MASS SPECTRA OF NEGATIVE IONS OF CONDENSED AROMATIC HYDROCARBONS AND BIPHENYL

I. Kh. Aminev, V. I. Khvostenko,
V. P. Yur'ev, and G. A. Tolstikov

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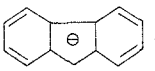
Substantial fragmentation of the molecule occurs in the resonance capture of electrons by alkylbenzene molecules [1, 2]. The process of ring decomposition was not detected for the condensed hydrocarbons like naphthalene (I), fluorene (II), anthracene (III), phenanthrene (IV), and biphenyl (V). A single fragmentary negative ion is formed by the cleavage of one hydrogen atom from the molecular ion. In energy, the maxima on the curves of the effective yield of the $(M-H)^-$ ions of these compounds coincide with the maximum for the corresponding benzene (VI) ion, but the processes of electron capture, with a cleavage of the hydrogen atom in (I), (II), and (V), occur in a broader range of electron energies. As can be seen from Fig. 1, the width of the curves for the effective yield of the $(M-H)^-$ ions at half-height is, respectively, equal to 1.7, 1.9, and 2 eV for (II), (V), and (I); the analogous curve for (VI) has a half-height width of 0.9 eV.

The reaction of electrons with (II) gives still another process for the formation of the $(M-H)^-$ ions, with a maximum yield at 1.6 eV. Apparently, this low-energy process corresponds to the cleavage of a hydrogen atom from the CH_2 group and the formation of the  ion, which finds an analogy with the process for the formation of the cyclopentadienyl anion from cyclopentadiene [3].

For (III) an inflection is observed on the curve of the effective yield of the $(M-H)^-$ ions, which can be interpreted as being a superposition of the decomposition peaks of two states of the molecular negative ion that differ in symmetry. For (IV) the inflection is expressed weakly, and here the lower symmetry of the phenanthrene molecule (C_{2v} vs D_{2h}) can lead to a blending of the states of the M^- ion that differ in anthracene. The undissociative capture by the molecules of electrons, the energy of which is close to zero, with the formation of molecular negative ions that are long-lived with respect to autoionization, is observed only for (III), which correlates with the relatively high electron affinity of (III) when compared with the other discussed compounds [4]. Taking the average life span of the SF_6^- ions with respect to autoionization as equal to 68 μsec [5], the average life span of the molecular ions with respect to autoionization was estimated as equal to ~21 μsec for (III). (The estimate was made by comparing the number of negative ions and the number of multiplier-recorded neutral particles that are formed as the result of autoionization of the ions.)

Employing the formation cross section of the $(M-H)^-$ ions for (VI) as a standard, the effective formation cross section of the M^- and $(M-H)^-$ ions for (III) was estimated as, respectively, being $1 \cdot 10^{-16}$ and $2 \cdot 10^{-17}$ cm^2. The different behavior of the isomeric (III) and (IV) molecules during reaction with electrons makes it possible to easily distinguish these compounds when recording the negative ions; the large formation cross section of M^- for (III) makes it possible to determine the presence of (III) (less than 1%) in other compounds.

EXPERIMENTAL METHOD

The study was made on an MX-13-03 mass spectrometer, which was adapted for recording negative ions. The energy scale of the electrons was calibrated and the energy distribution of the electrons was

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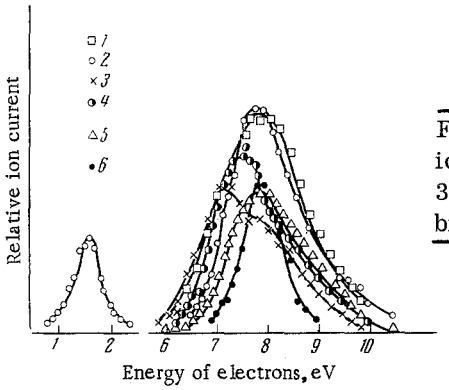

Fig. 1. Effective yield of $(M-H)^-$ ions: 1) naphthalene; 2) fluorene; 3) anthracene; 4) phenanthrene; 5) biphenyl; 6) benzene.

checked by the shape of the curve for the effective yield of SF_6^- ions from sulfur hexafluoride. During experiment the energy distribution of the electrons was ~0.4 eV at half-height, and the electron current was ~1 μA. The samples of the investigated compounds in a glass ampul were inserted into the region of the ionization source of the ions.

CONCLUSIONS

The positions of the maxima of the effective yield of the $(M-H)^-$ ions on the energy scale of the electrons for condensed hydrocarbons and biphenyl coincide with the maximum yield of the $(M-H)^-$ ions for benzene. The existence of a molecular ion M^-, with a life span with respect to autoionization of 21 μsec, was observed for anthracene.

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