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ARTICLES

Reduction Reactions in the Ion Source in Electron Ionization Mass Spectrometry

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Abstract—Theoretically, electron ionization mass spectra should contain exclusively peaks of ions due to the monomolecular fragmentation of molecular ions. However, spectra of aromatic compounds with halogen atoms and nitro groups contain ion peaks with the composition not consistent with this postulate. Based on a detailed study of such ions by high-resolution mass spectrometry, we showed that their formation is associated with the reduction of the initial molecules at the metal walls of the ion source before their ionization. As a result, products of the reduction reaction of the corresponding composition are ionized. Nitro compounds are reduced to the corresponding amines, while halogenated compounds lose the halogen atom, turning into unsubstituted substrates. Water molecules on the metal surface of the ion source act as reduction agents. This process does not depend on the geometry of the source and proceeds in any mass spectrometer.

Keywords: electron ionization, nitro compounds, halogen-containing compounds, reduction reactions
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INTRODUCTION

The patterns of fragmentation of organic compounds under the conditions of electron ionization (EI) are well studied [1]. It is generally accepted that, under the EI conditions, ion-molecular transformations do not occur, because deep vacuum is maintained in the ionization source (10^{-5} to 10^{-6} mmHg), and the ion residence time in the source is extremely short (~10^{-6} s). In other words, in such a short time and such a rarefied atmosphere, ions have no time to interact with each other or with any molecules.

In contrast to EI, chemical ionization (CI) is based on ion-molecular reactions [2, 3]. The presence of a reagent gas creates a pressure in the ion source of an order of 1 mmHg, and the residence time of the ion in the source increases to approximately 10^{-3} s. The ionization process is carried out by the interaction of analyte molecules with reagent gas ions. Chemical ionization is a well-studied method; however, alternative processes of ionization occurring in the source are of independent interest. These may be oxidation, reduction, or substitution reactions. Cases of the reduction of nitro-substituted aromatic compounds under CI conditions with hydrogen, methane, ammonia, isobutane, and water as a reagent gas are mentioned in [4–7]. For example, in studying the CI mass spectra of trinitro derivatives of aromatic compounds, high intensity of ion peaks was noted, m/z of which was by 30 Da smaller than the m/z value of protonated molecules [5]. The $[MH-30]^+$ ions can form either by reducing the nitro group to the corresponding amines or by the loss of an NO molecule in the fragmentation of the molecular ion. The authors used heavy water to study the composition of the formed ions in mass spectrometry experiments. The loss of NO from a protonated molecule leads to the formation of a $[MD-30]^+$ ion, and when it is reduced to a corresponding amine, the $[MD-28]^+$ ion is obtained (Scheme 1). It was found for 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzene, 3-methyl-2,4,6-trinitrotoluene, and picric acid that the $[MH-30]^+$ ion is a composite one. A loss of 30 Da may correspond not only to the elimination of the NO molecule, but also to the reduction of the nitro group.

$$R\text{–}NO_2 \xrightarrow{[D_3O]^+} [R\text{–}ND_3]^+ \Rightarrow [M\text{–}2O + 2D]^+.$$

Scheme 1. Study of the composition of the $[MH-30]^+$ ion formed in the fragmentation of nitroaromatic compounds in the EI source in the presence of D_2O.

The reduction of the nitro group was also observed under the conditions of negative ion mass spectrome-

try with electron capture, which was studied using dinitroaromatic compounds as an example [8]. The mass spectra of *N*-substituted dinitroanilines contained $[M-30]^-$ ion. To determine the origin of the $[M-30]^-$ ion, the mass spectra of trifluralin (2,6-dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)-aniline) containing three ^{15}N atoms were studied. In this case, the removal of the NO molecule corresponded to the $[M-31]^-$ ion. The trifluralin mass spectrum contained both $[M-30]^-$ and $[M-31]^-$ ions, which is typical for the simultaneous process of the reduction and fragmentation of the nitro group. Trifluralin mass spectra were obtained in the presence of D_2O and CD_4, for which a shift of reduced ions by mass from $[M-30]^-$ to $[M-28]^-$ and $[M-29]^-$, corresponding to $[M-2O + 2D]$ and $[M-2O + H + D]^-$ ions, was observed. The authors demonstrated that the reduction reaction depends on the temperature of the ionization source, pressure, concentration of the sample, and the amount of water contained. In particular, the ratio of the reduced $[M-2O + 2H]^-$ ion to the $[M-NO]^-$ ion characteristic of the fragmentation of nitro compounds increases with the introduction of a small amount of water into the source [8].

The most interesting is the fact that the reaction of reduction of nitroaromatic compounds to the corresponding amines takes place under the EI conditions at a pressure in the ion source of (10^{-5} to 10^{-6} mmHg) and the ion residence time in the source of ~10^{-6} s. Beynon et al. [9], using the Nir Johnson sector geometry instrument MS-9 for studying metastable ions resulting from the fragmentation of molecular ions of nitrobenzene, nitrophenols, and nitronaphthalene, found that a low-intensity isobar ion accompanies the ion $[M-NO]^+$. Using high-resolution mass spectrometry, they proved that the composition of this ion was $[M-O_2 + H_2]^+$; i.e. it was precisely the reduction of the nitro group under the conditions of electron ionization. Moreover, the authors detected the peaks of molecular ions of azobenzene and azoxybenzene, which are known intermediates for the reduction of nitrobenzene to aniline in solution. As the introduction of heavy water into the ion source led to the formation of deuteroderivatives of $ArND_2$, the authors concluded that the reduction reaction is due to the interaction of nitro compounds with water vapor and is catalyzed by metal oxide films on the source walls. Quilliam et al. [7] confirmed later the conclusion about the reduction of the nitro group in the ion source by using isotopic labels and showed that the reaction proceeds independently of the type of sample introduction into the device: direct inlet or introduction through a gas or liquid chromatograph.

Dehalogenation products, that is, the products of substitution of halogens in the initial aromatic substrates for hydrogen, are another type of nonstandard ions. This process can also be treated as reduction. Under the conditions of chemical ionization, the occurrence of this process can be explained by ion-molecular reactions [10–12], while under conditions, for example, of electron capture negative ionization (ECNI), this explanation does not work. The most diverse polyhalogenated aromatic compounds, including benzenes, naphthalenes, biphenyls, dibenzofurans [13–17], exhibit $[M-n\text{Hal} + n\text{H}]^-$ ions in the dissociative electron capture spectra. The substitution of the cyano group in aromatic compounds for hydrogen can occur similarly [18]. With decreasing source temperature or pressure in the ECNI source, the peak intensities of these ions increase [18]. Sears et al. [13] proposed a reaction for the reduction of substrates on the metal walls of an ion source again, as in the case of the reduction of a nitro group.

We decided to test a possibility of the reactions in gas chromatography–mass spectrometry (GC/MS) in EI sources of modern instruments of various types: Orbitrap Q Exactive with an orbital trap ((Thermo Fischer Scientific)), 7200 B/Q-TOF hybrid (Agilent), and Pegasus® GC-HRT time-of-flight (LECO).

EXPERIMENTAL

We studied ion-molecular reactions of the reduction and substitution of nitro and halogen derivatives using 20 compounds, constituents of the MegaMix commercial mixture (Restek, United States): *N*-nitroso-*N*-propyl-1-propanamine, nitrobenzene, 2-nitrophenol, *p*-chloroaniline, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, *o*-nitroaniline, 1,4-dinitrobenzene, 1,3-dinitrobenzene, 2-methyl-1,3-dinitrobenzene, *m*-nitroaniline, 4-nitrophenol, 1-methyl-2,4-dinitrobenzene, 2,3,5,6-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, *p*-nitroaniline, 2-methyl-4,6-dinitrophenol, 1-bromo-4-phenoxybenzene, hexachlorobenzene, and pentachlorophenol.

The analysis was performed using high-resolution mass spectrometers Orbitrap Q Exactive (Thermo Fischer Scientific, United States), 7200 B/Q-TOF (Agilent, United States), and Pegasus® GC-HRT (LECO, United States). The main experiments were conducted using a LECO time-of-flight instrument. Control of the system and accumulation and processing of data were performed using the ChromaTOF® software (LECO). Data were recorded at a rate of ten spectra per second (mass range m/z 10–500) using high-resolution mass spectrometry (resolution 25000), which enabled us to determine the elemental composition of all fragment ions reliably. The mass spectrometer was calibrated before analysis of the samples as part of the automatic tuning procedure using perfluorotributylamine. Unless otherwise specified, the temperature of the EI source was kept at 250°C, and the electron energy was 70 eV. Chromatographic separation was performed in an Rxi-5Sil MS column, the length of which was 30 m, the inner diameter was 250 mm, and the phase thickness was

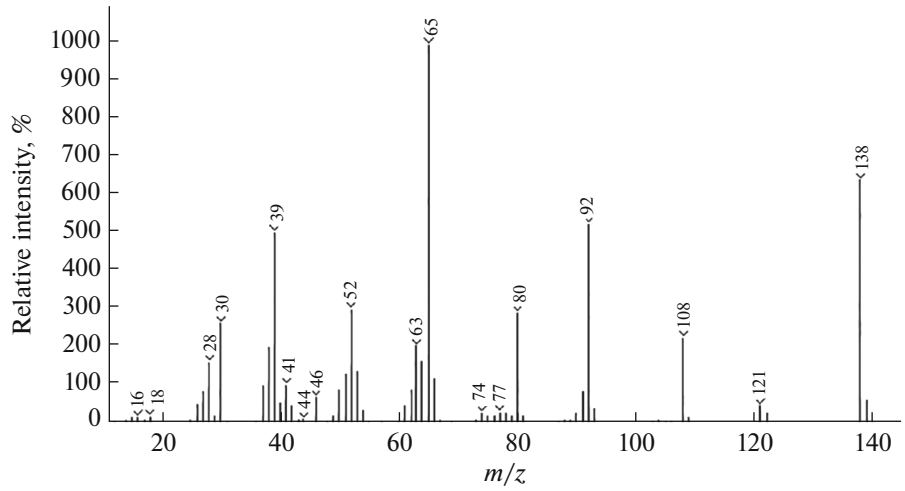

Fig. 1. EI mass spectrum of *o*-nitroaniline from the NIST electronic library.

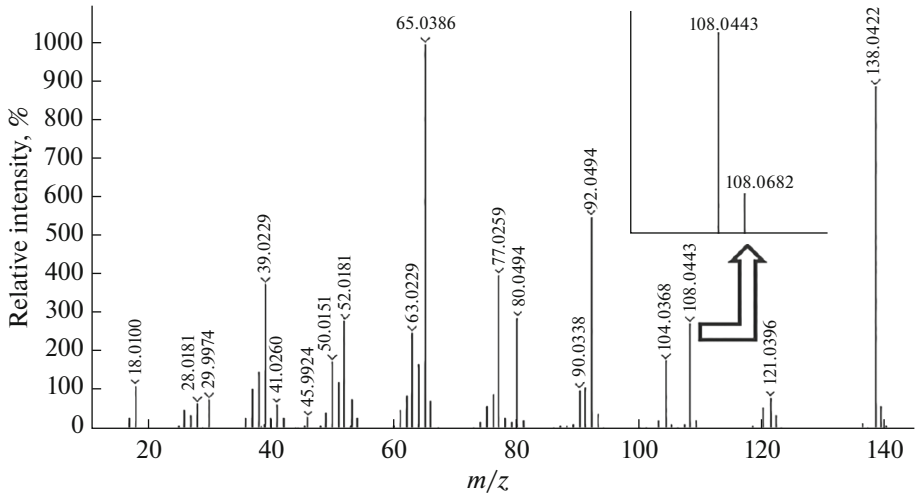

Fig. 2. Experimental high-resolution mass spectrum of *o*-nitroaniline (*m/z* 108.0682 $C_6H_8N_2$, *m/z* 108.0443 C_6H_6NO).

0.25 μm. Helium was used as a carrier gas at a flow rate of 1 mL min^{-1}. The column temperature was programmed as follows: initial temperature 50°C for 2 min, then, heating at a rate of 10°C min^{-1} to 280°C; the temperature of the transfer line was 320°C. One microliter of a dichloromethane solution of the test mixture was injected into the injector heated to 280°C, with a flow split ratio of 50 : 1.

RESULTS AND DISCUSSION

The abstraction of an NO molecule is one of characteristic mechanisms of the fragmentation of nitroaromatic compounds under EI conditions [19]. For *o*-nitroaniline (*m/z* 138), such a loss leads to the formation of a fragment ion of *m/z* 108 (Fig. 1).

Mass spectra contained in electronic libraries tend to have low resolution. Therefore, we cannot suggest the formation of any other isobaric ion. In the transition to high-resolution mass spectrometry (HRMS), new details are found in the spectra of some compounds (Fig. 2). An increase of the resolving power in the mass region of *m/z* 108 in the EI mass spectrum (Fig. 2, inset) demonstrates that this ion is composite. Two ions correspond to an ion with a nominal mass of 108 Da: *m/z* 108.0443 (C_6H_6NO) and *m/z* 108.0682 ($C_6H_8N_2$). The formation of the C_6H_6NO ion is due to the elimination of NO molecule from the molecular ion, while $C_6H_8N_2$ ion implies the replacement of two oxygen atoms by two hydrogen atoms; i.e., a reduction process takes place in the ion source of the mass spectrometer.

The mass chromatograms plotted for each ion (Fig. 3) show the closeness of their retention times. We are not talking about the coelution of chromatographic peaks of *o*-nitroaniline and phenylenedi-

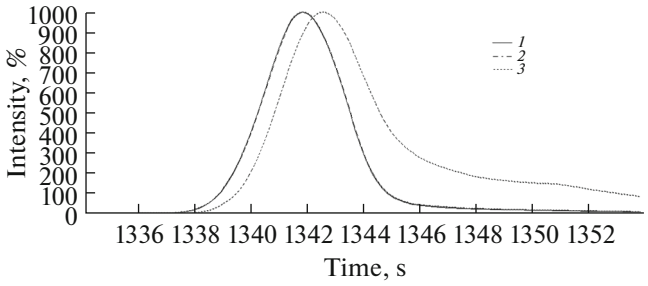

Fig. 3. Mass chromatogram for *o*-nitroaniline ions: (*1*) *m/z* 138.0422 $C_6H_6N_2O_2$, (*2*) *m/z* 108.0443 C_6H_6NO, and (*3*) *m/z* 108.0682 $C_6H_8N_2$.

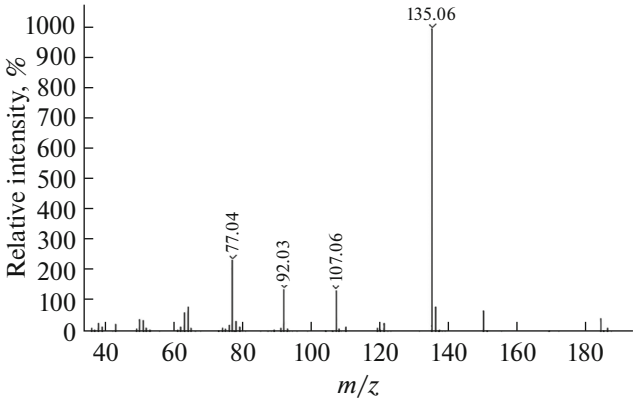

Fig. 4. Mass spectrum of α-chloro-4-methoxyacetophenone.

amine. Their retention times are significantly different, but they appear together in the mass spectrum. A small shift in the retention time of the ion of *m/z* 108.0682 indicates a somewhat longer stay of this ion in one of the units of the mass spectrometer, presumably, in the ion source. We can assume that the formation of this ion is due to the ionization of the product of the reduction of the initial nitro derivative into amine one directly in the mass spectrometer.

Similar processes of the reduction of the nitro group in aromatic compounds have been recorded in several cases (Table 1). The relative intensities of the peaks of such ions can be quite high. For example, when 20 ppm of nitrobenzene is injected into the source, the ratio of the peak intensity of the cation radical of the reduced amine is 43% of the molecular ion of nitrobenzene itself. For *p*-nitroaniline, this value is even higher, 62% (Table 1). The presence of two nitro groups in the molecule makes it possible to detect the product of the reduction of both (Table 1).

In addition to the reaction discussed above, another process was also discovered, namely, the replacement of a halogen atom in aromatic derivatives with hydrogen. Formally, this process can also be considered as a reduction. It is often not necessary to use high-resolution devices to detect such ions. We obtained a mass spectrum of α-chloro-4-methoxyacetophenone (Fig. 4) in an experiment on the study of aquatic chlorination of avobenzone [20]. The peak intensity of $[M-Cl+H]^+$ ion of *m/z* 150 is higher than the peak intensity of the molecular ion, and the peak of $[M-Cl]^+$ ion is almost completely absent. In the spectrum of α-bromo-4-methoxyacetophenone (Fig. 5), the intensity of a similar peak of *m/z* 150 is even higher [21]. This is the fourth most intense peak in the spectrum.

Although we are considering aromatic substrates, the reaction proceeds at an aliphatic carbon atom. As the elimination of both the chlorine atom and the HCl molecule by the molecular ions of these acetophenones does not lead to stable ions, the peak of reduced acetophenone becomes very noticeable in the spectrum.

In the presence of halogen atoms in the aromatic ring, their substitution by hydrogen proceeds in a similar way but is often masked by more intense peaks of $[M-Cl]^+$ isotopic ions. For example, consider the EI mass spectrum of the 2,4,6-trichlorophenol (the nominal molecular weight of 196 Da) in Fig. 6.

An increase in resolution in the mass region of *m/z* 162 (Fig. 7a) demonstrates that two ions correspond to a nominal mass of 162 Da. Using high-resolution mass spectrometry, we found out that *m/z* 161.9448 ion is part of the isotopic cluster of $[M-Cl]^+$ ion ($C_6H_2{}^{37}Cl^{35}ClO$). The composition of the second ion (*m/z* 161.9634) is $C_6H_4Cl_2O$; i.e., its formation can only be due to the reaction of substitution of a chlorine atom for a hydrogen atom in the ion source.

A similar situation was observed in the mass region of *m/z* 128 (Fig. 7b). In this case, the ion of *m/z* 127.9838 is a part of the isotopic cluster of $[M-2Cl]^+$ ion with composition $C_6H_3{}^{37}ClO$. The presence of the isobaric ion (*m/z* 128.0024) with composition C_6H_5ClO is the result of the substitution of two chlorine atoms for hydrogen atoms in the molecule of the initial 2,4,6-trichlorophenol in the ion source.

For all the compounds considered in this study, the relative intensities of the reduced ions were calculated as a percentage of the molecular ion intensity (Table 1), while different amounts of initial substrates were introduced into the instrument. At a concentration of substances below 1 ppm, the sensitivity of the mass spectrometers becomes insufficient to detect abnormal ions. Perhaps, this is due to a significant decrease in the rate of reduction reactions in the mass spectrometer. With an increase in the concentration of the substance, nonlinear dependence of the relative intensity was observed for most compounds (Table 2): with an increase in concentration, the intensity of the reduced ion first increases, passes through a maximum, and decreases. The nonlinearity of the dependence of the intensity of the reduced ions on the con-

Table 1. Intensity of reduced ions as a fraction of the intensity of the molecular ion (%)

No.	Name	*m/z*	Formula	100 ppm*	50 ppm	20 ppm	5 ppm
1	Nitrobenzene	93.0571 [M−2O + 2H]	C_6H_7N	16.9	32.1	43.4	33.7
2	2,4,6-Trichlorophenol	161.9634 [M−Cl + H]	$C_6H_4Cl_2O$	1.1	1.6	1.4	–
		128.0024 [M−2Cl + 2H]	C_6H_5ClO	0.2	0.3	–	–
3	2,4,5-Trichlorophenol	161.9634 [M−Cl + H]	$C_6H_4Cl_2O$	1.2	2.0	2.5	0.9
		128.0024 [M−2Cl + 2H]	C_6H_5ClO	0.3	0.4	0.3	–
4	*o*-Nitroaniline	108.0682 [M-2O + 2H]	$C_6H_8N_2$	5.0	4.3	3.4	–
5	1,4-Dinitrobenzene	138.0422 [M−2O + 2H]	$C_6H_6N_2O_2$	7.0	3.7	1.5	–
		108.0682 [M-4O + 4H]	$C_6H_8N_2$	9.7	9.3	2.0	–
6	*m*-Nitroaniline	108.0682 [M−2O + 2H]	$C_6H_8N_2$	7.4	16.1	17.5	–
7	4-Nitrophenol	109.0522 [M−2O + 2H]	C_6H_7NO	4.0	11.3	22.6	18.1
8	1,3-Dinitrobenzene	138.0423 [M−2O + 2H]	$C_6H_6N_2O_2$	4.2	2.9	1.5	0.2
		108.0682 [M−4O + 4H]	$C_6H_8N_2$	2.0	0.9	–	–
9	*p*-Nitroaniline	108.0682 [M−2O + 2H]	$C_6H_8N_2$	9.3	25.8	62.3	45.9
10	2,3,4,6-Tetrachlorophenol	195.9244 [M−Cl + H]	$C_6H_3Cl_3O$	1.8	2.5	1.1	–
		161.9634 [M−2Cl + 2H]	$C_6H_4Cl_2O$	0.2	0.1	0.2	–
11	2,3,5,6 Tetrachlorophenol	195.9244 [M−Cl + H]	$C_6H_3Cl_3O$	1.3	2.3	1.5	–
		161.9636 [M−2Cl + 2H]	$C_6H_4Cl_2O$	0.1	0.4	0.1	–
12	1-Methyl-2,4-dinitrobenzene	152.0582 [M−2O + 2H]	$C_7H_8N_2O_2$	121.7	122.3	–	–
		122.0838 [M−4O + 4H]	$C_7H_{10}N_2$	13.5	12.2	8.9	–
13	*N*-Nitrozo-*N*-propyl-1-propanamine	116.1308 [M−O + 2H]	$C_6H_{16}N_2$	–	–	–	–
14	2-Nitrophenol	109.0524 [M−2O + 2H]	C_6H_7NO	–	–	–	–
15	*p*-Chloroanilin	93.0572 [M−Cl + H]	C_6H_7N	–	–	–	–
16	2-Methyl-1,3-dinitrobenzene	152.0581 [M−2O + 2H]	$C_7H_8N_2O_2$	–	–	–	–
		122.0840 [M-4O + 4H]	$C_7H_{10}N_2$	0.1	0.9	0.4	–
17	2-Methyl-4,6-dinitrophenol	168.0529 [M-4O + 4H]	$C_7H_8N_2O_3$	–	–	–	–
		138.0784 [M-4O + 4H]	$C_7H_{10}N_2O$	–	–	–	–
18	1-Bromo-4-phenoxybenzene	170.0725 [M-Br + H]	$C1_2H10O$	–	–	–	–
19	Hexachlorobenzene	247.8515 [M-Cl + H]	C_6HCl_5	–	–	–	–
		213.8906 [M-2Cl + 2H]	$C_6H_2Cl_4$	–	–	–	–
20	Pentachlorophenol	229.8853 [M-Cl + H]	$C_6H_2Cl_4O$	2.54	3.25	1.74	–
		195.9250 [M-2Cl + 2H]	$C_6H_3Cl_3O$	0.34	0.53	–	–

* 1 g/L = 1000 ppm.

centration enables excluding the assumption of the implementation of chemical ionization where the initial substance itself could act as a reagent gas. In this case, the direct dependence of the fraction of reduced ions on an increase in the concentration of the substance would be observed. In similar processes, the source of hydrogen atoms can be water or hydrogen molecules [22]. According to the manufacturer, the purity of helium is >99.9999%, and the concentration of an impurity of water and hydrogen is <0.5 ppm. The high purity of the reagents used and the high vacuum make it possible to exclude the carrier gas and solvent used to prepare the solution of analytes as sources of hydrogen. Probably, such a source may be water, free or adsorbed on the walls of the source, present in any mass spectrometer.

Experiments with varying the temperature of the ion source (170, 200, and 270°C) showed that the intensity of the reduced/substituted ion signals directly depends on this factor. With the increasing

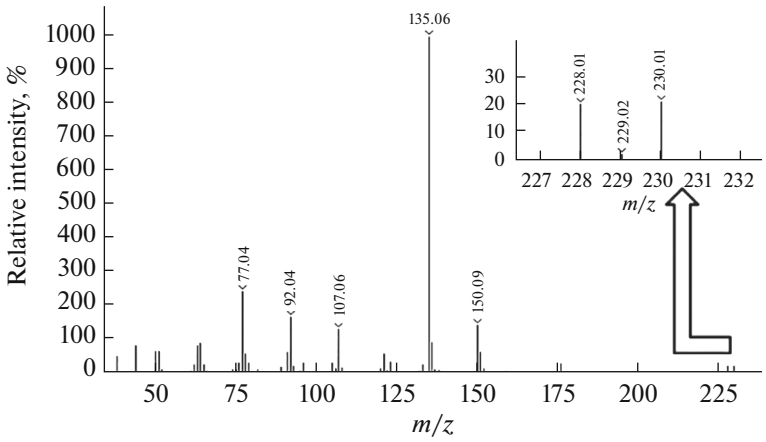

Fig. 5. Mass spectrum of α-bromo-4-methoxyacetophenone.

temperature of the ionization source, the intensity of the reduction/substitution processes in the examples considered increases (Table 2), which is also an argument in favor of a chemical reaction in the source before ionization of the initial compound.

EI mass spectra of the studied compounds recorded using other high-resolution gas chromatographs/mass spectrometers (Orbitrap Q Exactive (Thermo Fischer Scientific), 7200 B/Q-TOF (Agilent)) also contained peaks of all the reduced/substituted ions mentioned above (Table 3).

This issue evidences that the observed process is not random and does not depend on the geometry of the source, type of an analyzer, or other nodes of the mass spectrometer. Probably, as Beynon et al. [9] suggested, a catalytic reduction of the halogen- and nitroaromatic compounds occurs on the walls of the chamber of the ion source. The first act of the reaction is the adsorption of part of the incoming neutral molecules at the metal surface of the ion source. The oxide film on this surface acts as a catalyst, and adsorbed water serves as a source of hydrogen. Thus, the initial molecule rather than corresponding molecular ion, the lifetime of which in the source is microseconds, enters the reaction. Under GC/MS conditions, the width of the chromatographic peak of a few seconds means that it is precisely this time that the molecules of the substance are present in the source; all this time, neutral molecules of the studied compounds are in the source and can undergo some kind of chemical reaction. Under the conditions of direct inlet [9], the reaction time is practically unlimited.

CONCLUSIONS

Using high-resolution mass spectrometry, we detected ion peaks in EI mass spectra, the formation of which cannot be rationalized by the processes of the monomolecular fragmentation of molecular ions of the initial compounds. Their presence indicates that nitro- and halogen-containing aromatic compounds are reduced in the electron ionization source. The reactions proceed on metal walls of the source, and adsorbed water acts as a source of hydrogen. The geometry of the ion source has little effect on these reactions. The reduction reaction involves molecules

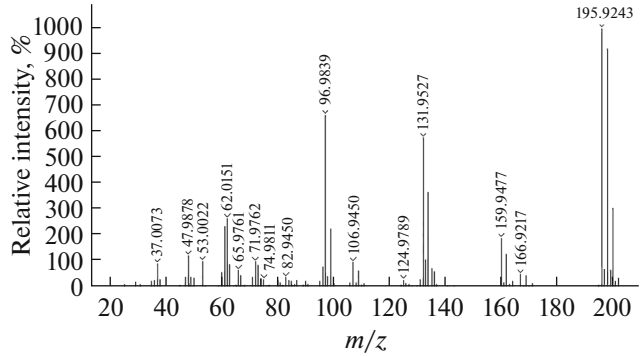

Fig. 6. Experimental high-resolution EI mass spectrum of 2,4,6-trichlorophenol.

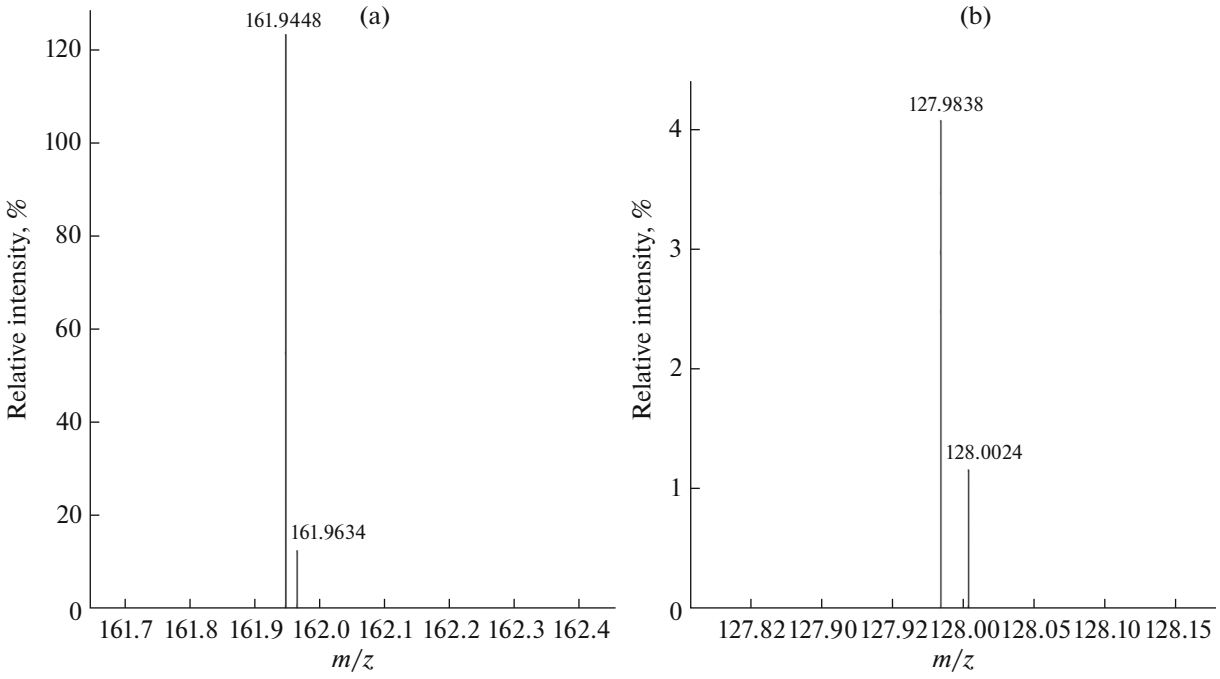

Fig. 7. Magnified mass spectra of (a) 2,4,6-trichlorophenol (*m/z* 161.9448 $C_6H_2{}^{37}Cl^{35}ClO$ and *m/z* 161.9634 $C_6H_4Cl_2O$) and (b) 2,4,6-trichlorophenol (*m/z* 128.0024 C_6H_5ClO and *m/z* 127.9838 $C_6H_3{}^{37}ClO$).

Table 2. Intensity of the reduced ions as a fraction of the intensity of the molecular ion (%) under different temperatures of the ion source

Compound	*m/z*	Source temperatuire, °C		
		270	200	170
o-Nitroaniline (*m/z* 138.0422 $C_6H_6N_2O_2$)	108.0682 [M−2O + 2H]	6.1	2.8	1.0
m-Nitroaniline (*m/z* 138.0422 $C_6H_6N_2O_2$)	108.0682 [M−2O + 2H]	6.9	6.5	3.0
p-Nitroaniline (*m/z* 138.0422 $C_6H_6N_2O_2$)	108.0682 [M−2O + 2H]	17.2	11.6	5.9
p-Nitrophenol (*m/z* 139.0263 $C_6H_5NO_3$	109.0522 [M−2O + 2H]	12.4	8.4	3.1
1,3-Dinitrobenzene (*m/z* 168.0164 $C_6H_4N_2O_4$)	138.0423 [M−2O + 2H]	7.5	8.4	5.6
	108.0682 [M−4O + 4H]	9.1	2.7	0.3

Table 3. Intensity of the reduced ions as a fraction of the intensity of the molecular ion (%); data obtained by the LECO, Thermo Fisher Scientific, and Agilent instruments (5 ppm)

Compound	*m/z*	Formula	I, % (LECO, 5 ppm, 250°C)	I, % (Thermo, 5 ppm, 200°C)	I, % (Agilent, 5 ppm, 200 °C)
Nitrobenzene (*m/z* 123.0315 $C_6H_5NO_2$)	93.0572 [M−2O + 2H]	C_6H_7N	33.7	3.5	3.75
o-Nitroaniline (*m/z* 138.0422 $C_6H_6N_2O_2$)	108.0682 [M−2O + 2H]	$C_6H_8N_2$	–	2.8	2.7
m-Nitroaniline (*m/z* 138.0422 $C_6H_6N_2O_2$)	108.0682 [M−2O + 2H]	$C_6H_8N_2$	–	3.5	3.7
p-Nitroaniline (*m/z* 138.0422 $C_6H_6N_2O_2$)	108.0682 [M−2O +2 H]	$C_6H_8N_2$	45.9	9.3	7.3
p-Nitrophenol (*m/z* 139.0263 $C_6H_5NO_3$	109.0522 [M−2O + 2H]	C_6H_7NO	18.1	8.2	6.1
1,3-Dinitrobenzene (*m/z* 168.0164 $C_6H_4N_2O_4$)	138.0423 [M−2O + 2H]	$C_6H_6N_2O_2$	0.2	29.2	10.8
	108.0682 [M−4O + 4H]	$C_6H_8N_2$	–	2.9	1.0

that are present in the source much longer than the molecular ions formed already from them.

CONFLICT OF INTERESTS

The authors declare no conflict of interest.

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