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Abstract

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EXCITED STATES OF POSITIVE IONS AND PROCESSES OF DISSOCIATIVE PHOTOIONIZATION OF AROMATIC AMINES

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We have previously shown that in the spectral region up to 1100 Å (11.2 eV) the only primary process of photoionization of benzene and its methyl and amino derivatives is the process of formation of molecular ions ([1]). The study of photoionization processes at higher photon energies has made it possible to obtain new data on the excited states of positive ions and to study the formation of a number of fragment ions during photoionization.

Extension of the spectral region to 885 Å (14 eV) was achieved by using differential pumping of the monochromator of a photo-mass-spectrometric apparatus, similar to that described earlier ([1,2]). The monochromator was pumped by two mercury diffusion pumps: DRN-50 (immediately behind the vacuum-tight entrance slit of the monochromator) and NR-50 (in the region of the diffraction grating). At a hydrogen pressure in the light source (a high-voltage hydrogen lamp) of about 2 torr, the pressure in the ion-source region of the mass spectrometer was $(7—10) \cdot 10^{-6}$ torr, and in the analyzer region $(3—5) \cdot 10^{-8}$ torr. The photon monochromaticity at half-height of the lines, with the monochromator slit width used in this work of 0.2 mm, was 6 Å (0.04 eV at a photon energy of 10 eV and 0.06 eV in the region of 12.5 eV).

The ion currents at the output of the mass spectrometer, at a pressure of the investigated substance of $10^{-4}—10^{-5}$ torr, for the most intense peaks were $10^{-14}—10^{-6}$ A. The ion currents were recorded with an SI-01 ion counter in the mode of measuring the average current of an electron multiplier. With a time constant of the recording circuit of 1 sec and a measurement accuracy of 15%, the detector sensitivity was $2 \cdot 10^{-18}$ A.

To reduce the background caused by ion-molecule reactions, a potential 0–100 V higher than the potential of the ionization chamber was applied to a special diaphragm in front of the electron multiplier.

This work discusses the results of a study of photoionization of aromatic amines

(aniline, N-methylaniline, N,N-dimethylaniline, and benzylamine). Figures 1–4 show the ionization-efficiency curves of the compounds investigated. Along the ordinate is plotted the ratio of the photoionization current to the incident radiation flux; along the abscissa, the photon energy. The points correspond to the mean values of three successive experiments. To obtain additional information on the mechanisms of dissociative photoionization and the structure of the fragment ions formed, samples of aromatic amines enriched with D in the amino group were prepared by isotopic exchange with D_2O, and their photoionization mass spectra were studied.

The excited states of molecular ions were determined from the bends in the ionization-efficiency curves, leading to an increase in the slope of these curves. The energies of the excited states of positive ions of the molecules investigated are given in Table 1. For comparison with aromatic amines, Table 1 includes data on the excited states of benzene and pyridine ions, which were obtained by us by an analogous method.*

* We intend subsequently to publish more detailed materials on the photoionization of benzene derivatives in the spectral region up to 850 Å.

The table also gives the values of the excitation energies of the ions obtained from the distributions of photoionization electrons over kinetic energies ([3]), and, in the case of aniline, the energies of the filled one-electron MOs of the ground state of aniline calculated by the LCAO MO method ([4]). The first of the calculated values given corresponds to a calculation by the Pariser–Parr–Pople method, and the second to the Hückel method.

In aniline the free electrons of the nitrogen atom are strongly conjugated with the π-electrons of the ring. Therefore the calculation ([4]) was carried out for a single system of 8π electrons. Removal, upon ionization, of an electron from the highest of the filled MOs gives an ion in the ground state. Ejection of an electron from the three lower-lying orbitals leads to the formation of molecular ions in excited states (8.8, 10.2, and 12.6 eV). The fourth state of aniline ions found by us (11.7_5 eV) is associated by us with ejection of a bonding electron, since excitation to this state is accompanied by a process of dissociative ionization with formation of a fragment ion with $M/e = 66$ (appearance potential of the fragment ion $= 12.3 \pm 0.1$ eV). The contribution of this process to the total photoionization cross section at a photon energy of 13 eV is about 3%. The ion with $M/e = 66$ is the most intense of the fragment ions in the electron-impact mass spectrum. A study of the mass spectrum of aniline N^{15} ([5]) showed that, at an electron energy of 70 eV, 92% of the total number of ions of this mass are formed as the result of the process:

Fig. 1. Photoionization efficiency curves of aniline. **1** $-M/e = 93$; **2** $-M/e = 66$

$$C_6H_5NH_2 + e \rightarrow C_5H_6^+ + HCN\ (HNC) + 2e \qquad (1)$$

Fig. 1. Photoionization efficiency curves of aniline. 1 –M/e = 93; 2 –M/e = 66

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Fig. 2. Photoionization efficiency curves of methylaniline. 1 –M/e = 107; 2 –M/e = 106

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Fig. 2. Photoionization efficiency curves of methylaniline. **1** $-M/e = 107$; **2** $-M/e = 106$

and 8% as the result of the process:

$$C_6H_5NH_2 + e \rightarrow C_4NH_4^+ + C_2H_3 + 2e. \quad (2)$$

Our results on the photoionization mass spectrum of aniline deuterated in the amino group lead to the conclusion that, at a photon energy of 13 eV, ions with $M/e = 66$ are formed only as the result of the process:

$$C_6H_5NH_2 + h \rightarrow C_4NH_4^+ + (C_2H_3) + e. \quad (3)$$

In this case, 46% of C_2H_3 contains two H atoms of the amino group and one from the ring, 19% contains one H atom of the amino group and two from the ring, and 35% contains three H atoms from the ring.

Replacement of the H atoms of the amino group of aniline by methyl groups does not noticeably change the conjugation of the free electrons with the π-electrons of the ring. Therefore, in methylaniline and dimethylaniline the lower excited levels of the ions characteristic of the conjugated system of aniline are retained. The slight decrease in the energy of these levels may be explained by induc–

···tion effect of the methyl groups. However, the introduction of methyl groups substantially changes the ionization processes at energies greater than 11 eV. In this spectral region, with a large yield (50% of the total ionization cross section at a photon energy of 13 eV for methylaniline and 60% for dimethylaniline), H is split off from the molecular ions. Mass spectra of the photoionization of deuterated samples show that H is not split off from the amino group. In view of the fact that the corresponding process does not occur in aniline, H must be detached from the methyl groups:

$$C_6H_5NHCH_3 + h\nu \rightarrow C_6H_5NHCH_2^+ + H + e, \quad (4)$$

Fig. 3. Photoionization-efficiency curves of dimethylaniline. 1 $-M/e = 121$; 2 $-M/e = 120$

Figure 3: Fig. 3. Photoionization-efficiency curves of dimethylaniline. 1 $-M/e = 121$; 2 $-M/e = 120$

Fig. 4. Photoionization-efficiency curves of benzylamine. 1 $-M/e = 107$; 2 $-M/e = 106$; 3 $-M/e = 30$

Figure 4: Fig. 4. Photoionization-efficiency curves of benzylamine. 1 $-M/e = 107$; 2 $-M/e = 106$; 3 $-M/e = 30$

$$\begin{matrix} \mathrm{CH_3} \\ \mathrm{C_6H_5N} \\ \mathrm{CH_3} \end{matrix} + h\nu \rightarrow \begin{matrix} \mathrm{CH_3} \\ \mathrm{C_6H_5N} \\ \mathrm{CH_2} \end{matrix}^{+} + \mathrm{H} + e. \tag{5}$$

The appearance potentials of the corresponding ions are equal to 11.0 ± 0.1 and 10.75 ± 0.05 eV.

Fig. 3. Photoionization-efficiency curves of dimethylaniline.
1 $-M/e = 121$; 2 $-M/e = 120$

In the photoionization mass spectra of aniline and methylaniline, ions with the structure $C_6H_5NH^+$ are absent, although calculation from thermochemical data [6] of the ionization potential of the radical C_6H_5NH [7] gives, for the appearance potential of this ion from aniline, 11.8 eV, and from methylaniline, 10.9 eV. Apparently, ions of such a structure are not formed during photoionization, or are formed with a very small yield (less than 0.1% of the total ionization at 13 eV).

In pyridine, in contrast to aniline, the free electrons of nitrogen are not conjugated with the π-electrons of the ring. Therefore, for the positive ion of pyridine one should expect the system of energy levels characteristic of benzene, which is confirmed by the experimental data (Table 1).

Conjugation of the free electrons of nitrogen with the π-electrons of the ring is also absent in benzylamine. However, already at energies 0.8 eV above the ionization potential (i.p.) of the molecule, an intense decomposition of molecular ions begins, with detachment of H (appearance potential $= 9.3 \pm 0.1$ eV; contribution to the total ionization cross section at 13 eV about 60%), which leads to the disappearance of structure on the ionization-efficiency curve with formation of molecular ions. A study of deuterated samples of benzylamine showed that in this case also the hydrogen is not detached from the amino group. Apparently, as in the case of methylaniline, the ion is formed as a result of detachment of a hydrogen atom from the methylene group:

Fig. 4. Photoionization-efficiency curves of benzylamine.
1 $-M/e = 107$; 2 $-M/e = 106$; 3 $-M/e = 30$

$$C_6H_5CH_2ND_2 + h\nu \rightarrow C_6H_5CHND_2^+ + H + e. \quad (6)$$

At photon energies exceeding 11.65 ± 0.1 eV, an increase is observed in the slope of the photoionization efficiency curve with formation of the ion $C_7NH_8^+$. This is probably connected with the formation of $C_6H_5CHNH_2^+$ ions in an excited state. In addition to process (6), the following processes of dissociative ionization were found in benzylamine:

$$C_6H_5CH_2ND_2 + h \rightarrow C_7H_7^+ + ND_2 + e \quad (a.p. = 11.7 \pm 0.1 \text{ eV}), \quad (7)$$

$$C_6H_5CH_2ND_2 + h \rightarrow C_6NH_2D_2^+ + (C_2H_5) + e \quad (a.p. = 11.0 \pm 0.2), \quad (8)$$

$$C_6H_5CH_2ND_2 + h \rightarrow CH_2ND_2^+ + C_6H_5 + e \quad (a.p. = 11.0 \pm 0.1). \quad (9)$$

The contributions of these processes to the total photoionization cross section at a photon energy of 13 eV are 2, 3, and 7%, respectively. In the formation of ions by reaction (8), both H atoms of the amino group remain in the charged fragment, while processes (7) and (9) correspond to simple cleavage of the N–C and C–C bonds. In terms of the types of processes of dissociative ionization and their energetics, benzylamine is more similar to aliphatic amines than to other aromatic amines.

Table 1

Energy levels of positive ions (relative to the ground state of the molecule, eV)

Molecule	Ground state of the ion (a.p.)	Excited states of the ion
Aniline ([3])	7.67 ± 0.03	8.8 ± 0.1; 10.2 ± 0.1; 11.8 ± 0.1; 12.6 ± 0.1;9.2 ± 0.1; 10.3 ± 0.2;
Aniline ([4])	8.18; 8.26	9.1; 9.2; 10.2; 10.0;
Methylaniline ([3])	7.30 ± 0.05	8.55 ± 0.05; 10.0 ± 0.1;9.0 ± 0.1; 10.0 ± 0.2;
Dimethylaniline ([3])	7.10 ± 0.05	7.75 ± 0.05; 8.6 ± 0.1; 9.8 ± 0.1;8.5 ± 0.1; 9.7 ± 0.2;

Molecule	Ground state of the ion (a.p.)	Excited states of the ion
Benzylamine	8.64 ± 0.05	
Benzene	9.20 ± 0.05	$10.3_5 \pm 0.1$; 11.5 ± 0.1;
Pyridine	9.20 ± 0.05	10.30 ± 0.05; 11.05 ± 0.1;

Thus, the a.p. of the ion corresponding to the detachment of H from methylamine is 10.2 ± 0.2 eV ([8]), and in more complex aliphatic amines the main process of dissociative ionization, both under electron impact and under photoionization ([8,9]), is associated with cleavage of the C–C bond nearest to the N–C bond. This allows the conclusion that, although the first ionization potential of benzylamine is associated with removal of one of the π-electrons of the benzene ring, the ionization processes at energies greater than 9.5 eV are mainly caused by absorption in the amino group.

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CITED LITERATURE

1. M. E. Akopyan, F. I. Vilesov, A. N. Terenin, DAN, **140**, 1037 (1961).
2. M. E. Akopyan, F. I. Vilesov, Kinetika i kataliz, **4**, 39 (1963).
3. F. I. Vilesov, B. L. Kurbatov, A. N. Terenin, DAN, **138**, 1329 (1961).
4. I. Fischer-Hjalmars, Arkiv Fysik, **21**, 123 (1962).
5. P. N. Rylander, S. Meyerson et al., J. Am. Chem. Soc., **85**, 2723 (1963).
6. G. L. Esteban, J. A. Kerr, A. F. Trotman-Dickenson, J. Chem. Soc., 1963, 3879.
7. T. F. Palmer, F. P. Lossing, J. Am. Chem. Soc., **85**, 1733 (1963).
8. J. Collin, Bull. Soc. chim. Belg., **62**, 411 (1953).
9. H. Hurzeler, M. G. Inghram, J. D. Morrison, J. Chem. Phys., **28**, 76 (1958).

Note: Figure translations are in progress. See original paper for figures.