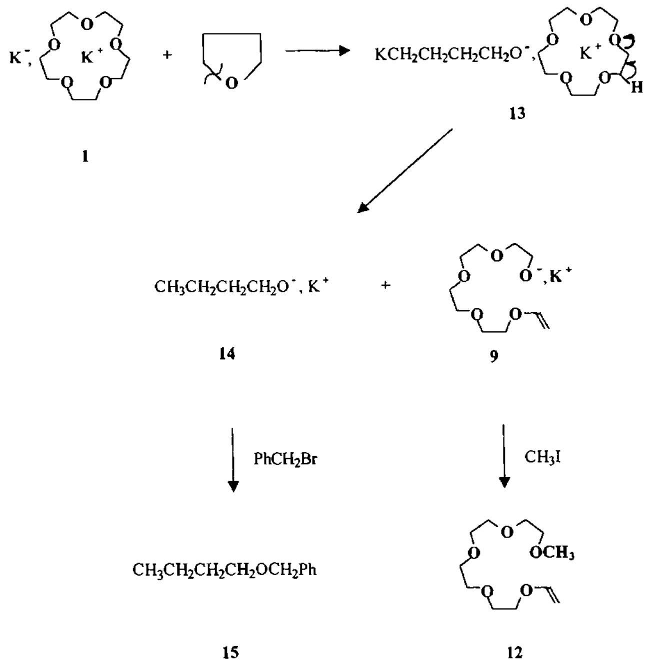
Scheme 2.

alkalide solutions but also the mechanism of their decomposition.

Based on all these findings it is proposed that in the first step of the process the cleavage of the C–O bond takes place in the crown ether molecule of K^-, K^+(15-crown-5)$_2$ **1** by K^- of **1** (Scheme 1). It results in the unstable potassium organometallic alkoxide **2**. After the reductive elimination of ethylene **3**, dipotassium tetraethylene glycoxide **4** is formed. The latter can partly decompose under the influence of **1** to potassium 2-potassioethoxide **6** and dipotassium triethylene glycoxide **7** (Scheme 2). Organometallic compound **6** then reacts rapidly with the crown ether molecule of **7** causing its ring opening and the formation of potassium ethoxide **8**, potassium tetraethylene glycoxide vinyl ether **9** and dipotassium triethylene glycoxide **7′**. The latter contains a crown ring opening product instead of one crown ether molecule. The cleavage of the 15-crown-5 ring by various organometallic intermediate products was reported already in Refs. [10,25,26]. Organometallic compounds formed in the reaction of **1** with methyloxirane [10], oxetane [25] or phenyl glycidyl ether [26] were also very unstable and reacted immediately with the crown ether. That was the reason why they were never isolated from the reaction mixture. However, the same crown ring opening product, i.e. **9** was found in each of those works.

Potassium anions are still present in the blue solution until its discoloration [16]. Therefore, it was assumed that they could react not only with 15-crown-5 but also with **9**. Decomposition products of the latter were found to be dipotassium tetra- and triethylene glycoxides (**4** and **7**), as mentioned in Ref. [10] concerning the reaction of **1** with methyloxirane. This might explain the low yield of **9** in the process under study. Recently, the reaction of methyloxirane with an excess of **1** was conducted by us. Methyloxirane tetrahydrofuran solution was slowly dropped into the freshly prepared blue potassium solution until the latter became colorless. The compounds **4** and **7** were the main reaction products in this case and the yield of **9** was low. It confirms that **9** is unstable in the mixture containing potassium anions. However, the explanation of its decomposition mechanism as well as of other unsaturated alkyl ethers needs more experiments and it will be the subject of a separate paper.

On the other hand, the presence of benzyl butyl ether in benzylated samples confirms the earlier statement that potassium anions cleave the solvent molecules [17]. It seems that the reaction of K^- with tetrahydrofuran leads to the formation of an intermediate product, i.e. potassium 4-potassiobutoxide **13** (Scheme 3). The latter opens the crown ether ring forming potassium butoxide **14** and potassium tetraethylene glycoxide vinyl ether **9**. Taking into account the hypothesis that **13** is a stable compound, benzyl 5-phenylpentyl ether would be ex-



Scheme 3.

pected in benzylated samples. However, that compound was not found in the analyzed systems. It points to a high reactivity of **13** and indicates that other reactions occurring with the participation of organometallic intermediates can also be very rapid.

In order to confirm the participation of solvent molecules in the decomposition process, the blue potassium solution was prepared using 2-methyltetrahydrofuran instead of unsubstituted tetrahydrofuran. However, in such a case benzyl isopropyl ether **21** was detected after benzylation of the colorless mixture instead of the expected benzyl 1-methylbutyl ether. It could indicate that potassium potassioisopropoxide **19** is formed initially in that reaction with the elimination of ethylene (Scheme 4). Then, the crown molecule of **19** is opened in an intramolecular reaction resulting in potassium isopropoxide **20** and potassium tetraethylene glycoxide vinyl ether **9**. It is not know if the open chain product **17** is really an intermediate during the fragmentation of **16** to the more stable branched radical anion **18** [27]. A concerted process would also be reasonable.

The reactions presented in Schemes 1–4 are very fast. No methylated or benzylated derivatives of organometallic compounds **2**, **6**, **13** as well as **19** were observed in the chromatograms because of their short life-time. Similar results were found in our earlier works [10,25,26]. On the other hand, a hypothesis assuming the existence of organometallic intermediates was till now not confirmed in a direct experiment. However, the structure of end products and the knowledge of the reactivity of such compounds show that they will take part in the studied process.

The difference between potassium alkalide containing 18-crown-6 and 15-crown-5 found in this work is most likely connected not only with the kind of crown ether but rather with the structure of its complex with the potassium cation. 15-Crown-5 forms a 2:1 sandwich complex with the potassium cation whereas 18-crown-6 gives a 1:1 flat one [2]. The structure of these complexes seems to be decisive for the course of side reactions. In the case of 15-crown-5 two sandwich complexes are situated on both ends of dipotassium tetraethylene glycoxide. In some of them, the potassium tetraethylene glycoxide vinyl ether molecule can be present instead of one crown ether molecule. This is possible because linear oligoethers also form stable complexes with alkali metal cations [28,29]. It can be assumed that such a structure causes steric hindrance diminishing the probability of the attack of **1**. Therefore, potassium anions should react rather with the next crown molecule than with the glycoxide one. Another situation takes place in the 18-crown-6 system. Smaller steric hindrance causes the easy further decomposition of dipotassium penta- and tetraethylene glycoxides, which results in a mixture of various products.

It is worth noting that in reactions of the potassium solution with methyloxirane [10] or oxetane [25] the solvent was found to be inert and crown ether reacted exclusively with organometallic intermediate compounds. However, those reactions were instantaneous. Potassium anions vanished immediately after the mixing of reagents. Therefore, they could not take part in the relatively very slow reaction with 15-crown-5 or with tetrahydrofuran observed in the present work.

3. Conclusions

The mechanism of self-decomposition of K^-, $K^+(15\text{-crown-}5)_2$ tetrahydrofuran solution was proposed. In the first step of this process, the cleavage of the C–O bond takes place in crown ether as well as in the solvent under the influence of potassium anions. Organometallic compounds with more or less ionic potassium–carbon bonds are formed as intermediate products. These compounds undergo further rapid reactions. Most interestingly, the organopotassium compounds do not cleave the solvent as usual [30] but the crown ether which is obviously more reactive due to its more extensive complexation of K^+. It confirms the results of our previous works concerning K^-, $K^+(15\text{-crown-}5)_2$ reactions with simple cyclic ethers, as methyloxirane [10] and oxetane [25], in which the crown ether ring was found to be unstable in the presence of organometallic compounds.

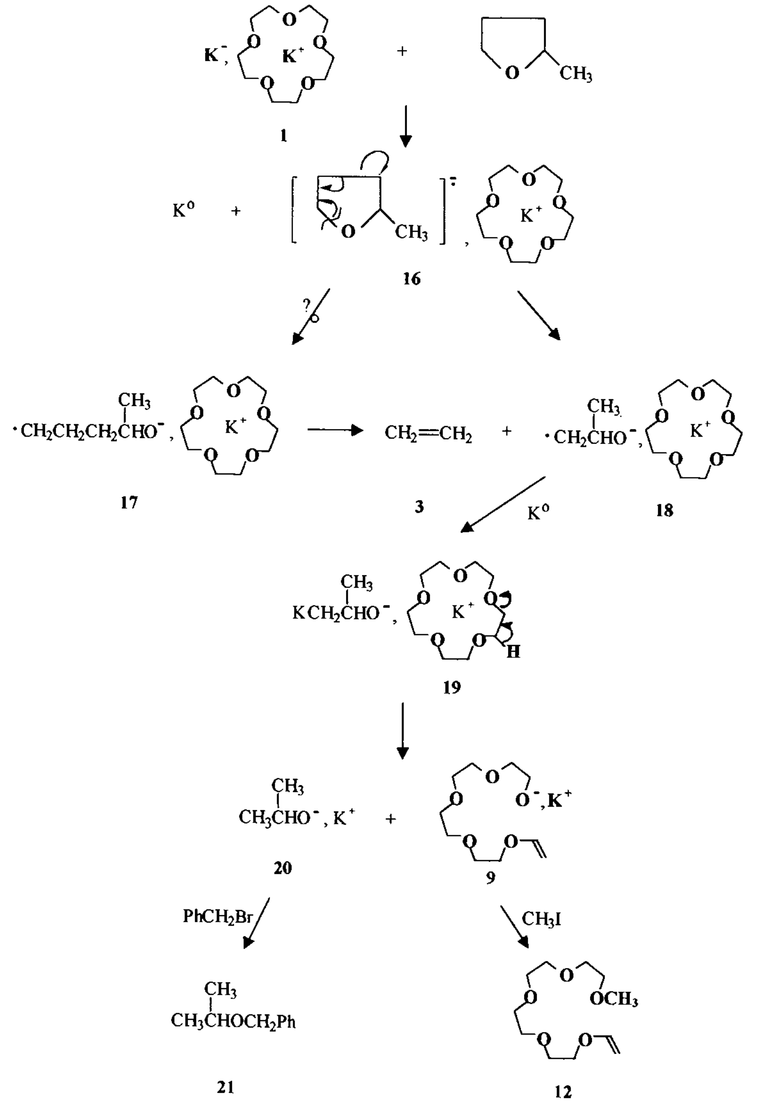
The hypothesis assuming the participation of organometallic species in the decomposition of alkali metal solutions was not discussed till now in the literature and it seems to be the main novelty of this work. It is also a very important finding of the present work that the kind of crown ether influences not only the stability of potassium solutions but also the mechanism of their decomposition.

4. Experimental

GC–MS analyses of liquid compounds were performed on a 30 m long fused silica capillary column DB-1701 using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. Diethylene glycol dimethyl ether was used as an internal standard. The gaseous components were examined on a Chromatron GCHF chromatograph, on a 2 m long metal column, filled with modified Al_2O_3, at 20°C. ^1H- and ^{13}C-NMR spectra were recorded at 20°C on a Varian VXR-300 multinuclear spectrometer at the ^1H resonance frequency of 300 MHz and ^{13}C resonance frequency of 75 MHz. $CDCl_3$ was used as the solvent. Chemical shifts were referenced to tetramethysilane (TMS) serving as an internal standard.

Tetrahydrofuran (POCH) was purified by the method presented in Ref. [16]. 2-Methyltetrahydrofuran was purified in the same way. 15-Crown-5 (Aldrich) was dried under vacuum at 50°C for several hours. Potassium (Aldrich) was distilled under high vacuum.

About 0.1 M K^-, $K^+(15\text{-crown-}5)_2$ dark blue solution was prepared by dissolving of the potassium mirror in 0.2 M 15-crown-5 tetrahydrofuran or 2-methyltetrahydrofuran solution at 20°C. The contact time was equal to 25 min. Details of the experimental procedure were described elsewhere in Ref. [18]. After filtering through the glass frit the solution was left for about 24 h at ambient temperature, until its blue color



Scheme 4.

faded. Then, the colorless mixture was quenched with methyl iodide or benzyl bromide and analyzed by GC–MS, GC and NMR. The methylated or benzylated decomposition products were identified by matching their mass spectra, retention times as well as ^{1}H- and ^{13}C-NMR spectra with those of original compounds. Data concerning the mass spectra and NMR spectra of the products were already presented in the literature. They included tetraethylene glycol dimethyl ether [10], triethylene glycol dimethyl ether [10], tetraethylene glycol methyl vinyl ether [10], benzyl butyl ether [31,32], benzyl ethyl ether [33–35] and benzyl isopropyl ether [31,34,36,37].

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