Hydroxyl radical, sulfate radical and nitrate radical reactivity towards crown ethers in aqueous solutions

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A R T I C L E   I N F O

Article history:
Received 19 July 2011
Accepted 16 January 2012
Available online 25 January 2012

Keywords:
Crown ether
Cation
Nitrate radical
Sulfate radical
Pulse radiolysis
Laser photolysis

A B S T R A C T

Reaction rate constants of crown ethers (12-crown-4, 15-crown-5, 18-crown-6) and their analogs 1,4-dioxane (6C2) with some important oxidative radicals, hydroxyl radical (·OH), sulfate radical (SO42−) and nitrate radical (NO3−), were determined in various aqueous solutions by pulse radiolysis and laser photolysis techniques. The reaction rate constants for 6C2 and crown ethers with ·OH and SO42− increase with the number of hydrogen atoms in the ethers, indicating that the hydrogen-atom abstraction is a dominant reaction between crown ethers and these two radicals. The presence of cations in solution has negligible effect on the rate constants of crown ether towards ·OH and SO42−. However, for the NO3−, the rate constants are not proportional to the number of hydrogen atoms in ethers, and 12-crown-4 (12C4) is the most reactive compared with other crown ethers. Except 12C4 and 6C2, the cations in the aqueous solution affect the reactivities of 15-crown-5 (15C5) and 18-crown-6 (18C6). The cations with high binding stability for crown ether would improve the reactivity of 15C5. For the studied crown ethers, the reaction rate constants of these oxidative radicals have the order ·OH > SO42− > NO3−. Furthermore, the formation of radicals after the reaction of crown ethers with sulfate radical could be observed in the range of 260–280 nm using laser photolysis and pulse radiolysis. This is the first report on the kinetic behavior of crown ethers with NO3− and it would be helpful for the understanding of stability of crown ethers in the processing of spent nuclear fuel.

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1. Introduction

Due to their selective binding capacity with numerous cations, the crown ethers have been investigated for the separation of Uranium (U) or Plutonium (Pu) (Foos et al., 1991) and radioactive Strontium (Sr) from spent fuel (Draye et al., 1997). They are proposed for usage in partitioning fission-products from acidic solutions and the future processes will be possibly based on the aqueous solvent-extraction technologies for nuclear reactors (Makhlyarchuk and Zatonskii, 1992; Mincher et al., 2009). In contrast to the radiolysis of neat crown ethers, the noncyclic polyethers could be formed when dicyclohexano-18-crown-6 (DCH18C6) was irradiated in 1.0 M nitric acid with a dose of 3290 kGy (Draye et al., 2008). The absence of recyclization in solution is possibly attributed to the reactive species created in irradiated solutes reacting with crown ether radicals and leading to the formation of the nanocyclic polyethers. All of these works focus on the radiolysis product of neat crown ethers and crown ethers in nitric acid. Few papers report on the transient species of crown ether during the irradiation. Zakurdaeva et al. studied the radiolysis of aqueous dicyclohexano-18-crown-6 (DCH18C6) by ESR spectroscopy at 77 K (Zakurdaeva et al., 2009). They confirmed that ·OH, trapped
electrons and macrocyclic radicals resulting from H-atom abstraction are predominant radiolysis products. Furthermore, the radiolysis effect on complex of crown ether with metals was studied. It was found that the C–O bond cleavage was greater when 15-crown-5 (15C5) was complexed with magnesium, because the increased yield of (–CHCH=O) radicals was found using ESR at 77 K (Grigorev et al., 1995). The effect of complexation on radiolytic damage to crown ethers was attributed to the degree of interaction between the donor oxygen atoms of the crown ethers and the metal cations. 

Although the steady-state radiolysis of crown ethers has been reviewed and the radiation-chemical behavior of crown ethers is considered to be similar to that of dioxane and poly(ethylene glycols) from the standpoint of radiation stability (Makhlyarchuk and Zatonskii, 1992), the quantitative kinetic information on their radiation chemistry is scarce now. Ershov et al. (1987) studied the radiolysis chemistry of aqueous crown ether; a common absorbance at 260 nm was observed under different irradiation conditions. They suggested that a radical was created by reaction of 18-crown-6 (18C6) and dicyclohexano-18-crown-6 (DCH18C6) with the solvated electron, \( \cdot \text{OH} \), oxide radical anion and H atom via hydrogen-atom abstraction, and the order of reactivity of these species towards 18C6 and DCH18C6 was \( \cdot \text{OH} > \cdot \text{O} > \cdot \text{H} > \text{e}^- \) (Ershov et al., 1987).

In the processing of spent nuclear fuel, the nitric acid is widely used to dissolve the spent fuel, and then the obtained nitric acid solutions will be mixed with diluent solutions containing crown ethers for the extraction of the U, Pu and fission products for the recovery of useful metal elements. The radiolytic damage to crown ethers is often expected to exist in the practical extraction (Asanuma et al., 2006; Raju and Subramanian, 2005; Zhang et al., 2009). For example, in the radiolysis of nitric acid (Katsumura et al., 1991), it is necessary to study their reactivity towards various crown ethers. Since the reactivity of crown ether analogs, 1,4-dioxane was studied as a model compound and compared with crown ethers. Since the hydroxyl radicals and sulfate radicals are two important oxidant radicals in an aqueous solution, the reactions of various crown ethers towards these two radicals were measured and compared.

2. Experimental

2.1. Chemicals

1,4-dioxane (6C2; purity 99.5%), 12-crown-4 (12C4; purity 98.0%), 15-crown-5 (15C5; purity 98.0%) and 18-crown-6 (18C6; purity 99.0%) were purchased from Wako Pure Chemical Industries, Ltd. with the highest available purity. Their chemical structures are shown in Fig. 1. Other chemicals such as sulfuric and nitric acids, K\(_2\)S\(_2\)O\(_8\) and Na\(_2\)S\(_2\)O\(_8\), sulfate and nitrate were of analytical grade with a purity of 99.0%. All the reagents were used as received.

2.2. Nanosecond laser photolysis

Laser photolysis was done using a KrF excimer laser \((\lambda=248\text{ nm}; \text{ Compex 102, Lambda Physik})\) with a pulse duration of 20 ns and an energy of 100 mJ. Ar-saturated K\(_2\)S\(_2\)O\(_8\) and Na\(_2\)S\(_2\)O\(_8\) solutions were used for the generation of sulfate radical. The optical path of the quartz cell was 2 cm. The formation mechanism of sulfate radical is given as

\[
\text{S}_2\text{O}_8^2^- + h\nu \rightarrow 2\text{SO}_4^-
\]

In laser photolysis, for the formation of nitrate radical, ceric ammonium nitrate (CAN) in water (Hermann et al., 1994; He et al., 2004) and acetonitrile (Ito et al., 1989; He et al., 2004) have been widely used. The mechanism is given as follows:

\[
[\text{Ce}^{IV}(\text{NO}_3)_6]^{2-} + h\nu \rightarrow [\text{Ce}^{III}(\text{NO}_3)_5]^{2-} + \text{NO}_3^-
\]

This technique was applied to this system but failed, because it was found that a spontaneous reaction takes place and the yellow color due to Ce\(^{IV}\) disappears when we mixed CAN and crown ethers.

2.3. Nanosecond pulse radiolysis

The nanosecond pulse radiolysis experiments were carried out at room temperature using a LINAC facility (35 MeV, 10 ns) coupled with an absorption spectroscopic detection system at the Nuclear Professional School, the University of Tokyo. Dosimetry was carried out using N\(_2\)O-saturated solutions of 10 mM KSCN aqueous solution having \(G(\text{SCN})_2^- = 5.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \text{ (100 eV}^{-1})\) at 472 nm (Buxton and Stuart, 1995). To determine the rate constants for the reaction of \( \cdot \text{OH} \) with the crown ethers, the competition method was adopted using SCN\(^-\) as a competitor. The absorbance of (SCN\(^-\))\(^2-\) at 472 nm was monitored.

N\(_2\)O-saturated 1 M Na\(_2\)S\(_2\)O\(_8\) solution and 5 M NaNO\(_3\), 5 M NH\(_4\)NO\(_3\) solutions were used to produce sulfate radical and nitrate radical, respectively. The NO\(_3\) radical is mainly produced by direct radiolysis of neutral nitrate ion or concentrated nitric acid according to our previous work (Katsumura et al., 1991):

\[
\text{NO}_3^- \rightarrow \text{NO}_3^- + e^-
\]

\[
\cdot \text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3^-
\]

During these experiments, different concentrations of 6C2, 12C4, 15C5 and 18C6 were used to react with these oxidative radicals. Transient absorption spectra and kinetic curves were obtained to study the transient reaction products and reactivity.
3. Results and discussion

3.1. Reaction with Hydroxyl radical

Since hydroxyl radical (‘OH) is one of the most important oxidizing radicals produced by radiolysis of water, the rate constants of crown ethers towards ‘OH were firstly determined and the results are shown in Table 1. The rate constant \( (3.4 \pm 0.2) \times 10^9 \text{M}^{-1}\text{s}^{-1} \) of hydroxyl radical with 6C2 agrees well with the reported value \( 3.1 \times 10^9 \text{M}^{-1}\text{s}^{-1} \) \( \text{(Buxton et al., 1988)} \). Compared with the data reported in literature \( \text{(Ershov et al., 1987)} \), our rate constant for 18C6 is close to that of 18C6-K with hydroxyl radical \( (1.0 \times 10^9 \text{M}^{-1}\text{s}^{-1}) \). It suggests that, in our case, the 18C6 could be complexed with K+ rapidly, and some complexation of 18C6 existed in the KSCN aqueous solution. The analogs of crown ethers, i.e. THF and 6C2, have similar reactivity with the ‘OH radical. For the crown ethers with the number of hydrogen atoms more than 16, the rate constants increase with increasing ring size. Interestingly, there is a very good linear relationship between the number of hydrogen atoms in ethers and rate constants \( \text{(Fig. 2)} \), indicating that the hydrogen-atom abstraction is the dominant reaction between crown ethers with hydroxyl radical.

3.2. Reaction with sulfate radical

In order to study the reaction between crown ethers and sulfate radical, we measured firstly the transient absorption spectra of 6C2 and crown ethers in K2S2O8 aqueous solution using laser photolysis. As shown in \text{Fig. 3}, the absorption band with \( \lambda_{\text{max}} = 460 \text{ nm} \) is the characteristic spectrum of sulfate radical. It decayed completely in 5 \( \mu \text{s} \) for 6C2 \( \text{(Fig. 3A)} \) and 1 \( \mu \text{s} \) for 18C6 \( \text{(Fig. 3B and C)} \). For the 6C2, an isosbestic point was found at 280 nm. At 260 nm, the absorbance slightly increases with time, demonstrating the formation of a radical due to the reaction between 6C2 and sulfate radical. Similarly, the transient absorption spectra of 18C6 show an isosbestic point at 280 nm and an increasing absorbance at 260 nm, which has no obvious decay in the studied time range \( \text{(Fig. 3B)} \); therefore, the absorption below \( \lambda < 280 \text{ nm} \) could be attributed to the radical of 18C6. The transient absorption spectra obtained from pulse radiolysis indicated that, like laser photolysis, the radicals of crown ether with long life-time were generated via hydrogen-atom abstraction.

![Fig. 2. Rate constants of ‘OH with ethers as a function of number of hydrogen atoms. The rate constants were obtained by pulse radiolysis of N2O-saturated 10 mM KSCN aqueous solution. Pulse dose: 21 Gy.](image-url)
Our results are consistent with the transient spectra obtained from the reaction of hydroxyl radical with crown ethers in literature (Ershov et al., 1987).

The rate constants of sulfate radical reacting with various crown ethers and 6C2 obtained from pulse radiolysis and laser photolysis are listed in Table 1. In the case of 6C2, the obtained rate constant with sulfate radical in this work is higher than the reported value, $1.6 \times 10^7 \text{M}^{-1}\text{s}^{-1}$, where they used 1 mM $\text{K}_2\text{S}_2\text{O}_8$ to produce sulfate radical (Eibenberger et al., 1978). For the studied crown ethers, increase in size of crown ethers, increases their rate constants. As shown in Fig. 4, it is clear that the rate constants with sulfate radical are proportional to the number of hydrogen atoms in the ethers. Although the rate constants obtained in pulse radiolysis are systematically larger than those obtained in laser photolysis, the reason is not clear yet. For the reaction of crown ethers with sulfate radical, the dominant reaction is hydrogen-atom abstraction in both photolysis and radiolysis.

### 3.3. Reaction with nitrate radical

The reactions of 6C2, 12C4, 15C5 and 18C6 with nitrate radical in 5 M $\text{NaNO}_3$ and 5 M $\text{NH}_4\text{NO}_3$ solutions were studied using pulse radiolysis method. NO$_3^-$ radical was produced by radiolysis of concentrated nitrate aqueous solutions. The inset of Fig. 5 shows the characteristic absorption spectrum of NO$_3^-$ radical obtained by radiolysis of NaNO$_3$ aqueous solution. The crown ethers can react with NO$_3^-$ and the decay at 630 nm becomes faster as the concentration of crown ether increases. Fig. 5 shows the kinetic curves of NO$_3^-$ at 630 nm in the presence of different concentrations of 18C6. The relationship between the decay rate of nitrate radical and the concentration of crown ethers is presented in Fig. 6. The reaction rate constants between nitrate radical and crown ethers are deduced by fitting kinetic curves with an exponential decay. The results are shown in Table 1. It can be seen that the rate constants of nitrate radical towards crown ethers with different sizes have similar order compared to 6C2 and THF. Comparing the reported rate constants of 6C2 with nitrate radical, the rate constant obtained in 5 M $\text{NaNO}_3$ solution ($k = 3.7 \times 10^6 \text{M}^{-1}\text{s}^{-1}$; Herrmann and Zellner, 1998) is higher than that in 6 M HNO$_3$ ($k = 1.3 \times 10^6 \text{M}^{-1}\text{s}^{-1}$; Herrmann and Zellner, 1998). The presence of $\text{NH}_4^+$ and $\text{Na}^+$ has no obvious influence on the rate constants of 6C2 with nitrate radical.

![Fig. 3.](image)

![Fig. 4.](image)
rate constants have the order \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) towards nitrate radical. For the \( \text{NH}_4^+ \), the reaction work have obvious influence on the reaction rate constants of \( \text{OH}^- \) and sulfate radical. Among these cyclic ethers, \( \text{C}_4\text{H}_{12} \) is the most active and \( \text{C}_2\text{H}_6 \) is the most stable in reaction with nitrate radical. It suggests that the reactions between nitrate radical and crown ethers are very complicated in the studied work. The reactivity depends not only on the chemical structure of crown ethers, but also on the cations and composition in the solution. For the reaction of nitrate radical towards crown ether, the measured rate constants are about \( 10^6 \) to \( 10^7 \) \( \text{M}^{-1} \text{s}^{-1} \). In the presence of cations, \( \text{C}_5\text{H}_{15} \) and \( \text{C}_6\text{H}_{18} \) might complex with cations. It was reported that the rates of complex formation of crown ethers are all in the range \( 2 \times 10^7 \) to \( 2 \times 10^8 \) \( \text{M}^{-1} \text{s}^{-1} \) (Jong and Reinholdt, 1981). In contrast, the rates of decomposition for crown-ether complexes range from \( 6.1 \times 10^2 \) to \( 2 \times 10^2 \) \( \text{M}^{-1} \text{s}^{-1} \) (Jong and Reinholdt, 1981). Thus, the reaction rate constant of crown ethers with nitrate radical is lower than that of complex formation and higher than that of decomposition, and then the complex of crown ether will react with nitrate radical. Consequently, the effect of cations in the solution on the reactivity of nitrate radical is more obvious than those for hydroxyl and sulfate radicals. In the presence of ammonium nitrate solution, the reactivity of crown ethers obtained by Sharma et al. (1984), who used a pulsed electron beam high ion source pressure mass spectrometer to determine the gas-phase basicities of crown ethers and \( \text{C}_2\text{H}_6 \). The measured proton affinities were \( 12\text{C}_4 > 15\text{C}_5 > 18\text{C}_6 > 6\text{C}_2 \). The measured proton affinities were \( 2 \times 10^7 \) to \( 2 \times 10^8 \) \( \text{M}^{-1} \text{s}^{-1} \) (Jong and Reinholdt, 1981).}

3.4. Discussions

3.4.1. Effect of chemical structure of crown ethers

Comparing all the rate constants of crown ether with \( \text{OH}^- \), sulfate radical, the rate constants are proportional to the number of \( \text{H}^- \) atoms in crown ethers, indicating the reaction between crown ethers and hydroxyl and sulfate radicals is primarily based on \( \text{H}^- \) abstraction. Then by increasing macrocycle size, the reactivity of crown ether towards these oxidizing radicals increases. While for the nitrate radical the reaction rate constant in the sodium nitrate solution has the order \( 12\text{C}_4 > 18\text{C}_6 > 15\text{C}_5 > 6\text{C}_2 \), in the ammonium nitrate solution it is \( 12\text{C}_4 > 15\text{C}_5 > 18\text{C}_6 > 6\text{C}_2 \), and no linear relationship was observed between the rate constant and number of hydrogen atoms in ethers. Thus, it suggests that the reactions between nitrate radical and crown ethers are very complicated in the studied work. The reactivity depends not only on the chemical structure of crown ethers, but also on the cations and composition in the solution. For the reaction of nitrate radical towards crown ether, the measured rate constants are about \( 10^6 \) to \( 10^7 \) \( \text{M}^{-1} \text{s}^{-1} \). In the presence of cations, \( 15\text{C}_5 \) and \( 18\text{C}_6 \) might complex with cations. It was reported that the rates of complex formation of crown ethers are all in the range \( 2 \times 10^7 \) to \( 2 \times 10^8 \) \( \text{M}^{-1} \text{s}^{-1} \) (Jong and Reinholdt, 1981). In contrast, the rates of decomposition for crown-ether complexes range from \( 6.1 \times 10^2 \) to \( 2 \times 10^2 \) \( \text{M}^{-1} \text{s}^{-1} \) (Jong and Reinholdt, 1981). Thus, the reaction rate constant of crown ethers with nitrate radical is lower than that of complex formation and higher than that of decomposition, and then the complex of crown ether will react with nitrate radical. Consequently, the effect of cations in the solution on the reactivity of nitrate radical is more obvious than those for hydroxyl and sulfate radicals. In the presence of ammonium nitrate solution, the reactivity of crown ethers obtained in the present work agrees well with the result on the protonation of crown ethers obtained by Sharma et al. (1984), who used a pulsed electron beam high ion source pressure mass spectrometer to determine the gas-phase basicities of crown ethers and \( \text{C}_2\text{H}_6 \). The measured proton affinities were \( 12\text{C}_4 > 15\text{C}_5 > 18\text{C}_6 > 6\text{C}_2 \).

3.4.2. Effect of cations

It has been reported that a solution containing a metal salt (MX) and a crown ether (Cr) may contain three different anionic species, the free anion \( X^- \), the tight ion pair \( \text{M}^+ \text{X}^- \) and the crown ether-separated ion pair \( \text{M}^+ \text{CrX}^- \), besides free crown ether (Jong and Reinholdt, 1981). During the pulse radiolysis measurement, all of these species may react with oxidative radicals and affect the reaction rate of free crown ether. For the hydroxyl and sulfate radicals, the reaction rate constants are higher than \( 10^9 \) \( \text{M}^{-1} \text{s}^{-1} \), and the effect of cations on reactivity...
of crown ethers is not significant. However, the reaction between nitrate radical and crown ethers is more complicated in the presence of cations. It is not simple hydrogen-atom abstraction reaction and the reaction rate constants do not increase with the number of hydrogen in crown ethers. Furthermore, the order of reactivity of crown ethers varies with chemical structure of crown ethers and cations in the solution.

If we consider the effect of complexing capacity of 15C5 and 18C6 with different cations, the reported values of the association constant log Kₐ for 1:1 complexes of 15C5 in water at 25 °C are log Kₐ=0.70  and log Kₐ=1.71 (Jong and Reinholdt, 1981). Kₐ is almost 9 times higher than Kₐ. It has been reported that cation–macrocycle complexes with high association constants are more susceptible to radiolytic degradation, as evidenced by high radical yields and high yields of gaseous hydrogen (Makhlyarchuk and Zatonskii, 1992; Mincher et al., 2009). Thus the reactivity of 15C5–NH₄ would be expected to be higher than that of 15C5–Na. The measured rate constant of 15C5 with nitrate radical in this work is consistent with the results of the analysis of radiolysis product. In the case of 18C6, log Kₐ and log Kₐ are 0.8 and 1.23, respectively; that is, Kₐ is about 2 times higher than Kₐ (Jong and Reinholdt, 1981). This means that the reactivity of 18C6–NH₄ will be higher than that of 18C6–Na according to the radiolysis study of 15C5. On the contrary, in the experiment, the reaction rate constant in NaN₃ for 18C6 is higher than that of NH₄NO₃. The reason is not easy to be explained. Further work should aim to study the effect of different cations on the reactivity of crown ethers in detail.

3.4.3. Effect of oxidizing radicals

For the studied crown ethers and 6C2, the reaction of ‘OH (k=0.18–1.09 x 10¹⁰ M⁻¹ s⁻¹) is the fastest among the three investigated radicals. The SO₄²⁻ (k=0.66–4.2 x 10⁸ M⁻¹ s⁻¹) and the NO₃⁻ (k=0.23–2.4 x 10⁷ M⁻¹ s⁻¹) reactions are two orders and three orders of magnitude slower than ‘OH, respectively. The rate constants obtained in the present work (see Table 1) indicated that the reactivity sequence of the three radicals towards crown ether in aqueous solutions is ‘OH > SO₄²⁻ > NO₃⁻. This order is the same as that of the reactions with poly-alcohols (Hoffmann et al., 2009). The difference is that the reaction rate of SO₂⁻ towards poly-alcohols (k=2.7–5.3 x 10⁷ M⁻¹ s⁻¹) is generally lower than that with crown ethers. They suggested that all three radicals react by an H-atom abstraction mechanism preferably at the α-carbon atom of the investigated alcohols. Similarly, in the present work, the dominant reaction of these three radicals with crown ethers is also considered to be an H-atom abstraction. The measured rate constants increase linearly with the number of hydrogen in the ethers during the reaction of crown ethers with ‘OH and SO₄²⁻, while for the NO₃⁻ reaction, the obtained rate constants depend on the chemical structure of crown ethers and cations in aqueous solution. We note that the redox potentials of sulfate and nitrate radicals are E(SO₄²⁻/SO₂⁻) =2.43 V and E(NO₃⁻/NO₂⁻) = 2.45 V, respectively, implying that these two radicals have similar oxidizability (Logager et al., 1993). However, the reactivity of sulfate radical with crown ethers is higher than that of nitrate radical in the present work. It suggests that for these two radicals, their reactivity towards the crown ethers is not explained only by the oxidizability of radicals, but rather the chemical structure of crown ethers and composition of the solution would play important roles.

4. Conclusions

The kinetic behaviors of hydroxyl, sulfate and nitrate radicals in the crown ethers such as 12C4, 15C5 and 18C6 aqueous solution with various cations were measured using laser photolysis and pulse radiolysis. In addition, 6C2 was studied as a model compound. Sulfate and hydroxyl radicals could mainly react with crown ethers and 6C2 via hydrogen-atom abstraction to produce ether radicals. The reaction rate constants increase linearly with the number of H-atom in crown ethers. For the reaction between nitrate radical and ethers, the rate constants decrease in the sequence 12C4 > 18C6 > 15C5 > 6C2 in sodium nitrate solution and in the ammonium nitrate solution, 12C4 > 15C5 > 18C6 > 6C2. Moreover, the reactivity of nitrate radical towards 15C5 and 18C6 depends on the types of cations in the solution; the rate constant of 15C5 increases with the increase of association constants with cations. For the studied crown ethers and 6C2, the reactivity of oxidizing radicals decreases in the order ‘OH > SO₄²⁻ > NO₃⁻. This work would be helpful for a better understanding of stability of crown ethers in spent nuclear fuel reprocessing, where oxidizing radicals, especially NO₃⁻, are present under irradiation environment.

Acknowledgment

We would like to thank Prof. M. Uesaka and Mr. T. Ueda at the Nuclear Professional School, the University of Tokyo, for their encouragement and technical assistance in the experiments.

References


