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Radiation Stability of 15-Crown-5 Complexes with Alkaline Earth Metal Chlorides

Evgenii I. Grigor'ev,* Olga V. Mikhalitsyna, Sergei V. Nesterov and Leonid I. Trakhtenberg

L. Ya. Karpov Research Physico-Chemical Institute, 103064 Moscow, Russian Federation. Fax: +7 095 975 2450

The radiation stability of complexes with 15-crown-5 and alkaline earth metal chlorides has been investigated by EPR spectroscopy and gas chromatography; the resistance of the complexes to rupture of the ring is determined by the energy of the interaction between the cation and the polyether and energy transfer from the metal to the organic ligand was noted.

A study of the effects of ionising radiation on macrocyclic polyethers (or crown ethers) and their compounds was undertaken in view of the prospects for the use of crown ethers as extractants in radiochemical systems for the reprocessing of waste from nuclear power plants.[1] The effectiveness of the extraction systems is influenced by the radiation stability of the crown ethers in the organic phase and by the reactivity of the radiolysis products formed.[2] Furthermore, an important factor affecting the technological stability of the system is the stability towards radiation of the crown-ether–metal cation complexes formed.

It was shown previously that the radiation stability of individual crown ethers depends on the size of the macrocycle and on the nature of its substituent,[3–5] *i.e.* on the structure of the polyether molecule. At the same time, the stability of the complex depends on the cyclic structure of the ligand molecule and it is essential to understand how the captured cation influences the radiation stability of the macrocycle towards rupture. There is at present virtually no information about the action of ionising radiation on macrocyclic complexes.

The aim of the present study was to investigate the radiation stability of complexes between 15-crown-5 and alkaline earth metal chlorides. The complexes $BeCl_2 \cdot 15C5$, $MgCl_2 \cdot 15C5$ and $CaCl_2 \cdot 15C5$ were chosen for study. The results of elemental analysis and NMR and IR spectroscopic data demonstrated the absence of impurities. The evacuated specimens were irradiated on K–120000 (^{60}Co) apparatus at 77 K. The absorbed dose rate, determined by the iron(II) sulfate dosimetric method, was 7 Gy s^{-1}. The intermediate γ-radiolysis products were recorded on a Rubin microwave spectrometer in the X-range at 77 K. The ^1H and ^{13}C NMR spectra of the solutions of crown ether complexes in [$^2H_6$]DMSO were recorded on a Tesla BS–497 spectrometer at 300 K. The IR spectra were measured on a Perkin Elmer-1430 apparatus. The gaseous products were analysed chromatographically. The yields of molecular hydrogen were determined as described by Kunin *et al.*[6] The gaseous hydrocarbons were separated on a Tsvet gas chromatograph with a flame-ionisation detector. Ethylene was used as the reference standard in the calibration of the chromatograph.

The stability of the crown ether complexes with respect to the action of ionising radiation may be estimated from the radiation-chemical yields of the final products in the condensed and gaseous phases and of the radical products stabilised at 77 K. The formation of new functional groups in the condensed phase after irradiation of the specimens with doses up to 0.7 MGy could not be detected by NMR and IR spectroscopy.

Significant differences are observed in the EPR spectra recorded after γ-irradiation of the complexes. As in the γ-radiolysis of pure 15C5,[5] in $BeCl_2 \cdot 15C5$ and $CaCl_2 \cdot 15C5$ it is mainly the radicals $-\dot{C}=O$ and $-\dot{C}H-CH=O$, *i.e.* the radicals corresponding to the dissociation of the C–O bond of the macrocycle, that are stabilised. After the irradiation of $MgCl_2 \cdot 15C5$, the appearance of new components, formed by dissociation of the C–C bond and not characteristic of the degradation of individual crown ethers, was noted.

The radiation-chemical yields of molecular hydrogen and the radical products are presented in Table 1, which shows that $G_R >> 2G_{H_2}$, indicating that the radical products and molecular hydrogen are generated in parallel independent processes and the reaction involving the abstraction of a hydrogen atom from the polyether ring makes only a slight contribution to the radiolysis of the complexes. Comparison of the yields G_R in the complexes investigated and the corresponding crown ethers shows that the additivity rule does not hold. This indicates the complete transfer to the ligand of the energy absorbed by the cation. Charge transfer from the metal to the ligand on γ-radiolysis of metalloporphyrins was observed previously.[7]

Table 1 The radiation-chemical yields of the radicals G_R (radicals/100 eV) and of the gaseous products (molecules/100 eV) in γ-irradiated 15-crown-5 and its complexes with alkaline earth metal chlorides at 77 K.

Complex	D_{cat}/Å[a]	Radiation chemical yields of radicals and molecular products					
		G_R	G_{H_2}	G_{CH_4}	$G_{C_2H_6}$	$G_{C_2H_4}$	$G_{C_2H_2}$
15C5[b]		5.9±0.6	1.6	0.012	—	0.081	—
$BeCl_2 \cdot 15C5$	0.62	6.5±0.4	0.9±0.2	0.02	0.006	0.003	0.0008
$MgCl_2 \cdot 15C5$	1.30	8.1±1.1	0.7±0.2	0.04	0.004	0.002	0.002
$CaCl_2 \cdot 15C5$	1.98	6.0±1.1	0.9±0.2	0.05	0.1	0.1	0.003

[a] D_{cat} = diameter of cations. [b] Radiation chemical yields of molecular products are given in ref. 3.

The paramagnetic radiolysis products stabilised in the γ-irradiated complexes at 77 K are formed mainly as a result of rupture of the polyether ring, *i.e.* G_R, unlike G_{H_2}, corresponds to the yield from rupture of the macrocycle.

The maximum in the dependence of G_R on the size of the cation can be explained as follows. The size of the Mg^{2+} cation corresponds to the size of the 15C5 cavity, which is 1.7–2.2 Å, while the ionic diameters of Be^{2+} and Ca^{2+} are smaller and greater, respectively. The resistance of the macrocycle to rupture should be determined by the structure of the ligand, while the conformational strain in the ligand depends on the energy of interaction of the donor atoms and the cation and is characterised by the M–O distance in the complex. The yields G_R in the individual crown ether 15C5 and in the complexes $BeCl_2 \cdot 15C5$ and $CaCl_2 \cdot 15C5$ are similar, which may indicate an insignificant conformational ring strain on introduction of the metal cation, whereas in $MgCl_2 \cdot 15C5$ the strain is significant. This hypothesis is confirmed by X-ray diffraction data.[8] The interatomic M–O distance, characterising the energy of the interaction between the cation and the ligand, is a minimum for Mg^{2+} in the Be:Mg:Ca series considered, *i.e.* in the case of $MgCl_2 \cdot 15C5$ the conformation of the macrocycle is most strained. The calculated radiation-chemical yields of the radicals G_R agree with the available structural literature data.

Thus the resistance of the complexes between crown ethers and alkaline earth metal chlorides to ring rupture depends on the strain in the macrocycle due to the interaction of the cation and the polyether. An effective energy transfer from the cation to the polyether ring alters the mechanism of radiolysis of the ligand.

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