380 Russian Chemical Bulletin, International Edition, Vol. 55, No. 2, pp. 380—383, February, 2006

Brief Communications

Hidden rearrangement processes in short-lived negative molecular ions

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The study of resonant electron capture by nitrobenzene molecules showed that some fragmentary negative ions are unstable toward electron autodetachment. The measured appearance energy of the neutral component of an $[M - H]^-$ ion beam does not agree with the energetics of direct dissociation in a molecular ion. The estimation calculations show that the low appearance energy of $[M - H]^0$ neutral components is caused by isomerization of a molecular ion of nitrobenzene to the 2-nitrobenzene structure followed by the formation of a phenoxide ion in the autodetachment state.

Key words: mass spectrometry, resonant electron capture, negative ions, rearrangements, nitrobenzene, 2-nitrosophenol, structure.

Negative ions (NIs) in the autodetachment states are formed due to resonant capture of electrons by molecules. The total cross section of electron capture (σ_C) and the cross section of dissociative electron capture (σ_{DEC}), which leads to the appearance of smaller fragments, are related by the correlation[1]

$$\sigma_{DEC} = \sigma_C \exp(-\tau_d/\tau_a), \qquad (1)$$

where τ_a is the lifetime of a molecular negative ion ($[M]^-$) with respect to electron autodetachment, and τ_d is the time necessary for its dissociation to smaller fragments. It follows from Eq. (1) that electron autodetachment competes with dissociative processes, due to which fast fragmentation channels occur mainly of possible routes for molecular ion decay. Rearrangement processes occur, as a rule, in such $[M]^-$, whose composition includes acceptor groups or atoms. Hidden processes of H-shift and isomerization can occur against the background of explicit rearrangements in $[M]^-$, which are identified by peaks of characteristic ions $[M - HHal]^-$, $[M - H_2O]^-$, and others in the mass spectra. It is difficult to identify them only from the mass spectrum, because the elemental composition of rearrangement ions and that of ions formed without rearrangements through dissociation are often the same. However, $[M]^-$ decay products in the fast and slow processes differ in structure and, hence, in enthalpy of formation. The energies of these processes are different, and the mechanism can be determined by analysis of the energy balance of monomolecular decomposition

$$E_{\text{app}}([A]^-) = \Delta H_f^\circ([A]^-) + \Delta H_f^\circ(B) - \Delta H_f^\circ(AB) + E', \qquad (2)$$

where $E_{\text{app}}([A]^-)$ is the experimentally measured appearance energy for the $[A]^-$ fragmentary ion; $\Delta H_f^\circ([A]^-)$,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 367—370, February, 2006.

$\Delta H_f°(B)$, and $\Delta H_f°(AB)$ are the standard enthalpies of formation of the $[A]^-$ ion, uncharged B fragment, and AB molecule, respectively; E' is the excessive energy of the process.

Nitroaromatic compounds are characterized by the skeletal rearrangement in $[M]^-$ to liberate the $[M - NO]^-$ fragmentary ions,[2] which indicates that an electron captured by the molecule can be kept for a long time. This fact allowed us to study nitrobenzene in order to detect other rearrangement processes.

Experimental

Experiments were carried out on an MI-1201 single-focus magnetic mass spectrometer modified for generation and detection of negative ions.[3] This instrument makes it possible to obtain a dependence of the mass peak intensity on the electron beam energy in a range of 0—80 eV. The ion source was equipped with an electron monochromator[4] that decreased the energy scatter of the electron beam at the half-height ($\Delta E_{1/2}$) to 0.05 eV at an electron current of 1 nA. The electronic and ionic optics of the ion source were tuned according to the requirements of a minimum possible value of $\Delta E_{1/2}$ with retention of an ion signal intensity sufficient for its reliable detection. The electron energy scale was calibrated by maxima in the curves of the effective yield of the SF_6^-/SF_6 (~0 eV) and NH_2^-/NH_3 (5.65 eV) ions. The appearance energy of ions was determined from the onset of the SF_6^- ion peak with an error of ±0.05 eV. An additional electrode was mounted in a region of the ion receiver to deviate the charged component of the ion beam in the transversal electric field and to detect neutral components formed by electron autodetachment when ions were flying through the second field-free region.[5] The average lifetime of NIs relatively to electron autodetachment was calculated by the equation[5]

$$\tau_a = t/\ln(1 + [N]^0/[N]^-), \quad (3)$$

where $[N]^0$ and $[N]^-$ are the relative peak intensities of neutral components and ions, respectively; t is the time-of-flight by ions of the second field-free region (for ions with m/z 122 at an accelerating voltage of 1300 V, t = 8.48 μs). Nitrobenzene was delivered to the ionization chamber by a standard injection system for liquids and gases. To decrease the influence of activation of ions upon collisions on experimental results, a moderate inlet of a sample was used: the vapor pressure in the ion source region, which was monitored by a magnetic ionization detector, did not exceed 10^{-3} Pa, and the residual pressure was not higher than $5 \cdot 10^{-5}$ Pa. For calculation of the thermochemical constants of molecules and radicals, we used the expression similar to Eq. (2)

$$D(A—B) = \Delta H_f°(A) + \Delta H_f°(B) - \Delta H_f°(AB), \quad (4)$$

where D(A—B) is the bond dissociation energy in the AB molecule.

Results and Discussion

The mass spectrum of nitrobenzene NIs obtained at a constant electron energy of 4 eV contains more than 20 mass peaks, whose intensity range is four orders of magnitude. Along with the peak of the above-mentioned $[M - NO]^-$ ion, we found peaks of the $[M - OH]^-$ and $[OH]^-$ ions, being the products of rearrangement processes in $[M]^-$. No other ions indicating explicitly the H-shift or isomerization reactions were observed, and the $[M - H]^-$ ions are not exception in this respect. The threshold energy for H-atom elimination was calculated from the values $\Delta H_f°(NO_2C_6H_4^-)$ = 19 kJ mol^{-1},[6] $\Delta H_f°(NO_2Ph)$ = 67 kJ mol^{-1}, and $\Delta H_f°(H)$ = 218 kJ mol^{-1} (see Ref. 7) using Eq. (2). This energy is 170 kJ mol^{-1} (1.76 eV).

$$NO_2C_6H_5 + e \longrightarrow NO_2C_6H_5^- \longrightarrow NO_2C_6H_4^- + H \quad (5)$$

This does not contradict the measured appearance energy (2.85 eV) for the first broad peak with a maximum at 3.7 eV in the curve of the effective yield of the $[M - H]^-$ ions (Fig. 1). This suggests preliminarily that fragmentary ions can be formed through simple bond cleavage. The peak under discussion is nonsymmetric, which is caused by $[M]^-$ decay from two resonance states close in energy. The second peak at 7 eV (more narrow and symmetric) indicates the single initial state of $[M]^-$. The curve of the effective yield of $[M - H]^0$ neutral components is presented in Fig. 1. This curve shows that the $[M - H]^-$ ions are formed in the autodetachment states. Mass spectro-

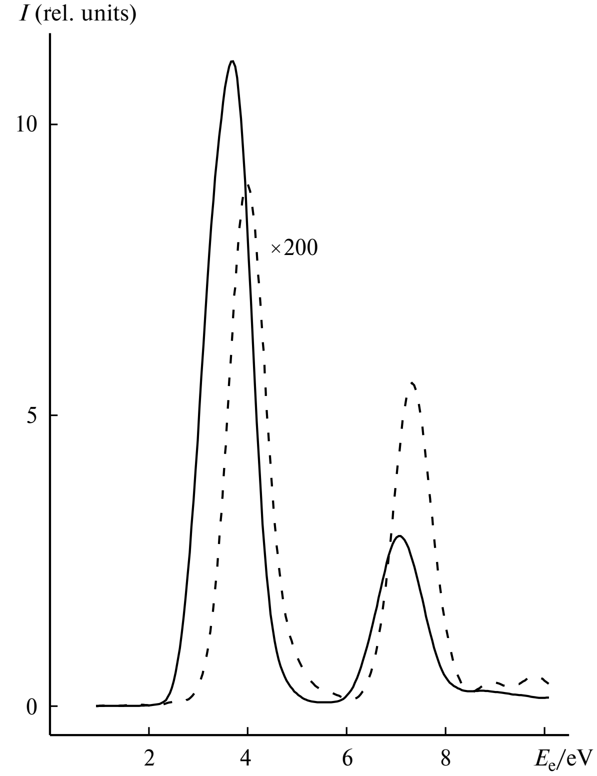

Fig. 1. Curves of the effective yield of the $[M - H]^-$ ions and $[M - H]^0$ neutral components (shown by dashed lines) from nitrobenzene at different electron energies (E_e).

metric observation of electron autodetachment by fragmentary NIs is a rare phenomenon. This process can occur only in polyatomic ions, whose internal energy exceeds the electron affinity energy of the corresponding neutral components. Similar phenomenon has been reported earlier.**[8]**

An interesting fact concerning nitrobenzene should be mentioned. The appearance energy for the first peak in the curve of the neutral component yield with a maximum at 4.0 eV is 3.51 eV. However, the threshold energy of electron autodetachment by the $NO_2C_6H_4^-$ ions is equal to the C—H bond dissociation energy in the molecule (ignoring the kinetic energy released at the moment of dissociation). Since in nitrobenzene and benzene ($D(C_6H_5—H) = 464$ kJ mol^{-1} (4.81 eV))**[7]** they differ insignificantly, we concluded that the measured appearance energy for $[M - H]^0$ is by 1.3 eV lower than the calculated energy. We found a similar divergence in the study of *p*-fluoroazobenzene. The analysis of this phenomenon suggested the formation of fragmentary ions with different structures.**[9]** Evidently, fragmentation of molecular NIs of nitrobenzene in the low-energy region is not restricted by simple bond cleavage. The estimation calculations show that the low appearance energy of neutral components corresponds to the isomerization process of phenoxide ion formation followed by electron autodetachment

$$\mathrm{NO_2C_6H_5^-} \longrightarrow \text{2-}\mathrm{NOC_6H_4OH^-} \longrightarrow$$
$$\longrightarrow \text{2-}\mathrm{NOC_6H_4O^-} + \mathrm{H} \longrightarrow \text{2-}\mathrm{NOC_6H_4O} + \mathrm{H} + e, \quad (6)$$

for which the threshold energy is 3.34 eV (calculations are given below). Skeletal rearrangement with the step of migration of the nitro group oxygen atom to the benzene ring has been substantiated previously**[2]** by the results of analysis of the metastable peak shape in the mass spectrum of the nitro compound corresponding to the process $[M]^- \rightarrow [M - NO]^-$.

Formula (4) was used to calculate the enthalpy of 2-phenoxide radical formation. In formula (4), the unknown ΔH_f°(2-NOC_6H_4OH) value was estimated as follows. Based on ΔH_f° for monosubstituted benzenes,**[7,10]** ΔH_f° of nitrosophenol was calculated using the additive macroincrementation scheme**[11]** (regardless of mutual arrangement of functional groups)

$$\Delta H_f^\circ(\mathrm{NOC_6H_4OH}) = \Delta H_f^\circ(\mathrm{NOPh}) +$$
$$+ \Delta H_f^\circ(\mathrm{PhOH}) - \Delta H_f^\circ(\mathrm{C_6H_6}) =$$
$$= 201 + (-96) - 83 = 22 \text{ kJ mol}^{-1}.$$

The resulting value was refined, because the additive scheme ignores the mutual influence of substituents in the benzene π-system. For instance, *p*-nitrophenol ($\Delta H_f^\circ = -117$ kJ mol^{-1})**[7]** exhibits stabilization compared to the calculated value ($\Delta H_f^\circ = -112$ kJ mol^{-1}), while the *ortho*-isomer is characterized, on the contrary, by destabilization ($\Delta H_f^\circ = -105$ kJ mol^{-1}).**[7]** Since the NO group is weaker than the NO_2 group in polarizability,**[12,13]** the stabilization effect in nitrosophenol should not exceed that in nitrophenols. Therefore, this value was accepted (estimated) as 5 kJ mol^{-1}. Taking into account this correction, the above calculated enthalpy of formation of 2-nitrosophenol ($\Delta H_f^\circ = 22$ kJ mol^{-1}) finally was 27 kJ mol^{-1}. The O—H bond dissociation energy in phenols is 362 kJ mol^{-1}.**[7]** Therefore, ΔH_f°(2-NOC_6H_4O) = 362 − 218 + 27 = 171 kJ mol^{-1}. Finally, for the threshold energy of the process described by Eq. (6) we have

$$E_{\mathrm{app}}([M - H]^0) = \Delta H_f^\circ(\text{2-}\mathrm{NOC_6H_4O}) +$$
$$+\Delta H_f^\circ(\mathrm{H}) - \Delta H_f^\circ(\mathrm{NO_2Ph}) =$$
$$= 171 + 218 - 67 = 322 \text{ kJ mol}^{-1} \text{ (3.34 eV)}.$$

The structure of the $[M - H]^-$ ions in the high-energy region differs from that in the low-energy region, which follows from analysis of the dependence of the average lifetime on the electron energy (Fig. 2). The τ_a value determined in mass spectrometric experiment is an integral characteristic of NIs decay in a strictly specified time interval of measurements. Since $1/\tau_a$ can formally be interpreted as a macrocanonical decay rate constant, the τ_a function should be continuous and monotonic within the energy region of the decay. Two peaks are far apart in the curve of the yield of the $[M - H]^-$ ions, and the

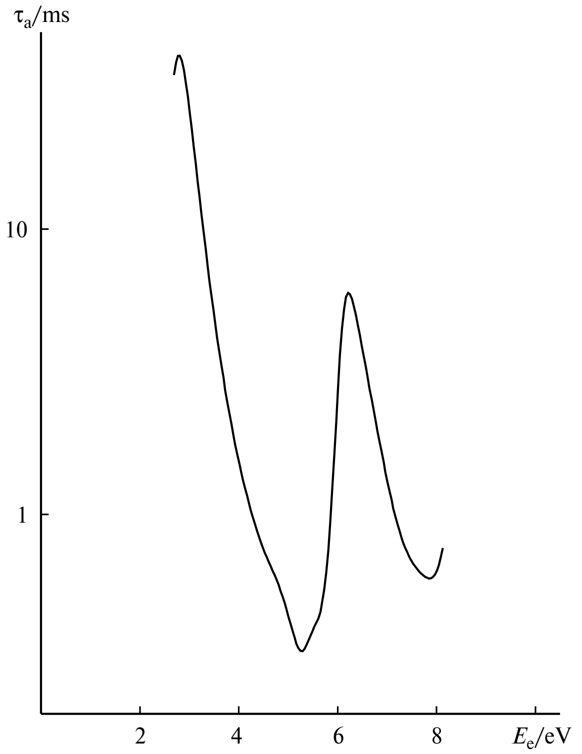

Fig. 2. Plot of the average lifetime of the $[M - H]^-$ ions from nitrobenzene relatively to electron autodetachment (τ_a) *vs.* electron energy (E_e).

regions of their abundance are not virtually overlapped. Electron autodetachment within each region is characterized by a pronounced dependence of τ_a: the lifetime decreases with an increase in the electron energy, which is caused by an enhancement of the efficiency of the process with an increase in the internal energy of ions. At the same time, the τ_a function is not monotonic in the energy region covering both peaks: the function undergoes a sharp jump at the boundary of two regions.

The shape of the τ_a function does not allow one to unambiguously determine the structure of ions in the high-energy region, because the efficiency of electron autodetachment is determined by the dependence of the microcanonical decay rate constant on the internal energy of NIs and their distribution function. The quantitative estimation of these parameters is a complicated procedure and represents an independent problem,[14] whose solution is beyond the present report. It is most likely that the cyclic structure of the $NO_2C_6H_4^-$ ion takes place in an energy region of 7 eV for the $[M - H]^-$ fragmentary ions. This structure corresponds to the requirement of minimum structural changes, which becomes decisive under the conditions of competition of electron autodetachment in $[M]^-$. At the same time, we do not ignore a possibility of $[M]^-$ dissociation with benzene ring opening and formation of linear $[M - H]^-$ ions, for example, $HC{\equiv}CCH{=}CHC(NO_2){=}CH^-$ or $H_2C{=}C(NO_2)CH{=}CHC{\equiv}C^-$. However, an electron cannot be autodetached by such ions. The $\Delta H_f°$ values of the corresponding radicals estimated by the additive microincrementation scheme[15] with allowance for group contributions[16] are 550 and 590 kJ mol^{-1}, respectively. The threshold energy for formation of the neutral components is ~7.3 and ~7.7 eV, respectively. The structure of the $CH_2{=}C(NO)C(O){=}CHC{\equiv}CH$ oxy radical, whose $\Delta H_f°$ is estimated as 420 kJ mol^{-1}, can correspond to the experimentally measured value of E_{app} = 6.85 eV for the $[M - H]^0$ neutral components.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 06-03-32412a) and the Russian Science Support Foundation.

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Received March 9, 2005;
in revised form December 22, 2005