MASS SPECTROMETRY OF MACROHETEROCYCLES.

2.* CHARACTERISTICS OF THE FRAGMENTATION OF AZA-CROWN ETHERS UNDER ELECTRON IMPACT

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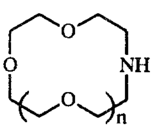
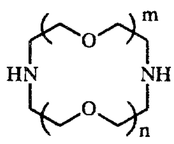
The fragmentation of aza-crown and diaza-crown ethers under electron impact was studied. It is shown that for the former the primary pathways of fragmentation of the molecular ions involve the intracyclic migration of a hydrogen atom and the elimination of $C_2H_3O\cdot$ *and* $\cdot CH_2OH$ *particles. A characteristic feature of the diaza-crown ethers is the ejection of a divinylaminyl radical.*

The fragmentation of crown ethers of the 3n-crown-n series (where n is the number of oxygen atoms in the ring) under electron impact has been studied thoroughly and described in [2-5]. At the same time, virtually no study has been devoted to the mass spectra of macrocyclic polyethers containing secondary amino groups in the ring. The mass spectrum of one of the representatives of this series of macroheterocycles was presented in graphical form in [6] without discussion. The principal pathways of the fragmentation of N-substituted diaza-crown ethers [7, 8] involve fragmentation of the substituents attached to the nitrogen atom and do not make it possible to single out features that are characteristic for macrocycles of this type.

The results of a study of the fragmentation of a number of aza- (I-III) and diaza-crown ethers (IV-VI) under electron impact are presented in this paper. The mass spectra of these compounds are presented in Table 1.



I-III



IV-VI

I n=1, II n=2, III n=3, IV n=m=1, V m=1, n=2, VI n=m=2

In [5] it is shown that the migration of a hydrogen atom along the CH...O intramolecular interactions in crown ether molecules leads to the realization of "crown ether" type of fragmentation involving the formation of ions, the mass numbers of which correspond to protonated lower homologs of the series 89, 133, 177.†

A similar series of ions (88, 132, 176) is also observed in the mass spectra of I-III. Their formation is preceded by elimination of $C_2H_3O\cdot$ radicals by the molecular ions (M^+) via a mechanism that is probably similar to that described for crown ethers [5]; the migration of a hydrogen atom occurs in the polyether part of the ring and does not involve the environment of the nitrogen atom. The increase in the intensity of the peak of $[M - 43]^+$ ions with an increase in the number of oxyethylene links in the series of examined substances (4%, 8%, and 9%, respectively) is in agreement with this conclusion.

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*For Communication 1 see [1].

†The numbers that characterize the ions are the m/z values.

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TABLE 1. Mass Spectra of I-VI*

Compound	m/z (relative intensity, %)
I	55(11), 56(57), 57(100), 58(19), 59(13), 70(10), 72(18), 74(31), 86(45), 87(26), 88(18), 100(27), 118(19), 175(M$^{\cdot+}$, 4)
II	55(30), 56(100), 57(57), 58(47), 59(22), 70(41), 71(25), 72(46), 73(46), 74(73), 86(57), 87(61), 88(50), 89(14), 100(47), 101(12), 102(11), 103(11), 116(11), 132(19), 162(20), 188(14), 219(M$^{\cdot+}$, 3)
III	55(28), 56(100), 57(90), 58(50), 59(40), 70(36), 71(25), 72(60), 73(33), 74(60), 86(70), 87(60), 88(70), 89(31), 100(56), 101(13), 102(14), 103(18), 114(15), 115(10), 116(15), 118(17), 130(10), 132(18), 144(10), 146(10), 160(11), 176(23), 263(M$^{\cdot+}$, 1)
IV	56(91), 57(100), 58(29), 69(29), 70(17), 71(18), 74(50), 86(55), 87(44), 88(61), 100(17), 106(F 53), 174(M$^{\cdot+}$, 0,3)
V	55(17). 56(100), 57(86), 58(42), 69(24), 70(44), 71(25), 72(23), 73(11), 74(66), 86(45), 87(41), 88(44), 100(60), 113(15), 114(11), 118(13), 132(66), 150(F 35), 218(M$^{\cdot+}$, 0,3)
VI	55(23), 56(84), 57(61), 58(61), 59(17), 69(20), 70(41), 71(21), 72(35), 73(17), 74(84), 85(14), 86(31), 87(53), 88(33), 98(11), 100(69), 102(23), 114(13), 118(53), 131(11), 132(100), 133(11), 194(F 20), 262(M$^{\cdot+}$, 0,5)

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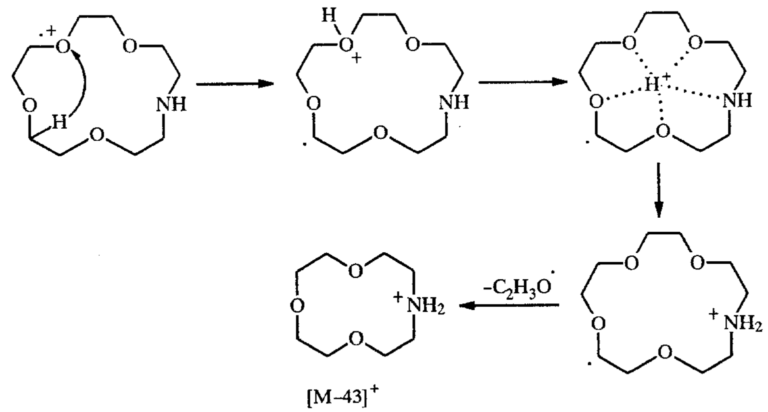
*The M$^{\cdot+}$ ions and the peaks of fragment ions with intensities ≥ 10% are presented.

TABLE 2. DADI Spectra of the F Fragments (194, VI) and the Protonated Molecular Ions of 6-Aza-3,9-dioxaundecane-1,11-diol (A)

Daughter-ion mass	Neutral-fragment mass	Ion-peak intensity, %	
		Φ (VI)	A
176	18	6,0	2,0
150	44	0,8	0,3
132	62	100,0	100,0
106	88	1,3	0,5

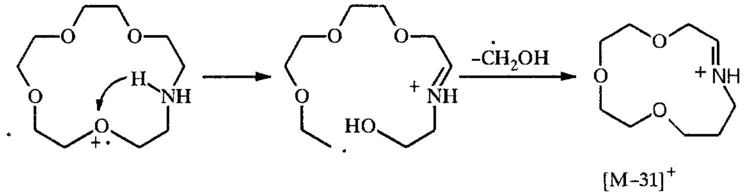
In the formation of protonated small rings in the case of crown ethers stabilization of the proton is achieved due to cooperative interaction with several oxygen atoms. In the case of I-III this is hindered by the higher basicity of the nitrogen atom, which promotes localization of the proton on the amino group.



$[M-43]^+$

Localization of the proton on an individual fragment of the molecule leads to the development of new fragmentation pathways that differ from the "crown ether" type. Thus in the DADI (direct analysis of the daughter ion) spectra of the $[M-43]^+$ fragments formed in the fragmentation of 15-crown-5 one observes a single peak corresponding to the elimination of a molecule of ethylene oxide. In addition to that, for the analogous ions in the case of II one observes a number of intense peaks corresponding to the elimination of H_2O, C_2H_4, and C_2H_4O particles, as well as ions at 72 (empirical formula $C_4H_{10}N$). This decreases the fraction of "crown ether" type of fragmentation in the total ion current and decreases the relative intensities of the peaks of ions formed via this type of fragmentation in the more profound degrees of fragmentation. Thus for 15-crown-5 the ratio of the intensities of the peaks of ions at 89 (protonated 1,4-dioxane) and ions at 177 (protonated 12-crown-4) is 50 [5]. In the case of II this ratio for the ions at 88 (protonated morpholine) and 176 [protonated monoaza-12-crown-4 (I)] is 7.8.

A characteristic of the behavior of monoaza-crown ethers under electron-impact conditions that distinguishes them from crown ethers of the 3n-crown-n series is fragmentation involving cleavage of the C—C bond and the elimination of CH_2OH radicals by M^+.



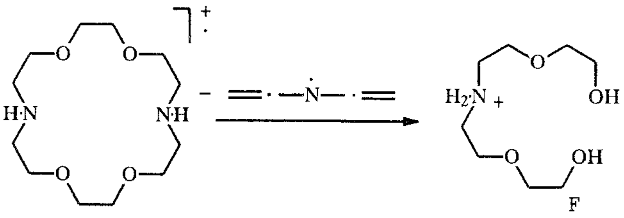
It is apparent from the scheme that the formation of an acyclic intermediate with a terminal hydroxy group occurs during this sort of fragmentation. This assumption is confirmed by the presence in the DADI spectra of the M^+ of I-III of a peak corresponding to the elimination of a hydroxyl radical.

The subsequent fragmentation of the $[M - 31]^+$ ions is accompanied by shortening of the polyether chain up to the formation of ions at 86 (empirical formula C_4H_8NO), the peak of which is the maximum peak in the DADI spectra of these fragments.

The introduction of a second amino group into the polyether ring (IV-VI) leads to a decrease in the intensities of the M^+ peaks as compared with I-III. In addition to this, a substantial change in the fragmentation pathways occurs. Peaks of $[M - 31]^+$ and $[M - 43]^+$ ions have low intensities or are absent in the mass spectra of IV-VI. Peaks of $[M - 68]^+$ (F) fragments (empirical formulas $C_4H_{12}NO_2$ and $C_8H_{20}NO_4$ for IV and VI, respectively) dominate in the high-mass region. Only molecular-ion peaks are present in the metastable-defocusing spectra of these fragments, and this does not make it possible to draw a conclusion in favor of a stepwise mechanism for the formation of the F ions.

In the mass spectra of the N,N^1-dideutero derivatives of IV-VI the peak of F ions is shifted two units to the high-mass region. In addition, it follows from the data in [6, 7] that the formation of ions similar to F fragments does not occur in the fragmentation of diaza-crown ethers that contain tertiary amino groups in their rings.

Taking into account what was stated above, one may assume that the formation of F fragment ions from M^+ most likely occurs in one step and is accompanied by the elimination of a divinylaminyl radical. Migration of a hydrogen atom along the interaction possible between the amino groups plays a substantial role in this process.



With an increase in the ring size this interaction should become weaker and lead to a decrease in the intensity of the peak of F ions; this is confirmed by the experimental data (Table 1).

It must be noted that similar interactions have been established in solution for cyclic polyamines [9].

To confirm the structure of the F ions presented in the scheme we studied the DADI spectra of these fragments, which are formed in the fragmentation of VI, and of the protonated molecular ions of 6-aza-3,9-dioxaundecane-1,11-diol (A, Table 2). It is apparent from the data presented that the relative intensities of the peaks of the daughter ions differ by a factor of two to three, which is permissible for isostructural ions formed from different precursors [10]. Thus a comparison of the DADI spectra of ions with known structures and the F fragments confirms the structure proposed for the latter.

It is apparent from Table 2 that the subsequent fragmentation of the F ions is accompanied by the elimination of fragments of the polyether chain with different lengths to give nitrogen-containing ions.

Thus, just as in the case of crown ethers of the 3n-crown-n series, the fragmentation of macroheterocycles that contain secondary amino groups is accompanied by migration of a hydrogen atom along CH...O and NH...N intracyclic interactions.

EXPERIMENTAL

The mass spectra and DADI spectra were obtained with an MAT-112 spectrometer at an ionizing voltage of 70 V, an ionization-chamber temperature of 220°C, and a resolution of 700 using a system for direct introduction of the samples. The metastable-defocusing spectra were recorded with an MKh 1321 mass spectrometer under the same conditions. The determination of the precise masses of the ions was accomplished with an MKh 1321 mass spectrometer at a resolution of 10,000 using polyphosphoric acid (PPA) as the standard.

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