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Radiation chemistry of crown-compounds

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ABSTRACT. **The results of studies on the radiation-chemical reactions in various systems containing crown-ethers and their analogues are surveyed and analysed in the review. The use of crown-compounds as extractants for the selective isolation of radionuclides is considered from the standpoint of radiation chemistry. Data concerning the radiolysis of individual crown-ethers as well as their aqueous and non-aqueous solutions are described. Good prospects for the application of macrocyclic compounds and their complexes in the study of the mechanisms of radiation-chemical processes are demonstrated.**

The bibliography includes 142 references.

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I. Introduction

Crown-compounds are macrocyclic compounds containing in their structures electron-donating heteroatoms such as those of oxygen (crown-ethers), nitrogen, or sulphur and possessing the ability to form with a high degree of selectivity stable "guest-host complexes" with cations and neutral molecules. Polycyclic compounds consisting of two (cryptands) and more rings can also be included among crown-compounds.[1–3] The chemistry of crown-compounds has been developing vigorously and the synthesis of numerous new macroheterocycles with unusual properties has stimulated studies not only in the field of organic chemistry but also in adjacent fields where these substances have found important practical applications.[4–6] The first studies concerning the radiation chemistry of crown-ethers were published in 1984.[7–12]

The capacity for the selective binding, separation, and transport of metal cations stimulated the use of crown-compounds as extractants for the selective isolation of radionuclides in radiochemical technology,[13] which in fact induced the initial practical interest in the radiation chemistry of macrocyclic polyethers and their solutions. The complex of a crown-ether and an inorganic salt is formed as a result of the ion–dipole interaction between the cation and the negatively charged oxygen atom of the polyether ring. The stability of the complex formed then depends on the relative diameter of the cavity within the crown-compound and the diameter of the cation. The complex-forming capacity is also influenced by the charge and hardness of the cation and the nature of the electron-donating heteroatoms of the crown-compounds and the substituents in the macrocycle.[1,3,14–16] As a result of the formation of a complex with a crown-compound, the relatively small alkali metal or alkaline earth metal ion is converted into a bulky organic cation capable of dissolving in the organic phase. Thus inorganic salts are solubilised in weakly polar organic solvents, which is favoured by the highly lipophilic properties of the ligand skeleton.[3,17] The weakly solvated, almost "bare" anions formed on complex formation in weakly polar solvents differ appreciably from their solvated analogues. The electron-donating properties of the weakly solvated anion are enhanced and it becomes a potentially strong base and nucleophile. Such an anion is activated by the crown-compound and its reactivity increases.[18] The degree of activation depends on the nature of the anion, the solvent, and the macrocyclic ligand.

The ability of crown-compounds to transport ionic reactants from the solid or aqueous phase to the organic phase and to act on the state of ion pairs in the solution influences the kinetics and stereochemistry of many reactions. Under these conditions, certain reactions can be carried out only in the presence of macrocyclic compounds.[19] This permits the application of these substances in the study of reaction mechanisms in organic chemistry. By virtue of the ability of crown-ethers and cryptands to dissolve alkali metals even in weakly polar organic solvents such as benzene and toluene,[20–23] it becomes possible to extent significantly the range of solvents in which the solvated electron and related species, which are the objects of study in radiation chemistry, may be obtained.[24] The weakly solvated alkali metal anions, present in such solutions, have very powerful reducing properties.[17] Strong oxidants, insoluble in the majority of organic solvents, such as potassium dichromate and permanganate, dissolve even in benzene in the presence of crown-ethers.[25–28] Thus a powerful instrument becomes available for the study of the oxidation-reduction processes occurring in the radiolysis of non-aqueous solutions.[29,30] Crown-compounds, which make it possible to alter the state and reactivity of not only ionic reactants but also of ionic reaction intermediates, can serve as an effective means for the study of the mechanisms of radiation-chemical reactions.[31,32] Macrocyclic polyethers and their analogues give rise to the possibility of increasing appreciably the number of compounds soluble in weakly polar media, which helps to create new antiradiation agents or reagents and phase-transfer catalysts for radiation-chemical synthesis.

II. Crown-compounds as extractants for radionuclides. Radiation-chemical aspects

Extraction is one of the most important fields in which macrocycles are used.[33] In particular, the employment of crown-compounds for the selective isolation of radionuclides is extremely

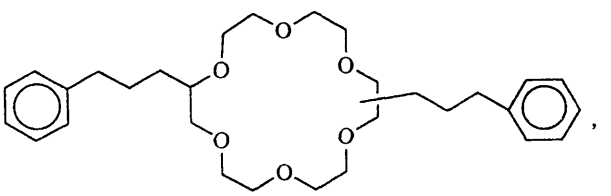
promising.[34,35] In the processing of spent nuclear fuel,[36] the extractant can receive a dose of the order of 0.4–40 kGy in one cycle depending on the organisation of the extraction process, while under conditions of multiple employment of the extractant the integral radiation dose received by the latter can reach tens of megagrays.[37] The radiolysis of extraction systems can also have negative consequences important for technology such as the degradation of the extractant and the decrease in the efficiency of the extraction, the formation of radiolytic products influencing unfavourably the selectivity of the extraction and the phase separation, and the formation of corrosive acids and oligomers which hinder the regeneration of the extractants. For this reason, the radiolytic reactions of organic compounds and of two-phase aqueous organic systems, the search for new more effective and radiation-resistant extractants which are satisfactorily compatible with the organic liquids used as diluents, as well as the behaviour of salts of the actinide elements, which are the main components of nuclear fuel, have been the subject of vigorous studies.[13,37–39]

Numerous studies have been devoted in this connection to crown-ethers. For example, a review[40] quotes data on the extraction of tervalent actinides by crown-compounds and their linear analogues. Another review[41] reports the complexes of divalent actinides with crown-ethers and their physicochemical properties and demonstrates the similarity to and differences from alkaline earth elements. The uranium(III) complexes of a series of crown-ethers have been investigated.[42] The processes involving the extraction of uranium, thorium, neptunium, and plutonium from nitric acid solutions by crown-ethers have also been studied.[43–46] A wide variety of compounds can be used as extractants and diluents, for example: 15-crown-5 (15C5) and dicyclohexano-18-crown-6 (DCH18C6) in nitrobenzene and 1,2-dichloroethane for uranium(VI), neptunium(IV), and americium(III); DCH18C6 in nitrobenzene for neptunium(IV);[47] 12-crown-4 (12C4), 15C5, 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), and DCH18C6 with 4-benzyl-3-methyl-1-phenylpyrazolone in toluene for uranium(VI), americium(III), and thorium(IV);[48] five different crown-ethers in 1,2-dichloroethane for uranium(VI),[49] DCH18C6, DB18C6, and 18C6 with thenoyltrifluoroacetone in benzene[50] and 12C4, 15C5, 18C6, DB18C6, and DBH18C6 in chloroform[51,52] for americium(III); DCH18C6 or benzo-15-crown-5 (B15C5) with 3-methyl-1-phenyl-4-trifluoroacetyl-5-pyrazolone in chloroform for trivalent americium, curium, californium, and europium.[53] The application of 18C6 makes it possible to carry out the selective extraction of thorium in the form of the picrate complex from a mixture containing cerium, uranium, zirconium hafnium, yttrium, and lead.[54]

The use of crown-ethers (for example, DCH18C6 or DB18C6) as extractants in the processing of irradiated nuclear fuel permits the isolation of uranium and plutonium from aqueous solutions containing nitric acid.[55,56] It has been shown that DCH18C6 (especially the *cis*, *syn*, *cis*-isomer of this macrocycle) is an effective extractant for plutonium present in highly radioactive solutions resulting from the processing of nuclear fuel. This crown-ether is more radiation-resistant and selective in the isolation of plutonium(IV) than tri-n-butyl phosphate (TBP) usually employed. Thus, in a study of a 10% solution of DCH18C6 in chloroform irradiated from a ^{137}Cs source (absorbed dose 168 kGy) by UV, IR, and ^{1}H and ^{13}C NMR spectroscopic methods as well as high performance liquid chromatography (HPLC), no products of the radiation-chemical reactions of the crown-ether were detected. In addition, a comparative study has been made of the extraction of plutonium from moderately active solutions by commercial DCH18C6 (mixture of isomers) and with the crown-ether subjected to preliminary washing with nitric acid. The extractant was irradiated during its contact with the solution containing plutonium(IV), uranium(VI), and fission products in the course of eight months. In this case, the overall absorbed energy was 611 kJ mol^{-1}, including 80.5 kJ mol^{-1} as the α-emission energy, which corresponds to 5000 cycles involving extraction from highly active solutions. It has been shown that, even if the selectivity in the isolation of plutonium does actually decrease as a result of the strong irradiation of the polyether, the decrease is extremely insignificant. The amount of extracted plutonium is 92 and 90% respectively for the commercial products and the irradiated DCH18C6. Thus, according to the authors,[56,57] the use of crown-ethers as extractants makes it possible to create a new industrial technology for the processing of nuclear fuel.

Apart from actinides, other radioactive elements and isotopes can be extracted with crown-ethers. The extraction of technetium(IV) with DB18C6 and 18C6 has been investigated in a study,[58,59] where the organic phase was nitrobenzene, benzene, and acetylacetone; the extraction of astatine-211 with crown-ethers from various media and its mechanism have been discussed.[60] The selective isolation of iodine-131 from irradiated uranium and tellurium oxides can be achieved with a high efficiency using DB18C6 in 1,2-dichloroethane as the extractant.[61] The equilibria in the extraction system involving the extraction of radium from an aqueous medium containing sodium nitrate and hydroxide into a solution of dicyclohexano-21-crown-7 in toluene in the presence of 2-heptyl-2-methylnonanoic acid has been investigated.[62] The possibility of the selective separation of radium from other alkali and alkaline earth elements was demonstrated.

The use of crown-ethers in the technology of the extraction of radioactive caesium-137 and strontium-90 from spent aqueous solutions in nuclear reactors is promising.[63,66] The study of the extraction of Sr^{2+} with the crown-ethers B15C5, DB18C6, dibenzo-21-crown-7, dibenzo-24-crown-8 (DB24C8), dibenzo-27-crown-9, dibenzo-30-crown-10, DCH18C6, and bis(4-phenylbutyl)-18-crown-6 (I), i.e.



(I)

for nitric acid solutions containing $NaNO_3$ showed that the crown-ethers (I) and DCH18C6 (mixture of two *cis*-isomers) can be used for this purpose. The latter extractant is more effective and the best diluent is 1,1,2,2-tetrachloroethane.[67] Similar results were obtained by Filippov, et al.,[68] who investigated the extraction of magnesium, calcium, strontium, and barium nitrates from nitric acid solutions with the crown-ether DCH18C6 in dichloroethane. The possibility of the selective extraction of Sr^{2+} was demonstrated, the crystalline complex $Sr(NO_3)_2$.DCH18C6 was isolated, and its IR spectroscopic characteristics were obtained. It has been noted[69] that DCH18C6 is an effective extractant not only for Sr^{2+} but also for Tl^{+} (diluent – 1,1,2,2-tetrachloroethane and trichlorobenzene).

A method is available for the isolation of strontium from spent solutions in the nuclear reactors in atomic power stations,[70] where ^{90}Sr is extracted with a solution of crown-ether in chloroform, benzene, toluene, or alkanes at pH 2–6 after adding picric acid, trialkylphenol, or phenyltetrazoline-5-thione. This method makes it possible to separate strontium from potassium, lead, silver, and mercury usually present in the solutions.

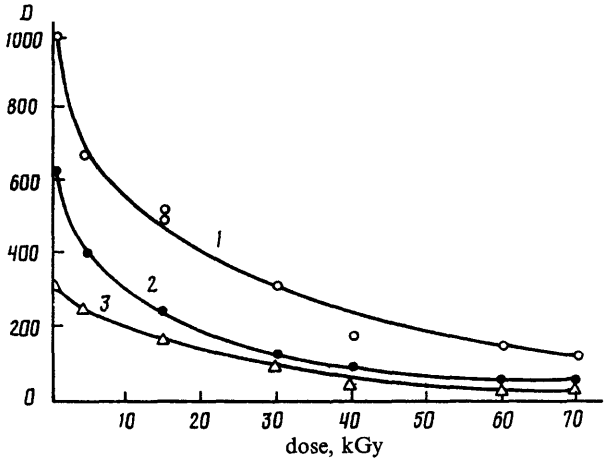


Figure 1. The effect of the absorbed radiation dose on the partition coefficient in the extraction of strontium by irradiated solutions of DCH18C6 in chloroform. Molar crown-ether concentration: *1*, 0.05; *2*, 0.01; *3*, 0.005. **^{60}Co γ-radiation dose rate 24 Gy s^{-1}.[71]**

The results of a study[71] of the extraction of strontium from aqueous solutions of picric acid with solutions of crown-ethers in chloroform subjected to ^{60}Co γ-irradiation are of interest in this connection. It was established that the partition coefficient *D* decreases significantly in the dose range up to 70 kGy for DCH18C6 (Fig. 1). Similar relations were observed also for solutions of 18C6 (Fig. 2), DB18C6, DB24C8, and D15C5 in chloroform, the effectiveness of the extractant decreasing in the sequence DCH18C6 > 18C6 > DB24C8 > DB18C6 > B15C5. This effect is due to the radiolytic reactions of chloroform, since the radioactive degradation or dehydrogenation of the crown-ether was not observed.

Comparison of the ^1H NMR spectra of pure DCH18C6 and of the crown-ether irradiated in chloroform (70 kGy) shows that either chlorination (1 or 2 halogen atoms) takes place or the complex H^+DCH18C6)Cl^- is formed under the influence of irradiation. However, later results of the study of γ-radiolysis of solutions of B15C5 in chloroform[72] failed to confirm the occurrence of radical reactions of the crown-ether and Cl atoms with formation of products mono- or di-chloro-substituted in either the aromatic or the polyether ring. On the basis of NMR and mass-spectrometric data, it was postulated that the radiolysis of chloroform containing B15C5 results in the formation of complexes of the type (H^5B15C5)Cl^- and (H^+B15C5)Cl^-_2 (the appearance of the red-violet colour on irradiation of the solution is attributed to this). The macrocycle decomposition products were not identified, although the appearance of carbonyl groups resulting from the opening of the polyether ring was detected by IR spectroscopy.

After the chloroform has been removed by evaporation from the irradiated DCH18C6 solution, the residue, dissolved in a fresh portion of choroform, was used to extract strontium.[71] In this case, the partition coefficient (D = 442) proved to be much higher than that obtained in the extraction of strontium with a solution of DCH18C6 in irradiated chloroform (D = 54). Evidently the decrease in the partition coefficient D is not a result of the reactions of the extractant. The data obtained[71,72] show that the main factor inducing the sharp decrease in the partition coefficient is the formation of HCl in the radiolytic decomposition of chloroform. Other products of the radiolysis of the latter influence the partition coefficient to a lesser degree. The formation of C_2Cl_6 diminishes the dielectric constant of the solvent, leading to a lower value of D at high concentrations. Comparison of the dose dependence of the partition coefficient D for 18C6 dissolved in irradiated chloroform and for the irradiated solution of this crown ether (Fig. 2) emphasises yet again that the decisive factor in the decrease of the effectiveness of the extraction is radiation-chemical processes occurring in the diluent.

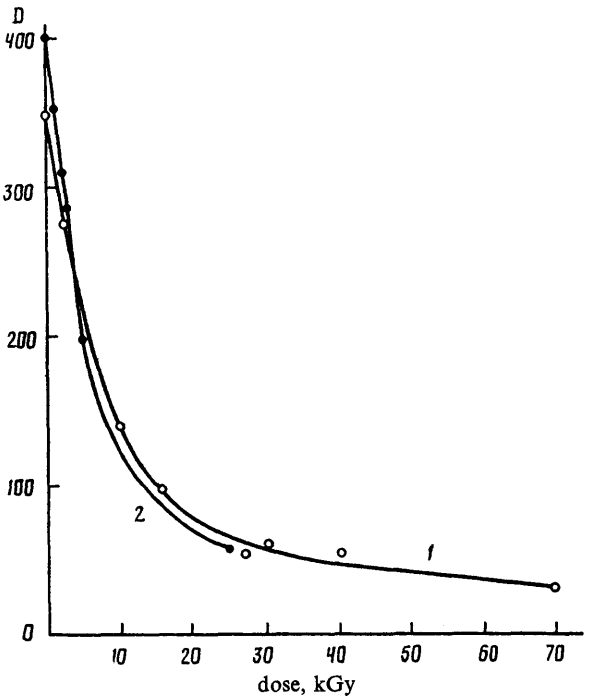


Figure 2. The effect of the absorbed γ-radiation dose on the partition coefficient in the extraction of strontium by an irradiated 0.1 M 18C6 solution in chloroform (curve *1*) and 0.13 M solution of 18C6 in chloroform subjected to preliminary irradiation (curve *2*).[71]

Interesting results were obtained in the study of the influence of γ-radiation on the ionophoric capacity of the ligand in the transfer of alkali and alkaline earth metal ions through a liquid membrane consisting of a 1×10^{-3} M solution of 18C6 in chloroform.[73] The

irradiated membrane has the greatest effect on the transport of cations in the case of caesium and barium (Table 1). The selectivity in the transport of ions shifts from K^+ to Cs^+ and from Sr^{2+} to Ba^{2+} under the influence of radiation. A similar effect has also been noted for another ligand—1,10-phenanthroline. The authors[73] have not reached unambiguous conclusions concerning the causes of the observed phenomenon and note that it can be due both to radiolytic reactions of the ligand and to a change in the properties of the organic phase, in particular the formation of HCl. The rate of the membrane transport is related directly to the extraction properties of the metal ion in the systems considered.

Table 1. The effect of γ-irradiation on the membrane transport of cations from 1×10^{-3} M aqueous solutions of picrates.[73]

Cation	Concentration of cation transferred to the aqueous phase 10^6C, M		$10^6\Delta C$, M
	non-irradiated 18C6–$CHCl_3$ system	irradiated* 18C6–$CHCl_3$ system	
Li^+	0.044	0.196	0.152
Na^+	0.399	0.458	0.115
K^+	8.900	11.970	3.070
Cs^+	7.640	21.840	14.200
Mg^{2+}	0.135	1.00	0.865
Ca^{2+}	0.360	3.990	3.650
Sr^{2+}	5.120	10.330	5.210
Ba^{2+}	6.790	18.680	9.100

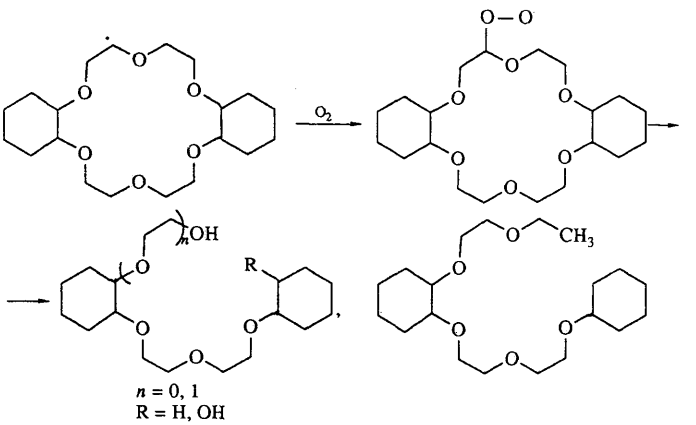
*The 1×10^{-3} M 18C6 solution in chloroform was irradiated from a ^{60}Co γ-source. Dose rate 1.5 Gy s^{-1}, absorbed dose 450 Gy.

An appreciable increase in the radiation-chemical yield $G(HCl)$ on passing from the individual compounds to two-phase aqueous organic systems has been noted for trichlorobenzene and tetrachloroethane.[74] The presence of the crown-ether DCH18C6 or DB18C6 leads under these conditions to an appreciable decrease in $G(Cl^-)$. This can be explained by the proton-solvating properties of the crown-ethers and their ability to form complexes of the type DCH18C6.HCl.

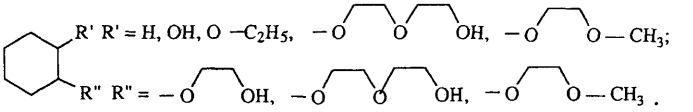
The presence of lanthanum(III) nitrate does not affect the accumulation of Cl^- ions in the 0.1 M crown-ether in tetrachloroethane–3 M HNO_3 extraction system.[75] The radiation-chemical reactions of DCH18C6 and DB18C6 in such aqueous organic systems have been examined.[76] The products of the radiolysis of the crown-ethers after irradiation from a ^{60}Co γ-source (absorbed dose ~100 kGy) were identified with the aid of UV, IR, and ^1H NMR spectroscopy. On the basis of the data obtained, in combination with the results of elemental analysis, the authors[76] proposed a probable mechanism of the formation of nitro- and chloro-derivatives of the products of the radiolysis of macrocyclic polyethers in the extraction system containing tetrachloroethane.

Further studies of the qualitative composition and of the pathways leading to the formation of the products of the radiolysis of DCH18C6 forming part of the 0.1 M DCH18C6 in 1,1,2,2-tetrachloroethane–3 M HNO_3 model extraction system by chromatograph-linked mass spectrometry[77,78] made it possible to refine the process mechanism. More than 40 products of the reactions of the crown-ether were identified and it was established that their structure is determined to a large extent by the nature of the diluent and the composition of the aqueous phase of the extraction system. The proposed mechanism of the radiation-chemical reactions of DCH18C6 includes five main product formation pathways.

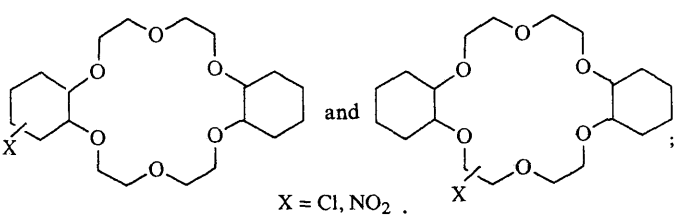
The radical with the unpaired electron localised on a carbon atom of the macrocycle, produced in the first stage, can interact with oxygen, further reactions of the peroxide radical formed leading to the appearance of degradation products (pathway *1*) with partial retention of the polyether bridge between the cyclohexane rings.



Further degradation to products containing only one cyclohexane fragment is postulated (by analogy with the behaviour of the peroxide radicals of ethers).

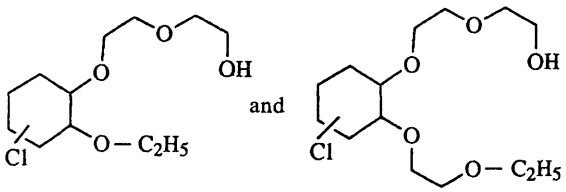


The formation of different chloro- and nitro-substituted crown-ethers



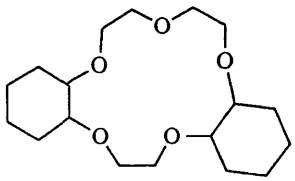
is a result of the reactions of the products of the radiolysis of tetrachloroethane and HNO_3 with DCH18C6 (pathways *2* and *3*).

For the chloro-derivatives, degradation with formation of structures of the type

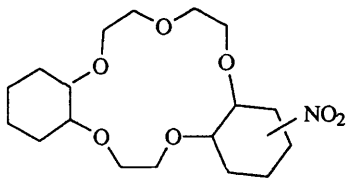


is also postulated.

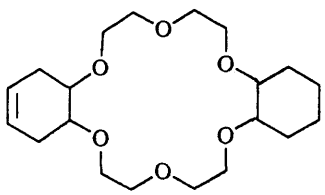
The decomposition of the crown-ether with loss of the epoxyethane fragment and retention of the ring



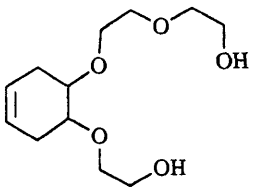
in the case of the liquid-phase radiolysis of DCH18C6 (pathway *4*) is probably analogous to the previously observed process occurring under electron impact in the mass spectrometer[79] and also leads, according to the authors,[78] to the appearance of nitro-substituted cyclic structures.



The partial dehydrogenation of the cyclohexane ring in the DCH18C6 molecule (pathway *5*) leads to the corresponding unsaturated compounds

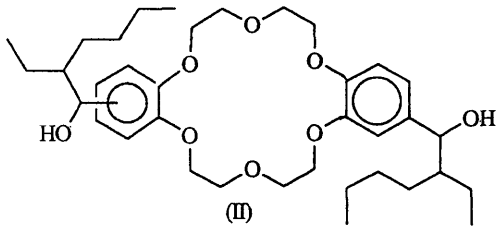


and subsequent fragment of the type



In addition, monocyclohexyl-substituted crown-ethers and the products of the methylation of DCH18C6 were identified in the irradiated extraction system.

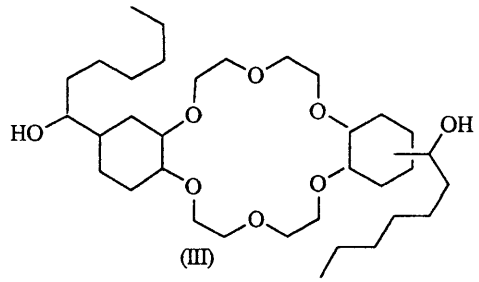
Another approach to the extraction of caesium and strontium from solution in nitric acid with the aid of crown-ethers has been used by Schulz and Bray[80] and Bowers and co-workers.[81,82] They used for the extraction four-component organic systems containing tributyl phosphate (28 vol.%), dinonylnaphthalenesulphonic acid (NNS) or didodecylnaphthalenesulphonic acid (5 vol.%), a macrocyclic polyether (0.05 M), and a hydrocarbon diluent (kerosene, 68 vol%). In these systems, dinonylnaphthalenesulphonic acid is used to substitute the relatively hydrophilic nitrate by a much more lipophilic anion, which increases the partition coefficient of strontium. Tributyl phosphate acts as a modifying agent, inhibiting the formation of a third phase and increasing the solubility of the crown-ether and dinonylnaphthalenesulphonic acid. It is recommended that 4,4′(5′)-bis(2-ethyl-1-hydroxyhexyl)benzo-18-crown-6 (II) be used for the effective extraction of caesium.



(II)

In this case, about 60% of the caesium is transferred from the spent model solution to the organic phase, whereas for solutions of a number of other crown-ethers the above quantity is only approximately 30%.[82]

Similarly, the selective extraction of strontium is promoted by the presence of 0.02 M 4,4′(5′)-bis(1-hydroxyheptyl)cyclohexano-18-crown-6 (III) in the four-component system.



(III)

It was established in comparative experiments that, when the TBP–NNS–crown-ether (II) or (III)–kerosene system is irradiated from a ^{60}Co γ-source up to an absorbed dose of 100 kGy, the partition coefficient of caesium falls from 1.6 to 1.0 and that of strontium diminishes from 2.0 to 1.6.[81]

The selective isolation of Sr^{2+} and Cs^{+} from nitric acid solutions with the aid of liquid membranes containing dinonylnaphthalenesulphonic acid and DCH18C6 dissolved in n-dodecane has been described.[83] The likely usefulness of immobilised liquid membranes for the regeneration and separation of strontium and caesium ions in industry and in analytical chemistry has been demonstrated. The crown-ether DCH18C6 and its derivatives have found applications in the extraction[84–87] and extraction-chromatographic[88–90] isolation and concentration of strontium radioisotopes in the analysis of waste waters, biological samples, and objects in the environment. With the

aid of DB24C8 and dichloromethane as the diluent, it is possible to separate caesium not only from alkali and alkaline earth metals but also from zirconium, hafnium, thorium, lead, bismuth, and other elements usually present in fission products.[91] Sorbents and membranes based on crown-ethers immobilised on different carriers and designed for the extraction and concentration of the ^{137}Cs and ^{90}Sr radionuclides from the alkaline waste produced by atomic power stations have been investigated[92,93] and optimum conditions for the selective transport of the $^{137}Cs^{+}$ ions through the crown-ether-containing membrane have been developed.

The latest studies by Horwitz and co-workers[94,95] showed that strontium can be effectively extracted from nitric acid by the crown-ether DCH18C6 or its derivatives in various oxygen-containing aliphatic diluents (for example, in alcohols and ketones), which are less toxic than chlorine-containing solvents and do not form corrosive HCl on radiolysis.

Table 2. The effect of radiolysis on the extraction system of the SREX process.[95]

Absorbed dose*, kGy	Partition coefficient of strontium D	
	0.01 M HNO_3	3 M HNO_3
0	0.020	39.6
116	0.056	41.5
244	0.080	36.3
317	0.038**	27.0**
321	0.12	18.5
386	0.11	14.1

* γ-radiation dose rate from a ^{60}Co source 0.7 Gy s^{-1}.
** The values obtained for a 0.2 M solution of DBC18C6 in 1-octanol subjected to preliminary irradition are presented.

In a new process,[95] called SREX, which has many advantages over the methods proposed earlier, the selective extraction of strontium from acid spent solutions is achieved using a 0.2 M solution of di-t-butylcyclohexano-18-crown-6 (DBC18C6) in 1-octanol. It has been shown experimentally that 99.7% of the strontium present initially in the solution can be extracted after only three extraction cycles. Table 2 summarises the results of the study of the influence of γ-radiolysis on the effectiveness of the SREX process. For absorbed doses not exceeding 240 kGy, the partition coefficient of strontium between the organic phase and 3 M HNO_3 does not change appreciably, but for higher doses D falls significantly and at ~390 kGy it diminishes by a factor of almost three compared with the initial value. On the other hand, the data obtained for 0.01 M HNO_3 show that, even for the lowest absorbed radiation dose investigated, the system undergoes radiolytic reactions leading to an almost threefold increase in the partition coefficient. It has been noted that radiolysis does not impair the selectivity of the strontium extraction process.

In connection with the high radiation stability of crown-ethers noted in a number of studies,[7,12,71,72] Horwitz, et al.[95] decided to check whether the observed change in the partition coefficient is merely a consequence of the radiation-induced degradation of the diluent. For this purpose, a 0.2 M solution of DBC18C6 was prepared in 1-octanol subjected to preliminary irradiation (317 kGy) and the strontium partition coefficients were determined. The measured values of D for 0.01 and 3 M HNO_3 occupy an intermediate position between the values obtained for the initial solution and the irradiated solution used in the extraction process. Thus the radiolysis of the system entails the degradation of both the diluent and the extractant. In the absence of other data apart from the measured partition coefficients, it is impossible to establish definitely the nature of the influence of the irradiation on the extraction system, although the rupture of the crown-ether ring and the formation of hydrocarbons with a smaller chain length and low-molecular-weight alcohols and aldehydes from 1-octanol is likely. It is important to note that the absorbed radiation doses used in the experiments appreciably exceed the values which may be expected in the processing of real radioactive liquid waste. Consequently, the radiation-chemical reactions do not create serious obstacles to the extraction process over a long period.

The complexity of the radiation-chemical behaviour of crown-compounds in multicomponent two-phase aqueous organic extraction systems used under the conditions of the industrial processing of radioactive materials necessitates a profound study of the mechanisms of the formation of the main products of the radiolysis of the extractants on the basis of simpler systems,[96] which may permit the determination of the details of the reaction mechanisms presented above as well as similar mechanisms.

It is therefore useful to examine in the Sections below the radiolysis of individual crown-compounds as well as their aqueous and non-aqueous solutions.

III. Radiolysis of macrocyclic polyethers

As a rule, the description of the radiation-chemical reactions in various systems is usually begun with the consideration of the primary radiolysis products and the reactive intermediates participating in such reactions. It has been shown that the products of this kind in liquid polar media are solvated electrons, various ions, free radicals, and excited molecules.[24] However, the available information about the primary products of the radiolysis of crown-ethers and their analogues is so far scanty and does not permit the formulation of a detailed picture of the primary processes occurring.

The formation of solvated electrons in the radiolysis of liquid crown-ethers has been observed by a pulse method in relation to 12C4 and 12C5.[97,98] The optical spectrum of e^{-}_{solv} in 12C4, obtained in the pulse radiolysis of the pure crown-ether, is illustrated in Fig. 3. The assignment of the peak in the wavelength range between 1100 and 1500 nm to e^{-}_{solv} is based on the complete disappearance of this peak when the solution is saturated by the N_2O electron acceptor. The wavelength at the absorption maximum of the solvated electron in 12C4 is close to the corresponding wavelength in ammonia (1504 nm).[97]

When 15C5 is subjected to pulse radiolysis and also when metallic potassium and caesium are dissolved in it, a very broad absorption band (from 0.8 to 1.8 μm) predominates in its near IR optical spectrum. By analogy with pulse radiolysis data for pure 15C5, the band was assigned to the solvated electron e^{-}_{solv}. The spectra of the

potassium solutions show a shoulder at 0.85 μm, which is characteristic of the K^- anion. On the other hand, solutions of alkali metals in 12C4 do not exhibit an appreciable absorption due to the solvated electron (Fig. 4). Instead, the presence of appreciable concentrations of the alkali metal anion is manifested in the spectrum. It is of interest to note that solutions of metals in 15C5 are less stable than their analogues in 12C4. Studies by pulse radiolysis showed that the rate constant for the first-order reaction involving the disappearance of the electron in 15C5 ($\sim 5 \times 10^6$ s^{-1}) is appreciably lower than in 12C4 ($\sim 2.5 \times 10^7$ s^{-1}).,[98] i.e. the solvated electron is longer-lived (or is more solvated) in liquid 15C5 than in the smaller ionophore 12C4.[99]

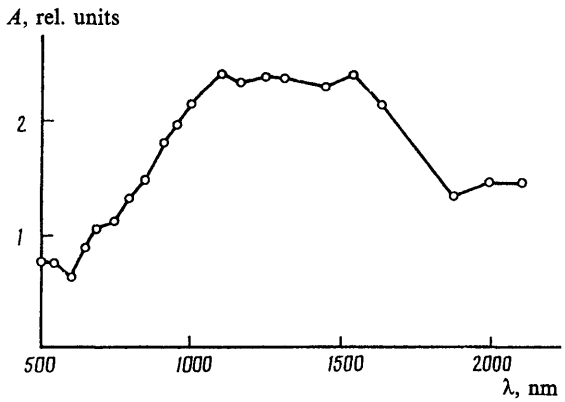


Figure 3. The optical spectrum of the solvated electron obtained on pulse radiolysis (0.2 μs) of 12C4 at room temperature.[97]

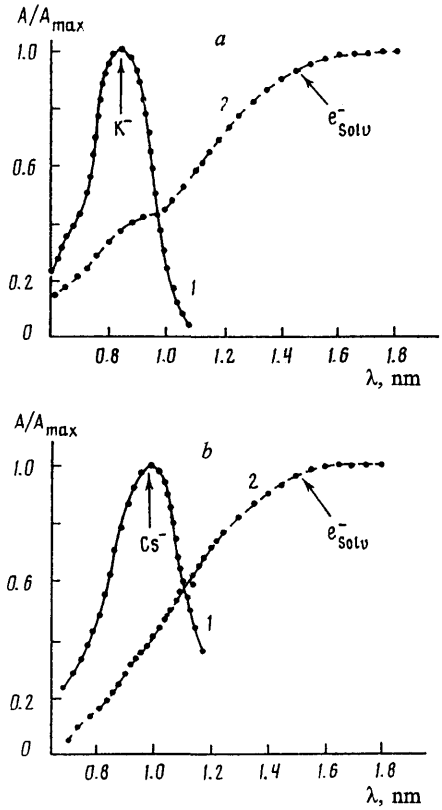


Figure 4. The optical absorption spectra at room temperature of metallic potassium (*a*) and caesium (*b*) dissolved in 12C4 (curves *1*) and 15C5 (curves *2*).[98]

Table 3. The radiation-chemical yields of molecular hydrogen and stabilised paramagnetic species in crown-ethers (absorbed doses 10–180 kGy).[101]

Crown-ether	$G(H_2)$	G(R)		
	T_{irr} = 77 K	T_{irr} = 77 K	after UV irradiation	T_{irr} = 300 K
18C6	0.3	5.7	5.7	0.8
DCH18C6	0.2	3.3	3.0	0.2
DB18C6	0	1.9	1.6	–

The radical intermediates formed in the low-temperature γ-radiolysis of a number of crown-ethers and their analogues with different ring sizes[100] as well as crown-ethers having an 18-membered macroheterocycle with different substituents[101–103] have been investigated by EPR spectroscopy. The results of the study of the primary products of the radiolysis of the polyethers 18C6, DCH18C6, and DB18C6 as well as mass-spectrometric data are presented in Table 3.

The introduction of substituents into the macrocycle leads to an appreciable change in the EPR spectra of the irradiated compounds and the specimens become coloured brown. The effect of UV radiation leads to the decolorisation of the specimen and to the disappearance of one of the spectral lines, which permits its assignment to stabilised electrons. After the "annealing" of the stabilised electrons, the concentration of the paramagnetic species does not increase. On raising the temperature to the melting point of the crown-ethers, the EPR spectra vanish. The appearance of a yellow colour and the presence of stabilised electrons in the irradiated 12C4, 15C5, DCH18C6, and their analogues tetrahydrofuran (THF) and 1,4-dioxane (the smallest member of the family of cyclic epoxyethane oligomers), has also been observed in the study of Kuruc and Sersen,[100] who also noted the instability of the radical intermediate at temperatures above 297 K.

The inconsistency between the radiation-chemical yields of molecular hydrogen and of the paramagnetic species formed (Table 3) and also the complexity of the EPR spectra of the irradiated crown-ethers are a consequence of the simultaneous occurrence during radiolysis of several primary processes, the main one being, according to the authors,[101–103] the rupture of the macrocycle at the C–O bonds. However, Kuruc and Sersen[100] believe that the formation of radicals containing the $-O-\dot{C}H-CH_2-$ fragment is more likely in the given instance, by analogy with the reactions in dioxane and THF.

The EPR study of γ-irradiated solutions of 1,4-dioxane in Freon matrices permitted the conclusion that the primary radical-cation undergoes an ion-molecule reaction with a neutral molecule and leads to the formation of a radical, resulting from the α-abstraction of hydrogen, and of a protonated dioxane molecule.[104] Other data[105] show that the THF radical-cations in the ground state, generated in freon matrices, are resistant to ring rupture reactions, but in the parent compound matrix the radical-cations, having an excess energy, are capable of forming radicals as a result of ring rupture.

In the case of mono- and di-alkyl derivatives of DB18C6, the abstraction of a H atom from the CH_2 groups of the macrocycle and the alkyl substituents in the crown-ether has been postulated.[102,103] The C-centred nature of the radicals is confirmed by the results of a study by the spin trapping method,[106] since it was established that the EPR spectra of the radical adducts formed on capture by the spin-trapping agent of the crown-ether radicals (generated at 77 K) on heating the specimen and measuring the spectrum at room temperature as well as the spectra of the radical adducts observed on irradiation at room temperature are identical. The EPR spectra of the radicals generated at 77 K, measured at the same temperature in the presence of a spin-trapping agent are consistent with the spectra of the pure crown-ethers.

The analysis of the EPR spectra obtained after irradiating the crown-ethers 12C4, 15C5, DCH18C6, as well as THF and 1,4-dioxane in the presence of a spin-trapping agent established the formation of spin adducts with H atoms and C-centred radicals. Under these conditions, it cannot be that the radical centre is located on the polyether or cyclohexane ring of the substituted macrocycle. We may note that in the case of THF two spin adducts are detected, which indicates the formation of both α- and β-radicals.[105]

Table 4. The radiation-chemical yields of free radicals in organic compounds at 77 K.[109]

Compound	G(R), radical/100 eV
Ethanol	4.0
Ethylene glycol	5-6
Diethyl ether	3.7
THF	1.7
Furan	1.1
Trioxane	1.1
Tetrahydropyran	4
Cyclohexane	3.8
Benzene	0.15

The introduction of substituents, especially aromatic rings, into the polyether ring increases the radiation stability of the crown-ethers as a result of the intramolecular energy transfer from the macrocycle to the substituent.[100-103]

The effect of γ-radiation on solid complexes of crown-ethers with metal salts has been investigated by EPR spectroscopy.[107,108] The radiation-chemical yields of the radicals were measured for $MgCl_2$.18C6, $CaCl_2$.18C6, and $CaCl_2$.15C5. They are 3.3, 8.1, and 3.1 radical/100 eV respectively. The presence of atomic hydrogen was detected in the irradiated specimens of $FeCl_3$.18C6 and $FeCl_3$.15C5.[108] It was noted that the radiation-chemical processes in the molecular complexes of the crown-ethers are determined not only by the nature of the macrocyclic ligand but to a large extent by the properties of the metal cation.

Comparison of the yields of radicals (Table 3) in crown-ethers irradiated at 77 K with the analogous values obtained at the same temperature for a number of other organic substances[109] (Table 4) does not indicate any kind of unusually high radiation stability of the crown-ethers. Their properties are similar to those of ethers and alcohols. The yields of the final radiolytic products are extremely important for the characterisation of the radiation stability of the compounds (as the factor influencing their practical employment).

The γ-radiolysis of DB18C6, DCH18C6, and 18C6 in the condensed phase in the presence and absence of air has been investigated in a series of studies[7,9,79,101] by gas–liquid chromatography and UV and NMR spectroscopy. No radiolysis products were found under these conditions in the condensed phase in the range of absorbed doses up to 640 kGy. Mass spectrometry of the gas phase of the irradiated crown-ethers made it possible to detect the formation during radiolysis of molecular hydrogen and of traces of epoxyethane (Table 5), but the yields of these products were not quoted.[7,9] Since the irradiation of DB18C6 and DCH18C6 results in the formation of $\sim 7 \times 10^{-5}$ and $\sim 8 \times 10^{-3}$ mol of H_2 per mole of the crown-ether,[7] it was possible to estimate the radiation-chemical yield of hydrogen taking into account the molecular weights of the crown-ethers and the absorbed dose of ionising radiation ($\sim$640 kGy). It amounts to $\sim$0.003 molecule/100 eV for DB18C6 and $\sim$0.3 molecule/100 eV for DCH18C6. In a later study by the same workers,[79] yields of hydrogen, amounting to 0.12, $\sim$0.01, and $\sim$0.01 molecule/100 eV were obtained respectively for DCH18C6, DB24C8. The upper limits of the decomposition are $\sim$0.004 and $\sim$0.2 molecule/100 eV for DB18C6 and DCH18C6 respectively.[7]

Table 5. Mass spectra of the gas-phase products of the radiolysis of DCH18C6 and DB18C6 (absorbed dose rate 0.51 Gy s^{-1}, dose $\sim$640 kGy).[7]

m/e	Peak intensity, rel. units		Proposed structure of fragments
	DB18C6	DCH18C6	
2	70	1000	H_2^+
15	10	20	CH_3^+
26	10	10	$C_2H_2^+$
28	10	20	$C_2H_4^+$, CO^+
44	60	50	$C_2H_4O^+$, CO_2^+

In the proposed radiolysis mechanism,[7,79] it is assumed that epoxyethane is formed in a small amount from the cyclic polyether as a result of ion-molecule reactions and that, after the elimination of the C_2H_4O fragment from the molecular ion of the crown-ether,

the opening of the macrocycle does not occur, a cyclic structure with a smaller ring size being formed instead. It is assumed that the source of hydrogen in the irradiation of DCH18C6 is the cyclohexyl fragments.

The study by Langrock, et al.[12] was also devoted to the radiation stability of crown-ethers. They investigated the γ-radiolysis of B15C5, DB18C6, DB24C8, and dithio-18C6 in the presence of air in the temperature range 293–313 K (absorbed dose range 0.1–1 MGy). The yields of the gaseous radiolysis products were determined by gas chromatography and those of the decomposition of the polyethers were found by ^{1}H NMR spectroscopy (Table 6). The authors[12] state that the resistance of the crown-ethers to γ-radiation can be regarded as satisfactory in the dose range up to 0.2 MGy and is acceptable up to 1 MGy. The radiation stability diminishes in the sequence DB24C8, B15C5 > DB18C6 > dithio-18C6. Crown-ethers containing only oxygen heteroatoms in the macrocycle are recommended for practical use in radiochemical separation processes.

Table 6. The yields G of the products of the γ-radiolysis of crown-ethers for an absorbed dose of 0.1 MGy.[12]

Crown-ether	Yields of gaseous products			Yield in the decomposition of the solid substance
	H_2	CH_4	C_2H_6/C_2H_4	
B15C5	0.00145	0.000203	0.000340	0.1428
DB18C6	0.00166	0.000267	0.008193	0.4928
DB24C8	0.00194	0.000239	0.003506	0.1284
Dithio-18C6	0.00206	0.000273	0.069085	0.6466

Table 7. The radiation-chemical yields of the products of the γ-radiolysis of polyethers at different temperatures (dose rate 4 Gy s^{-1}, absorbed doses 2–15 kGy).[110]

Compound	State of aggregation	$G(H_2)$		$G(C_2H_4)$	
		290K	300K	290K	300K
1,4-Dioxane	Liquid	–	1.41	–	0.364
PEG-300	"	1.46	–	0.048	–
PEG-600	Oil	2.06	–	0.043	–
	Liquid	–	1.51	–	0.026
15C5	"	1.60	1.94	0.081	0.158
18C6	Crystalline	2.14	–	0.020	–
	Liquid	1.62	1.85	0.108	0.163
DB18C6	Crystalline	0.175	–	0.014	–
DCH18C6	Oil	1.03	–	0.078	–
	Liquid	0.86	1.18	0.089	0.118

The results of studies on gaseous products of the γ-radiolysis of deaerated specimens of the cyclic polyethers 15C5, 18C6, DB18C6, and DCH18C6, their acyclic analogues—the poly(ethylene glycols) PEG-300 and PEG-600, and also 1,4-dioxane have been described.[110] It was established on the basis of the results of chromatographic analysis that the principal gaseous products are hydrogen and ethylene (Table 7), together with which a small amount of methane (G = 0.012 molecule/100 eV for 15C5) and traces of acetylene and carbon monoxide [G(CO) < 0.002] were detected. The low yield of ethylene formed in the γ-radiolysis of crown-ethers as well as polyglycols, compared with $G(C_2H_4)$, for dioxane is associated with the fact that the probability of the simultaneous dissociation of two C–O bonds in a single $-O-CH_2-CH_2-O-$ unit is greater for the dioxane molecule.

Thus the radiation-chemical behaviour of crown-ethers is similar to that of dioxane and poly(ethylene glycols) and, from the standpoint of radiation stability, macrocyclic polyethers do not differ fundamentally from the acyclic analogues and also from 1,4-dioxane which is in its turn more stable in this respect by a factor of 1.5–2 than, for example, diethyl ether.[109]

Table 8. Kinetic characteristics of the products of the interaction of certain crown-compounds, ethers, and oxygen-containing heterocycles with the primary water radiolysis products.

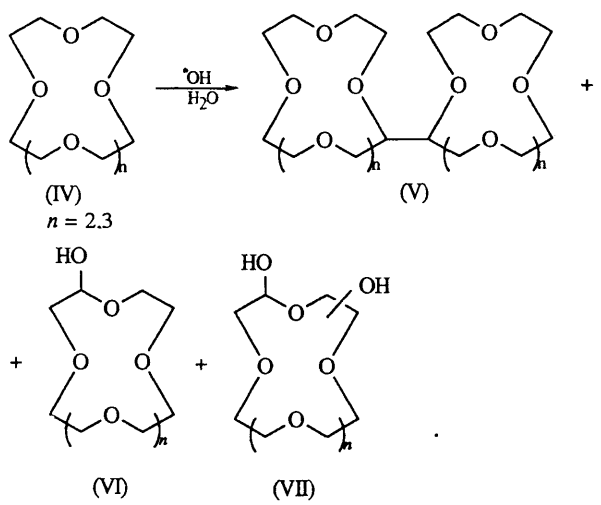
Reaction	Medium	Rate constant, litre mol^{-1} s^{-1}	Rate constant for the recombination of crown-radicals 2k, litre mol^{-1} s^{-1}	Refs.
18C6+e^-_{aq}	pH 6.7	$4\cdot10^6$	–	[111]
18C6+OH	pH 6.7, sat. N_2O	$6.0\cdot10^9$	$4.0\cdot10^8$	[111]
18C6+H	pH 1.2	$1.9\cdot10^8$	$5.0\cdot10^8$	[111]
18C6+O^-	pH 13.3, sat. N_2O	$5.0\cdot10^9$	$1.0\cdot10^9$	[111]
$KClO_4$.18C6+e^-_{aq}	pH 6.6	$< 10^6$	–	[111]
$KClO_4$.18C6+OH	pH 6.6, sat. N_2O	$1.0\cdot10^{10}$	$5.0\cdot10^8$	[111]
$KClO_4$.18C6+H	pH 1.2	$5.4\cdot10^7$	$5.0\cdot10^8$	[111]
$KClO_4$.18C6+O^-	pH 13.6, sat. N_2O	$9.2\cdot10^9$	$8.0\cdot10^8$	[111]
$NaClO_4$18C6+OH	–	$1.6\cdot10^{10}$		[114]
$NaClO_4$18C6+H	–	$2.5\cdot10^8$	–	[114]
$RbClO_4$.18C6+OH	–	$8.9\cdot10^9$	–	[114]
$RbClO_4$.18C6+H	–	$7.9\cdot10^7$	–	[114]
DCH18C6+e^-_{aq}	pH 6.5	$5.0\cdot10^6$	–	[113]
DCH18C6+OH	pH 6.5, sat. N_2O	$1.0\cdot10^{10}$	$5.0\cdot10^8$	[113]
DCH18C6+H	pH 1.0	$9.0\cdot10^7$	$2.9\cdot10^9$	[113]
DCH18C6+O^-	pH 13.5, sat. N_2O	$3.0\cdot10^9$	$3.6\cdot10^8$	[113]
C[2.2.1]+OH	sat. N_2O	$5.2\cdot10^9$	–	[115]
C[2.2.2]+OH	ditto	$6.0\cdot10^9$	–	[115]
$Cd(ClO_4)_2$C[2.2.1]+e^-_{aq}	–	$1.0\cdot10^{10}$	–	[115]
$Cd(ClO_4)_2$.C[2.2.2]+e^-_{aq}	–	$7.7\cdot10^8$	–	[115]
Ethyl ether+e^-_{aq}	–	$< 10^7$	–	[116]
Ethyl ether+OH	pH 1.2–7	$2.6\cdot10^9$	–	[116]
Ethyl ether+H	pH 1	$4.7\cdot10^7$	–	[116]
Dioxane+H	pH 2–9	$2.2\cdot10^9$	–	[116]
Dioxane+H	pH 1	$1.3\cdot10^7$	–	[116]
THF+OH	pH 9	$2.7\cdot10^9$	–	[116]
THF+H	pH 1	$7.8\cdot10^7$	–	[116]
1,2-Diethoxyethane+OH	pH 9	$2.2\cdot10^9$	–	[116]

IV. Radiation-chemical reactions in solutions of crown-compounds

1. Radiolysis of crown-ethers in aqueous solutions

Aqueous solutions of crown-ethers have been the objects of study by pulse radiolysis.[111–114] The study of the interaction of 18C6 (as well as its complexes with alkali metal perchlorates) and DCH18C6 with the primary water radiolysis products showed that crown-ethers exhibit a high reactivity in relation to hydrogen atoms and OH and O^- radicals and are significantly less reactive in relation to hydrated electrons (Table 8). It has been found[111,113] that at pH 6.5–6.7 the radiation-chemical yield of hydrogen is 0.9 molecule/100 eV both for 18C6 and DCH18C6, i.e. is close to the sum $G(H) + G(H_2) = 1.0$ in the radiolysis of pure water. In acid solutions (pH 1.0), the yield of hydrogen is $G(H_2) = 3.8$ molecule/100 eV for 18C6 and 3.0 molecule/100 eV for DCH18C6, i.e. is close to the sum of the yields $G(H) + G(H_2) + G(e_{aq}) = 4.1$. On this basis, it was concluded that hydrogen atoms interact with crown-ethers in the dehydrogenation reaction.

It follows from the identity of the optical absorption spectra of the short-lived products (λ_{max} = 260 nm) in acid as well as neutral and alkaline solutions of crown-ethers that H atoms, OH radicals, and O^- radical-ions dehydrogenate the polyether molecule with formation of the same radical. On the basis of EPR spectroscopic data, it is claimed[111,113] that both in the radiolysis of aqueous solutions of 18C6 and in the case of DCH18C6 the radical centre is located on the carbon atom of the polyether ring $-O-CH_2-CH-O-$, while the cyclohexyl groups in DCH18C6 are not involved to an appreciable extent. This mechanism has been confirmed also in the study of the dehydrodimerisation of crown-ethers in aqueous solution in the presence of hydrogen peroxide and iron(II) sulphate:[117]



Apart from the dimerisation products (V), the hydroxy-substituted crown-ethers (VI) and (VII) were isolated from the reaction mixture. The formation of the latter is possible as a result of the recombination of the corresponding radicals. Compounds (V)–(VII) are colourless oily substances whose composition and structure have been confirmed by elemental analysis, ^1H NMR, and mass spectrometry.[117]

It has been established[111,114] that absorption with $\lambda_{max} \simeq 260$ nm arises also in the pulse radiolysis of solutions of complexes of alkali metal perchlorates with 18C6. The presence of the potassium ion increases the rate constant for the reaction of the OH radical with the crown-ether but reduces the rate constant for the reaction of the H atom (Table 8). The disappearance of crown-radicals obeys the kinetic equation for second-order reaction (the values of $2k$ are listed in Table 8). Thus the presence of the alkali metal ion does not affect the mechanism of the interaction of OH and H radicals with the macrocyclic ligand and the reaction results in the appearance of analogous crown-radicals. On the other hand, the nature of the cation bound in the complex influences the reactivity of the crown-ether. It follows from the data in Table 8 that the rate constants for the interaction with the OH radical diminish from sodium to rubidium. Such variation is probably associated with the decrease in the energy of the C–H bond in the metal complex of the crown-ether as a consequence of the polarisation of the C–O bonds, which is greater the smaller the ionic radius of the metal.

Table 9. The rate constants for the reactions of complexes incorporating macrocyclic tetraaza-ligands with the primary water radiolysis products in aqueous solutions.

Reaction	Medium	Rate constant, litre mol^{-1} s^{-1}	Refs.
$[Mn(L^2)Cl_2]^+ + OH$	sat. N_2O	$5.2 \cdot 10^9$ ($125 \cdot 10^3$)*	[118]
$[Mn(meso\text{-}L^5)Cl_2]^+ + OH$	"	$3.1 \cdot 10^9$ ($5.0 \cdot 10^3$)*	[118]
$[Mn(rac\text{-}L^5)Cl_2]^+ + OH$	"	$1.9 \cdot 10^9$ ($9.0 \cdot 10^3$)*	[118]
$Ni(L^1)(ClO_4)_2 + OH$	pH 3.3, sat. N_2O	$3.5 \cdot 10^9$	[119]
$Ni(L^1)(ClO_4)_2 + e^-_{aq}$	pH 6.0, sat. Ar	$3.3 \cdot 10^{10}$	[120]
$Ni(L^2)(ClO_4)_2 + e^-_{aq}$	"	$3.8 \cdot 10^{10}$	[121]
$Ni(L^3)(ClO_4)_2 + OH$	pH 3.3 sat N_2O	$4.0 \cdot 10^9$	[119]
$Ni(L^3)(ClO_4)_2 + e^-_{aq}$	pH 5.5, sat. Ar	$1.2 \cdot 10^{10}$	[120]
$Ni(L^4)(ClO_4)_2 + e^-_{aq}$	pH 6.0, sat. Ar	$1.2 \cdot 10^{10}$	[121]
$Ni(meso\text{-}L^5)(ClO_4)_2 + e^-_{aq}$	pH 6–10, sat. Ar	$5.6 \cdot 10^{10}$	[122]
$Ni(meso\text{-}L^5)(ClO_4)_2 + H$	pH 1.0, sat. Ar	$3.2 \cdot 10^8$	[122]
$Ni(meso\text{-}L^6)(ClO_4)_2 + e^-_{aq}$	pH 6.0, sat. Ar	$8.7 \cdot 10^{10}$	[121, 123]**

*The rate constants (k, s^{-1}) for the decomposition of the manganese(IV) complexes formed are indicated in brackets. Their final decomposition reaction product is manganese(IV) oxide.[118]

**Certain spectroscopic characteristics of the complex $[Ni(L^6)]^+$, obtained on γ-irradiation of a solution of $Ni(L^6)(ClO_4)_2$ (saturated with helium at pH 7.6) with a dose of ~0.5 kGy have been published.[124]

Reduction of the cadmium(II) complexes of the cryptands [2.2.1] and [2.2.2] {C[2.2.1] and C[2.2.2]} by hydrated electrons has been investigated by pulse radiolysis.[115] The study of the interaction of

the primary water radiolysis products with cryptands showed that there are reactions of the OH radical (with abstraction of a hydrogen atom from a C—H bond in the cryptand) which are virtually controlled by diffusion (Table 8), while the reactions of the hydrated electron with C[2.2.1] and C[2.2.2] have not been observed. The hydrated electron reacts with the cadmium ion as follows:

$$e^-_{aq} + Cd^{2+} \rightarrow Cd^+.$$

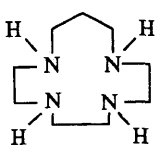
The rate constant for this reaction involving the aqueous $Cd(ClO_4)_2$ solution is $k_{\Psi=0} = 4.8 \times 10^{10}$ litre mol^{-1} s^{-1} after extrapolation to zero ionic strength. In solutions of cadmium(II) perchlorate in the presence of an excess of the cryptand, the disappearance of hydrated electrons via the reactions

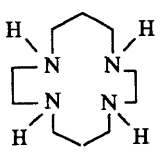
$$e^-_{aq} + [Cd\{C[2.2.2]\}]^{2+} \rightarrow [Cd\{C[2.2.2]\}]^+,$$

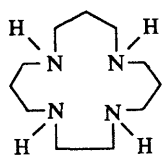
$$e^-_{aq} + [Cd\{C[2.2.1]\}]^{2+} \rightarrow [Cd\{C[2.2.1]\}]^+$$

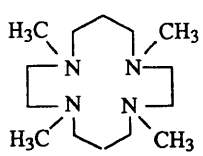
is described by a pseudo-first order kinetic equation; the reaction rate constants are listed in Table 8. The appreciable differences between the reactivities of cadmium cryptates in relation to e^-_{aq} have been related[115] to the crystallographic ionic radii, the size of the cryptand cavity, and the stability constant of the corresponding cryptates.

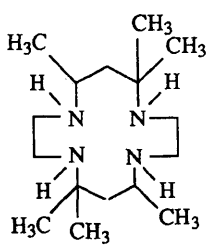
Table 9 lists the kinetic characteristics of certain oxidation-reduction reactions with participation of the primary water hydrolysis products obtained in the pulse radiolysis of solutions of manganese(III) and nickel(II) complexes of cyclam (L^2) and other nitrogen-containing analogues of crown-ethers.

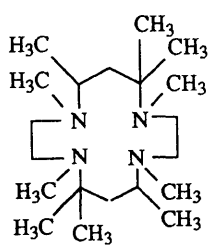

(L^1)


(L^2)


(L^3)


(L^4)


(L^5)


(L^6)

Irradiation of aqueous solutions of 18C6 up to large absorbed doses (0.25 MGy) does not lead to the formation of insoluble products.[113] The formation of compounds containing an aldehyde group with a radiation-chemical yield $G = 0.4$ was established from the results of the chemical analysis of the residue after the removal of water and from IR spectroscopic measurements. The overall yield in the decomposition of 18C6 is 0.6 molecule/100 eV. In aqueous solutions of DCH18C6, starting from a dose of 5 kGy, a pale-yellow deposit is formed. It contains compounds with an aldehyde group which are insoluble in the usual organic solvents. The overall decomposition yield is 0.9 molecule/100 eV for DCH18C6. Since the cyclic structure does not decompose in the stage involving the interaction of the primary water radiolysis products with crown-ethers, it has been suggested[113,114] that the aldehydes are formed in secondary reactions. The aldehydes are probably formed mainly as a result of the interaction of the crown-ether with hydrogen peroxide:

$$-CH_2-\dot{C}H-O-CH_2-CH_2- + H_2O_2 \longrightarrow$$
$$\longrightarrow -O-CH_2-CH_2-O-CHO + \dot{C}H_2-O-CH_2- .$$

Another possible pathway is the disproportionation reaction of the radicals:

$$2\,-CH_2-\dot{C}H-O-CH_2-CH_2- \longrightarrow$$
$$\longrightarrow -CH_2-CHO + CH_2{=}CH-O- +$$
$$+ -CH_2-CH_2-O-CH_2-CH_2- .$$

On irradiation of solutions of DCH18C6, a deposit may appear as a result of the formation of aldehydes and also as a result of the dimerisation of radicals.[113]

We may note that, when poly(ethylene glycols)—high-molecular-weight linear analogues of crown-ethers—are acted upon by radiation in aqueous solutions in the absence of dissolved oxygen, gel formation takes place and the radiation-chemical yield of the cross-linking reaction is 0.27 in 0.5% solution, but the ratio of the cross-linking yield to the polyether chain degradation yield in a neutral medium is 4:1.[125] Degradation predominates in acid solutions. The hydrogen formed in the radiolysis of a 2% solution of poly(ethylene glycol) in D_2O consists mainly of HD (G = 0.59 molecule/100 eV) whereas $G(H_2)$ = 0.05 molecule/100 eV. When recalculated in terms of the dose absorbed by the solute, this gives $G(H_2) \simeq 2.5$ molecule/100 eV, which agrees with data[110] for poly(ethylene glycols) (Table 7).

Chain degradation of poly(ethylene glycol) takes place in the presence of oxygen. The reactive products of the radiolysis of the solvent (H, OH) abstract hydrogen from the α-position in the ether linkage and oxygen adds to the macroradical arising in this way and gives rise to a peroxide radical. The chain propagation reaction is that between the peroxide radical and the initial molecule with formation of a hydroperoxide:

$$-CH_2-\underset{\displaystyle O-O^{\cdot}}{\overset{|}{CH}}-O- + -CH_2-CH_2-O- \longrightarrow$$
$$\longrightarrow -CH_2-\underset{\displaystyle O-OH}{\overset{|}{CH}}-O- + -CH_2-\dot{C}H-O- .$$

The decomposition of the hydroperoxide and the recombination of the peroxide radicals afford the alkoxyl radicals $-CH_2-\underset{\displaystyle O}{\overset{|}{CH}}-O-$, which rapidly decompose with rupture of the molecular skeleton.[125,126]

The radiation-chemical reactions of the macrocyclic polyethers examined above may be compared with the behaviour in 0.1 M aqueous solutions of heterocyclic compounds such as 1,3-dioxolans,

1,3- 1,4-dioxanes, etc.[127] The main products of the radiolysis of these compounds are ethylene, carbon monoxide (or dioxide), and aldehydes. The radicals, formed predominantly as a result of the dissociation of the C–H bond in the α-position relative to the heteroatom by the H and OH radical species into five- and six-membered oxygen-containing heterocycles, can rearrange to linear radicals on ring cleavage. However, among the products of the radiolysis of dioxanes, there are substances whose formation cannot be explained by the occurrence of the above processes. The initial radical species derived from dioxanes can decompose, as in the case of 1,3-dioxolans, in accordance with a concerted mechanism (with the simultaneous dissociation of two bonds), which results in the formation of the degradation products. The occurrence of this process in the radiolysis of 1,4-dioxane leads to the formation of acetaldehyde (G = 0.03 molecule/100 eV). Other products of the radiolysis of this compound are ethylene and CO. Under these conditions, $G(C_2H_4)$ = 0.07 and $G(CO)$ = 0.0014 molecule/100 eV in 0.1 M aqueous solution.[127] The radiation-chemical yields of ethylene and carbon monoxide exceed respectively by one and two orders of magnitude the values which would be expected in the case of the formation of the given compounds as a result of the direct action of γ-radiation on the dissolved 1,4-dioxane (the calculation was performed using the values of G for pure dioxane quoted by Zatonsky and Povolotskaya[110]). Thus the radiation-chemical degradation of the cyclic and macrocyclic ethers in aqueous solutions is associated with the indirect action of ionising radiation.

2. Radiolysis of solutions of crown-compounds in aromatic hydrocarbons

Together with the systems, examined in Section II, based on organochlorine solvents, numerous studies, concerned with the radiation-chemical reactions in non-aqueous solutions of crown-compounds, have been devoted to the radiolysis of their solutions in arenes. Aromatic hydrocarbons are much more reactive than aliphatic compounds and solutions of DCH18C6 and other crown-ethers in toluene and benzene are used for the effective extraction isolation from nitric acid solutions of radioactive elements such as uranium(VI) and plutonium(IV).[128]

Table 10. The radiation-chemical yields of the gaseous products of the γ-radiolysis of benzene solutions of crown-ethers.

Crown-ether	Concentration, M	G, molecule/100 eV				Refs.
		H_2	C_2H_2	C_2H_4	CH_4	
–	0	0.038	0.016	–	–	[129]
18C6	0.05	0.046	0.013	0.0010	0.00015	[129]
18C6	0.1*	0.009	–	0.005**	0.002	[130]
18C6	0.05	0.064***	–	0.0020***	0.00018***	–
DBB18C6	0.05	0.045	0.014	0.0027	0.0058	[129]

* Solution of crown-ether in C_6D_6; irradiation in the presence of air.

** The sum of $G(C_2H_4)$ and $G(C_2H_6)$ is quoted.

*** Calculated taking into account the direct effect of radiation on the solute using the corresponding values of G for 18C6 in the liquid state taken from the literature.[110]

Table 10 presents data characterising the radiolytic formation of gaseous products in benzene solutions of crown-ethers. The presence of crown-ethers has only a slight effect on the gas evolution caused by the radiolysis of solvents; the increase in the radiation-chemical yield of hydrogen and the appearance of ethylene and methane are associated in this instance with the direct action of ionising radiation and the solute. This is confirmed by the results of the study of the γ-radiolysis of a solution of 18C6 in fully deuteriated benzene[130] and also by the calculated values of G presented in Table 10. The presence of t-butyl substituents in the molecule of 4,4′(5′)-di-t-butyldibenzo-18-crown-6 (DBB18C6) is responsible for the high yields of ethylene and methane — the polyether degradation products — in a benzene solution of DBB18C6 compared with 18C6.[129] The yield in the radiation-chemical decomposition of 18C6 on γ-irradiation of its solution in C_6D_6 (initial concentration 0.435 M) is ~1.25 molecule/100 eV,[130] which corresponds to the decomposition of about 15% of the compound on absorption of a dose of 1 MGy.

Table 11. The influence of crown-compounds and their complexes on the formation of dimeric benzene γ-radiolysis products.

Additive	Concentration of crown-compound, M	Yield of products G, molecule/100 eV		Refs.
		biphenyl	phenylcyclohexadienes	
–	0	0.120	0.050	[131]
15C5	0.01	0.096	0.052	[131]
	0.1	0.090	0.054	[131]
18C6	0.05	0.080	0.045	[31]
	0.1	0.069	0.037	[31]
DB18C6	0.0001	0.097	0.050	[131]
	0.001	0.101	0.052	[131]
DCH18C6	0.01	0.091	0.042	[131]
	0.1	0.089	0.042	[131]
DBB18C6	0.05	0.091	0.048	[29]
	0.075	0.072	0.032	[132]
DB24C8	0.01	0.106	0.057	[131]
	0.05	0.072	0.044	[131]
C[2.2.2]	0.05	0.060	0.043	[31]
18C6+K	0.05*	0.096	0.000	[31]
	0.1*	0.088	0.000	[31]
18C+KOH	0.1*	0.134	0.000	[132]
18C6+KO_x	0.1*	0.201	0.000	[132]
C[2.2.2]+K	0.05*	0.035	0.000	[31]
DCH18C6+KBr	0.1*	0.118	0.051	[32]
DCH18C6+KI	0.1*	0.115	0.038	[32]
DCH18C6+KOH	0.1*	0.141	0.000	[32]
DBB18C6+$KMnO_4$	0.05**	0.218	0.000	[29]
DBB18C6+KOH	0.05*	0.090	0.051	[132]

* Saturated solution of the inorganic component.

** $KMnO_4$ concentration 0.013 M.

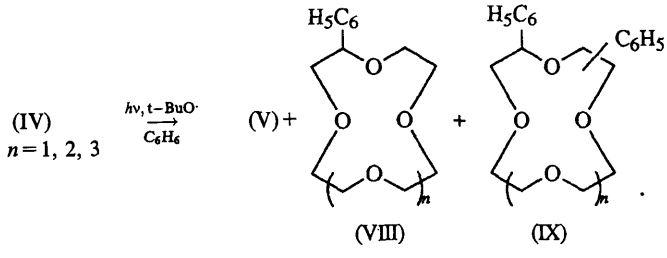
Thus from the standpoint of gas evolution processes and also the degradation of crown-ethers dissolved in benzene, macrocyclic polyethers are extremely radiation-resistant compounds for absorbed

doses not exceeding 200 kGy and can be used for many radiochemical separation processes as selective extractants.

Another process determined by radiolysis and inducing an impairment of the extraction-technological characteristics of the system is the formation of high-boiling products. Studies of the formation of dimeric products of the radiolysis of aromatic hydrocarbons in the presence of various crown-ethers have shown[8,131] that crown-compounds do not induce an additional reaction of the matrix via this pathway. On the contrary, in most cases, they, as it were, protect the solvent against the action of radiation. Examples of a decrease in the yield of biphenyl and phenylcyclohexadienes — the main benzene radiolysis products — in the presence of crown-compounds are presented in Table 11. This effect of crown-ethers agrees with the model of the formation of high-boiling products via the cationic polymerisation mechanism (including the addition of primary arene radical-cations to neutral molecules).[30,31]

Bearing in mind the powerful proton-accepting properties of crown-ethers,[133,134] one may expect the occurrence of reactions involving proton transfer from the molecular arene ion to the polyether molecule. The introduction of benzene rings into the polyether molecule lowers its proton affinity[133] and the effect of dibenzocrown-ethers on the yield of dimeric products is therefore much weaker than that of, for example, 18C6. On the other hand, a cryptand acts more effectively than crown-ethers because it is a stronger proton-solvating agent.

We may note that, although phenyl radicals are in fact formed as a result of the deprotonation of the benzene radical-cation, they may react further with the crown-ether without giving rise to biphenyl and phenyl cyclohexadienes. Thus the decrease in the yield of dimers in the radiolysis of benzene solutions of 1,4-dioxane has been explained[135] by the interaction of phenyl radicals with solute molecules leading to α-abstraction of a hydrogen atom. In the study of the dehydrodimerisation of 12C4, 15C5, and 18C6 in benzene in the presence of t-butyl peroxide, whose decomposition was initiated photochemically, phenyl-substituted crown-ethers (VIII) and (IX), formed on recombination of the corresponding radicals, were isolated and characterised in addition to the expected dimerisation products (V):[117]



Similar processes occur in the radiolysis of toluene in the presence of crown-ethers. Since the deprotonation reaction

$$C_6H_5CH_3^+ \longrightarrow C_6H_5CH_2^{\cdot} + H^+$$

is extremely important for the toluene radical-cations in the liquid phase while the benzyl radicals formed are less reactive than phenyl radicals and are destroyed predominantly as a result of recombination, in the presence of 18C6 there is some increase in the yield of the dimeric radiolysis products. In the case of a solution of DB24C8, the yield of bibenzyl falls somewhat, although the overall yield of the dimers remains unchanged.[131]

Another aspect of the use of crown-compounds in radiation-chemical studies is associated with attempts to act on the processes involving the radiolysis of liquid matrices of aromatic hydrocarbon,[29–32,132,136–138] based on the hypothesis that electron-donating agents present in solution should diminish the probability of the formation of radiolysis products, whereas electron-accepting agents (i.e. substances with oxidising properties) should promote radiolysis. The unique properties of crown-ethers, which make it possible to solubilise inorganic substances of different nature in organic (including hydrocarbon) solvents, provide very extensive possibilities for this purpose.

For example, dissolution of metallic potassium in arenes containing a crown-ether or a cryptand results in the formation of systems with a homogeneous distribution of electron-donating species, namely K^- anions or electrons, which are present in the form of crown-separated pairs $[K^+, L]K^-$ or $[K^+, L]e^-_{solv}$, where L is the macrocyclic ligand. On irradiation of such benzene solutions, the yield of biphenyl is extremely low, while phenylcyclohexadienes are not formed at all (Table 11). The yield of bibenzyl is also significantly reduced in the toluene–18C6–potassium system, while benzylmethylcyclohexadienes are detected only in trace amounts. The inhibition of the formation of dimeric products in the radiolysis of aromatic hydrocarbons, induced by the charge-transfer process (the transfer of an electron to the parent radical-cation)

$$ArH^+ + K^- \longrightarrow ArH + K$$

probably proceeds extremely effectively, because the reactant with a low ionisation potential (the reductant) is not simply the neutral solute molecule but an active weakly solvated electron-donating species bearing a negative charge.[31]

Potassium hydroxide and halides solubilised by crown-ethers do not manifest pronounced reducing or oxidising properties and do not lead to such appreciable inhibition of the formation of dimers,[136,137] while additives with oxidising properties induce the opposite effect. Thus the presence of $KMnO_4$ suppresses the formation of phenylcyclohexadienes, but increases appreciably (by 80%) the yield of biphenyl.[29,138] The electrons arising in the primary radiolytic steps interact with additives of this type, being converted into chemically more inert species and increasing thereby the lifetime of the benzene radical-cations and hence the probability of the occurrence of ion–molecule reactions. The absence of phenylcyclohexadienes is caused by the complete oxidation of their precursors to biphenyl by permanganate ions.

Combination of additives of different types, for example, crown-ethers and spin-trapping agents[139] or crown-ethers and transition metal acetylacetonates,[140,141] in the radiolysis of aromatic hydrocarbons can serve as an extremely effective instrument for the study of the mechanism of the formation of the products. Investigation of the latter systems is of independent importance because the combination of the crown-ether–β-diketone–diluent components is encountered in real extraction systems used for the isolation of radionuclides.[59,142]

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