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Dissociative ionization of 1,4-bis(2,5-phenyloxazolyl)benzene

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ABSTRACT

Dissociative ionization of 1,4-bis(2,5-phenyloxazolyl)benzene (POPOP) molecule by electron impact in gaseous phase is studied. Potentials of appearance of some fragments of the molecule under study are determined from the experimentally measured dependences of ionization cross-section on the ionizing electron energy. A new ion with $m/z = 144$ $[C_9H_6ON]^+$ is detected in the mass spectrum of the POPOP molecule, being complementary to the fragment with $m/z = 220$ $[C_{15}H_{10}ON]^+$. The threshold of appearance of this ion is determined ($E_{ap} = 9.51$ eV) as well as the first ionization potential of the POPOP molecule and fragment ion appearance potentials.

1. Introduction

Complex organic compounds are now widely used in high-end technologies, in particular, in manifold devices of molecular electronics [1]. In such devices molecules interact with electrons having various energies [2]. Stability of molecules to fragmentation is an important characteristic for their interaction with electrons. It is determined by the molecule structure, the molecule surrounding and the electron energy. $C_{24}H_{16}N_2O_2$, 1,4-bis(2,5-phenyloxazolyl)benzene (POPOP) linear molecule, is widely applied as a component of laser active media, liquid and plastic scintillators (see, for example, [3]). Linear derivatives of oxazole and ozadiazole have been also extensively used as electron-transporting and emitting layers of thin-film electroluminescent devices [1,4]. Fragmentation of the molecule at the interaction with electrons results in the formation of radical ions leading to the luminescence quenching as well as in ion–molecule reactions what finally causes the device degradation. Here we report on the mass spectrometric studies of dissociative ionization of the POPOP molecule by electron impact in the gaseous phase without intermolecular interactions.

2. Experimental set-up

The experiments have been carried out using a set-up with oil-free pumping. An MX-7304A monopole mass spectrometer was used as an analytical device, providing digital indication of the mass number and intensity at manual, cyclic, or program scanning of the mass spectrum and the bombarding electron energy. A detailed description of the experiment is given in [5]. Here we give only the most important experimental details. A beam of the POPOP molecules is formed by a multichannel effusion type source providing the molecule concentration in the area of interaction with the electron beam within 10^{10}–10^{11} cm^{-3}. The source of ions with electron bombardment operates in the electron current stabilization mode and enables one to obtain the electron beams of controllable energy at the current values 0.5–1.5 mA and $\Delta E = 500$ meV. The mass scale was calibrated using Ar and Xe beams, the energy scale was calibrated from the initial part of the Kr atom ionization cross-section enabling the electron energy scale to be determined with the accuracy better than ± 0.25 eV. The mass spectra were measured at various temperatures (420–520 K) and ionizing electron energies up to 70 eV. Based on the experimentally measured dependences of the ionization cross-section on the incident electron energy, the thresholds of appearance of some molecule fragments were determined. The experiment consisted of two stages: at the first the mass spectra were thoroughly measured in the mass range of 0–350 amu at the ionization energies $E_i = 20, 30, 40, 50, 70$ eV, in the second stage relative cross-sections of dissociative

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ionization were studied in the incident electron energy range 6–40 eV. Note that for dynamic (and partly monopol) mass spectrometers the ion mass discrimination is typical. Our set-up operates in the scanning regime with a constant resolution dM = const. resulting in resolution decrease with ion mass peak growth. We have made special experiments on the determination of discrimination coefficient in mass range of 40–350 amu taking into account the sensitivity changes.

3. Results and discussion

3.1. Mass spectrum

The mass spectrum of the POPOP molecule is characterized by high selectivity and low fragmentation depth [6]. Fig. 1 represents a mass spectrum of POPOP molecule measured at $T = 480$K and ionizing voltage $U_i = 40$ V. Note that the intensity of some peaks differs from the spectrum measured at $U_i = 70$ V that is apparently connected with the value of effective fragment ionization cross-section reaching maximum at different incident electron energies. For example, for ions with $m/z = 77$ and $m/z = 105$ the ionization cross-section maximum is observed in the energy range of 30–50 eV. The distinctive feature of the presented mass spectrum is the presence of new ion with $m/z = 144$ $[C_9H_6ON]^+$, which is absent in the NIST data [7]. The $[C_{24}H_{16}N_2O_2]^+$ $m/z = 364$ molecular ion peak is the most intense in the spectrum, and small amount of ion fragment peaks with a low intensity.

The fragmentation degree F is given by

$$F = 1 - \frac{G}{M}, \quad \text{where} \quad G = \frac{\sum M_i I_i}{\sum I_i} \qquad (1)$$

Here M is the molecular mass of the substance, M_i is the ion mass number, I_i is its peak intensity in the overall ion current. The calculation according to Eq. (1) for the POPOP molecule gives the fragmentation degree value $F = 0.17$ what is rather typical for compounds with conjugated aromatic systems.

The traditional approach to the analysis of the regularities of organic molecules fragmentation is based on the views on the charge localization in molecular ions. At the formation of the latter, the most probable is loss of an electron from upper occupied molecular orbitals. If the molecule contains heteroatoms with lone electron pairs or multiple bonds, such orbitals are non-bonding n-orbitals or bonding π-orbitals localized mostly on the above mentioned structural elements. The fragmentation mostly occurs at simple bonds nearest to the charge localization site. The decay of molecular ions at multiple bonds or at simple bonds included in different conjugation systems, is hardly probable and revealed very weakly in the absence of competitive processes.

The presence of three aromatic rings connected by oxazole nuclei in the POPOP molecule (see inset in Fig. 1) enables a common system of conjugated π-electrons to be considered. Nitrogen and oxygen heteroatoms, contained in this molecule, enable the most probable charge localization sites at the formation of the molecular ion to be supposed. According to Ref. [8], the relative probability of ionization of structural fragments of the molecule, containing =N–, is 100%, while for those containing –O– it is 70%.

As known from Refs. [8,9], while describing the fragmentation processes in the course of molecular ion decay, traditional representations of the ion structure and mechanism of their formation are not applicable since ions in the mass spectrometer exist in different hardly predictable vibrationally and electronically excited states and only elemental composition of daughter ions can be reliably determined. A generally established approach describes dissociative ionization as a process occurring at the bond opening or recombination of minimal number of bonds. Based on this principle, we propose the description of the POPOP molecule fragmentation by electron impact [6].

The analysis of the ways of the POPOP molecule dissociation enables one to conclude that at the electron impact the bond opening occurs first of all in the oxazole ring vicinity resulting in the diversity of the final products of the dissociative ionization. Phenyl groups possess stronger bonds due to their uniformity and their opening is less probable. The presence of heteroatoms, resulting in the variation of electronic density in the oxazole rings, in spite of the π-electron conjugation, is the decisive factor in the fragmentation of the molecule under study.

Fig. 2 represents the most probable ways of the formation of ion-fragments appearing as a result of dissociative ionization. Peak $m/z = 309$ $[C_{22}H_{15}NO]^+$ is formed in the case the molecular ion loses fragment $[C_2H_2NO]^+$ (m = 55), owing to opening the bonds C_2–C_3 and C_2–O (Fig. 2a) in oxazole rings, and proton migration. Peak $m/z = 164$ ($[C_{13}H_8]^+$) can be formed in the process of secondary fragmentation of $[C_{15}H_{10}NO]^+$ ion appearing after opening the single bond between carbon atom C_5 (C_5') in the oxazole ring [6] and adjacent phenyl ring. In this case the groups C_2ON, C_2HON and C_2H_2ON are eliminated from the oxazole ring.

3.2. Threshold dependences of cross-sections of single and dissociative ionization

The main regularities in the threshold behaviour of effective cross-section of atoms ionization were shown by Wannier for the hydrogen atom [10]. The threshold behaviour of the ionization

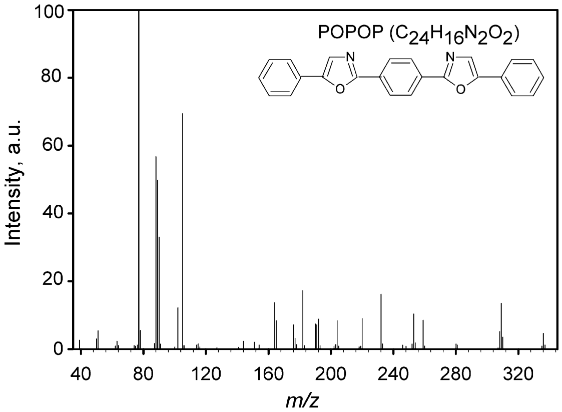

Fig. 1. Mass-spectrum of POPOP molecule, $T = 480$ K, $U_i = 40$ eV.

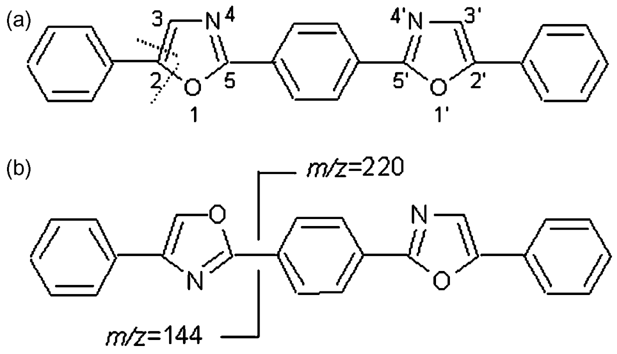

Fig. 2. (a) The most probable ways of the formation of the fragments with $m/z = 309$ and 90. (b) Breaking of a C–C bond in the $C_{24}H_{16}N_2O_2$ molecule resulting in the formation of the fragments with $m/z = 220$ and 144.

Table 1
Threshold appearance energies for fragment ions and ionization potential of the POPOP molecule (boldface).

Ion	m/z	E_{ap} (eV)
$C_6H_5^+$	77	12.26 ± 0.30
$C_7H_4^+$	88	12.86 ± 0.25
$C_7H_5^+$	89	13.50 ± 0. 25
$C_7H_6^+$	90	13.90 ± 0.25
$C_7H_5O^+$	105	13.17 ± 0.25
$C_9H_6NO^+$	144	9.48 ± 0.25
$C_{13}H_8^+$	164	11.72 ± 0.25
$C_{24}H_{16}N_2O_2^{2+}$	182	20.39 ± 0.25
$C_{15}H_{10}NO^+$	220	9.05 ± 0.25
$C_{22}H_{15}NO^+$	309	12.21 ± 0.25
$C_{24}H_{16}N_2O_2^+$	**364**	**8.74 ± 0.25**

cross-section of molecules can be expressed as a superposition of several exponential functions. For the exact determination of the ionization potentials of molecules (or atoms) and appearance energy of ion fragments at dissociative ionization, we applied a technique elaborated in Ref. [11]. The experimentally measured dependence of the ionization cross-section σ on the ionizing electron energy E near the threshold is fitted to a functional dependence $F(E)$. The fitting algorithm is implemented in special software enabling all the fitting parameters for the case of single ionization of molecules, to be obtained with a great number of iterations, taking into account the standard deviation values.

Thus obtained data sets are summarized in Table 1 containing the appearance threshold energies E_{ap} for the $[C_6H_5]^+$, $[C_7H_4]^+$, $[C_7H_5]^+$, $[C_7H_6]^+$, $[C_7H_5O]^+$, $[C_9H_6NO]^+$, $[C_{13}H_8]^+$, $[C_{15}H_{10}NO]^+$, $[C_{22}H_{15}NO]^+$ fragment ions, $[C_{24}H_{16}N_2O_2]^{2+}$ double-charged ion, and the first ionization potential for the $C_{24}H_{16}N_2O_2$ molecule, determined from the initial parts of the dissociative ionization cross-sections for the POPOP molecule.

3.3. Full ionization cross-section

This dependence was obtained by the following method. The mass spectrometer has been tuned for passing of ions, formed in the beam interaction area, without mass separation. The ionic current was measured at a collector (Faraday cup) and corresponded to the ionic current arising from the ionization of molecules by electron impact. In an automatic mode (cyclic signal accumulation) the dependence of ions formation on the electron energy was measured. The measurements were performed in two stages: at the first stage the energy dependence of the ionization process was measured with the POPOP molecular beam (useful signal + background), while at the second stage it was measured without the molecular beam (background). By subtraction of the second data array from the first one the POPOP molecule cross-section by electron impact in the given energy range has been obtained.

The energy dependence of the full ionization cross-section for the POPOP molecule within the energy range 6–50 eV is shown in Fig. 3. The cross-section varies gradually with features in the energy range 8–37 eV, some of which, as follows from their energy position, can be treated as related to the dissociative ionization process since their energy is close to the fragment ion appearance potentials. The threshold region of the curve in Fig. 1 was thoroughly measured. Using the algorithm of Ref. [11], we have determined the first ionization potential $E_i = 8.74$ eV. This value is in good agreement with the results of Ref. [12] where the first ionization potential of 8.7 eV is determined from the electron energy loss and optical absorption spectra.

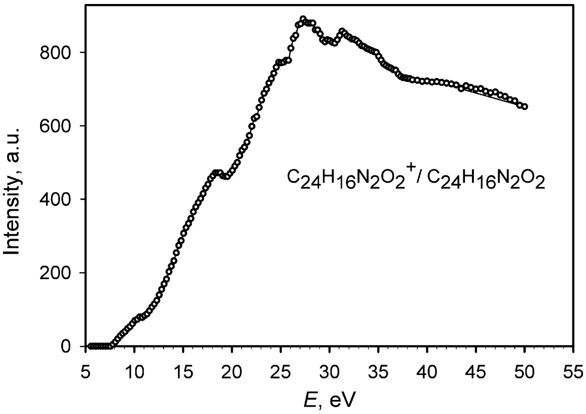

Fig. 3. Energy dependence of the full ionization cross-section for the POPOP molecule.

3.4. Daughter ion appearance cross-sections

The upper part of inset in Fig. 1 shows the POPOP molecule structural scheme while the lower part shows the scheme of the C–C bond opening in the $C_{24}H_{16}N_2O_2$ molecule which results in the formation of $[C_{15}H_{10}ON]^+$ and $[C_9H_6ON]^+$ fragments. According to our experimental data regarding the fragment ion appearance potentials (see Table 1), one should note that minimal values of E_{ap} for the POPOP molecule fragment ions correspond to $[C_{15}H_{10}ON]^+$ ions with $m/z = 220$, and $[C_{15}H_{10}ON]^+$ with $m/z = 144$. With the account of certain assumptions [9], the dissociation of the C–C bond between the PO– and –POP fragments of the initial molecule (Fig. 2) occurs at the energies by 0.3–0.7 eV above the molecular ion appearance potential. Such value of the dissociation energy is much below the handbook data for the single C–C bond binding energy [13]; however, there are experimental and calculation data available, according to which the energy required the C–C bond dissociation in single-charged ions, is by factor of 2–3 [9] or 6 [14] smaller than the binding energy in the unionized molecule. That is, a loss of electron by a molecule results in an essential weakening of one of the bonds of the hydrocarbon skeleton of the molecule. Evidently, in the case of POPOP molecule, ionization results in the weakening of the bond between the PO– and –POP fragments.

Energy dependences of dissociative ionization, resulting in the appearance of the $[C_{15}H_{10}ON]^+$ fragment ion and a complementary $[C_9H_6ON]^+$ ion, are shown in Fig. 4. In the ionizing electron energy range under study both dependences have maxima at 27 eV. The relative yield of the fragment ion with $m/z = 220$ is much higher

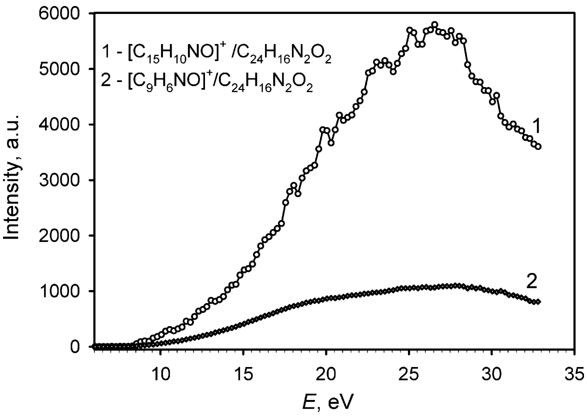

Fig. 4. Energy dependences of formation of $[C_{15}H_{10}NO]^+$ fragment ion and a complementary $[C_9H_6NO]^+$ ion.

than for the complementary ion that enables one to judge upon the predominant formation of a bigger fragment at the C–C bond opening in the POPOP molecule, resulting in the formation of PO– and –POP fragments (Fig. 2). Thus, at the molecular ion decay with this bond opening, the charge is localized mostly on the fragment containing two phenyl groups; it should be emphasized that both fragments contain equal numbers of similar heteroatoms. The appearance thresholds E_{ap} for these ions, calculated from the experimental plots, are 9.48 eV for $[C_9H_6ON]^+$ and 9.05 eV for $[C_{15}H_{10}ON]^+$. Evidently, formation of the $[C_{15}H_{10}ON]^+$ fragment is more favorable energetically, and in the course of charge localization at the POPOP molecular ion decay the fragment with three systems of conjugated bonds has an advantage because, probably, in this case the energy of the bonding electron orbitals is partially reduced.

Dissociation of the C–C bond between the phenyl and oxazole rings of the initial molecule, resulting in the formation of ions with $m/z = 74, 75, 76, 77, 78$ occurs at the energies, by 3.5 ± 0.25 eV exceeding the potential of appearance of the molecular ion. The $[C_6H_5]^+$ ion peak ($m/z = 77$), formed from the lateral phenyl groups of the initial molecule, is predominant in the present series. The low relative intensity of the peaks with $m/z = 74, 75, 76, 78$ and the absence of the complementary ions in the spectrum make the evidence for the charge localization predominantly on the phenyl fragment in the case of opening of the single bond between the phenyl and oxazole rings. The opening energy for this bond is in a good agreement with the handbook data for the C–C binding energy, that can be an indirect confirmation of the bond length or energy remaining unchanged at the ionization of the initial molecule.

3.5. Formation of a doubly charged ion

According to our experimental data, the maximal value of E_{ap} among the fragment ions of the POPOP molecule corresponds to an ion with $m/z = 182$ (see Table 1). Fig. 5 shows the threshold part of the energy dependence of formation of this ion which we identify as a double-charged $[C_{24}H_{16}N_2O_2]^{2+}$ molecular ion. Note that the behaviour of this curve essentially differs from the energy dependences for the daughter ions being formed in the course of the dissociative ionization: it has no maximum in the energy range 10–30 eV and the curve does not reach saturation in the energy range under study. The appearance threshold value for this ion is $E_{ap} = 20.39$ eV that is more than twice higher than the appearance potentials for single-charge ions. Besides, its peak is not accompanied by fragment peaks with masses $m_i \pm 1$, $m_i \pm 2$ amu, related to proton transfer, which are typical for fragment ions of organic molecules.

3.6. Temperature dependences for fragment ions

The importance of the study of the temperature effect on the fragment ion formation efficiency is shown in a number of recent studies. In particular, the effect of temperature on the appearance energies of daughter ions for ethane [15], methane [16], and propane [17] was studied. It is shown for these gases that the appearance energies change from 0.21 to 0.42 eV as the temperature is changed by 400 K. Unfortunately, in our experiment it was not possible to perform a similar study due to a rather high energy spread of the electrons. Therefore, we have studied the effect of temperature on the intensities of the daughter peaks in the mass spectrum. For this purpose the POPOP molecule mass spectrum was measured in the temperature range 420–520 K, the rest of the mass spectrum parameters remains constant. Note that the temperature increase results in the growth of the substance partial pressure in the molecular source and, as a consequence, in a variation of the fragmentation depth.

Fig. 6 shows the temperature dependences of the daughter ion formation measured at ionization energy $E_i = 40$ eV. $[C_6H_5]^+$ ion with $m/z = 77$ is formed from lateral phenyl groups of the initial molecule; $[C_7H_5O]^+$ ion with $m/z = 105$ is formed at the opening of C_2–C_3 and C_5–O bonds of the oxazole rings of the POPOP molecule; $[C_{13}H_8]^+$ ion with $m/z = 164$ is formed due to secondary fragmentation of the $[C_{15}H_{10}ON]^+$ ion, C_2ON, C_2HON and C_2H_2ON groups being eliminated from the oxazole ring; $[C_{22}H_{15}NO]^+$ ion with $m/z = 309$ is formed when the molecular ion loses a $[C_2HON]^+$ fragment ($m = 55$) which is formed due to the opening of the C_2–C_3 and C_2–O bonds of the oxazole rings of the POPOP molecule and recombination of the C_2–C_5 bond [6], as has been mentioned above. A characteristic feature of the curves presented in Fig. 6 is a natural almost linear growth of intensity with temperature in the range of $T = 455$–495 K. Note that the same temperature dependences measured in the range 420–520 K at $E_i = 70$ eV (not presented) have almost linear growth of intensity in the temperature range $T = 455$–495 K at first, then we observe a saturation followed by the intensity decrease. This decrease is possible owing to either space charge increase or different degree of daughter ions fragmentation and intensive molecule sublimation at critical temperatures (for POPOP the sublimation temperature is 512 K at pressure of 750 Torr [7]). More detailed interpretation could be done having

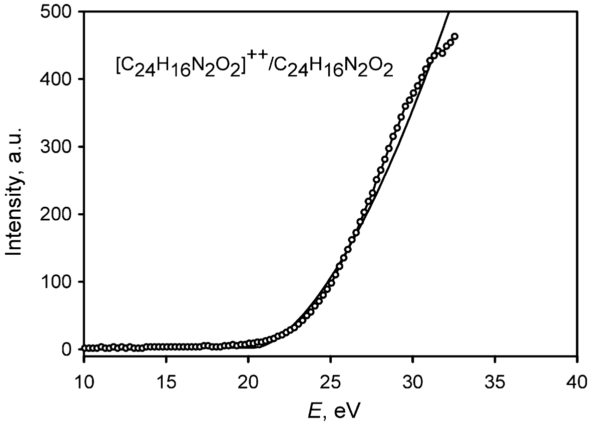

Fig. 5. Near-threshold part of the energy dependence of the doubly charged POPOP molecular ion formation. The measured data are shown as open circles, the fit curves are shown as solid lines.

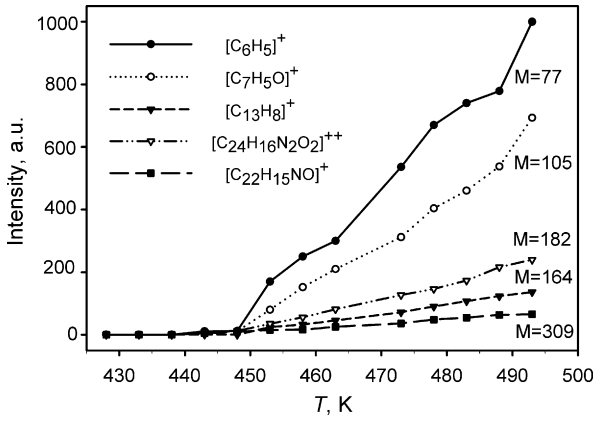

Fig. 6. Dependences of daughter ions formation intensities on temperature: $[C_6H_5]^+$ $m/z = 77$, $[C_7H_5O]^+$ $m/z = 105$, $[C_{13}H_8]^+$ $m/z = 164$, $[C_{22}H_{15}N_2O_2]^{2+}$ $m/z = 182$, $[C_{22}H_{15}NO]^+$, $m/z = 309$.

the dependence of saturated POPOP vapour pressure on temperature. In any case, no noticeable increase of the fragmentation depth with temperature was observed in our case being typical for organic compounds with conjugated bonds [8].

4. Conclusions

The ways of fragmentation of the molecule under study are proposed based on the presence of a common system of conjugated π-electrons and heteroatoms in the POPOP molecule. On the base of experimentally measured dependences of ionization cross-section on the electron energy the thresholds of appearance of some fragments of the molecule under investigation are determined. A new ion with $m/z = 144$ $[C_9H_6ON]^+$ in the mass spectrum of the POPOP molecule is detected. This ion is complementary to the fragment with $m/z = 220$ $[C_{15}H_{10}NO]^+$; the appearance threshold for this ion ($E_{ap} = 9.48$ eV) was determined.

The energy dependence of the POPOP molecule single ionization cross-section is measured in the energy range 6–60 eV, from the threshold part of which the first ionization potential for the molecule was determined as $E_i = 8.74$ eV; from the initial parts of the dissociative ionization cross-section plots the appearance threshold energies E_{ap} for $[C_6H_5]^+$, $[C_7H_4]^+$, $[C_7H_5]^+$, $[C_7H_6]^+$, $[C_7H_5O]^+$, $[C_9H_6NO]^+$, $[C_{13}H_8]^+$, $[C_{15}H_{10}NO]^+$, $[C_{22}H_{15}NO]^+$ fragment ions and a $[C_{24}H_{16}N_2O_2]^{2+}$ double-charged ion were determined.

A characteristic feature of the temperature dependence is the intensity increase with temperature; however, no noticeable increase of the fragmentation depth with temperature is observed that is related to the specific structural features of organic compounds with conjugated bonds.

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