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1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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MASS-SPECTROMETRIC STUDY OF THE PHOTOIONIZATION AND PHOTODISSOCIATION OF AMINE VAPORS

In our measurements of the photoionization potentials of vapors of organic compounds (1), it was assumed that, under irradiation of molecules by wavelengths in the vacuum ultraviolet region of the spectrum, elementary photoionization of the molecule occurs with removal of an electron.

On the other hand, it is known that, when molecular vapors are irradiated with short-wavelength radiation down to 1050 Å (quantum energy 11.8 eV), photodissociation of molecules also occurs; this has been studied in a number of works (see, for example, (2)).

For a detailed study of these processes we constructed a 90-degree mass spectrometer with an ion mean-trajectory radius of 126 mm*. The mass scan was automatic–exponential–with recording of the spectrum by a PS-01 self-recording instrument. The ion source was designed so that ionization of the gas under study could be produced separately by electrons or by photons, or by both simultaneously. The electron beam, as usual, was directed along the slit of the ion source; the photon beam was perpendicular to the slit.

With the clearly unfavorable irradiation of the space of the ionization chamber by undecomposed light from a hydrogen lamp (discharge current 2 A, voltage 1000 V) through a LiF window (transparent down to 1050 Å), the ion current at the collector was of the order of 10^{-13}–10^{-14}, while the pressure of the gas under study in the ion source was 10^{-4}–$5 \cdot 10^{-5}$ mm Hg. The following gaseous amines were studied: ammonia NH_3, hydrazine NH_2—NH_2, benzylamine C_6H_5—CH_2—NH_2, and aniline C_6H_5—NH_2. The mass spectra of these compounds obtained under irradiation are presented in Fig. 1. In them only elementary photoionization of the molecules is observed according to the scheme:

$$\mathrm{AB} + h\nu \rightarrow \mathrm{AB}^{+} + e.$$

Fig. 1. Mass spectra of amines obtained by ionization with light. 1 –ammonia, 2 –hydrazine, 3 –aniline, 4 –benzylamine.

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Fig. 2. Mass spectra of radicals upon photodissociation under the action of light. 1—ammonia, 2—hydrazine.

Figure 2: Fig. 2. Mass spectra of radicals upon photodissociation under the action of light. 1—ammonia, 2—hydrazine.

This result confirms our supposition that the photoionization currents observed in work (1) were indeed caused only elementary photoionization of molecules, and that, in any case, ionization processes with decomposition of the type

$$\mathrm{AB} + h\nu \rightarrow \mathrm{A}^+ + \mathrm{B}^- \quad \text{or} \quad \mathrm{AB} + h\nu \rightarrow \mathrm{A}^+ + \mathrm{B} + \mathrm{e}$$

were unlikely (less than 1% of the principal process).

If aniline and benzylamine vapors are irradiated not with photons but with electrons of energy about 11.5 eV, more complex mass spectra are observed, caused by processes of decomposition of molecules into ions.

It follows from this that the use of even a nonmonochromatic photon beam is more suitable in performing mass-spectrometric analyses of complex organic compounds and their mixtures than the use of an electron beam.

Fig. 2. Mass spectra of radicals upon photodissociation under the action of light. 1—ammonia, 2—hydrazine.

Fig. 3. Mass spectra of radicals upon photodissociation of benzylamine.

The use of monochromatic light, which makes it possible to determine ionization potentials with an accuracy of 0.02–0.03 eV, will make it possible to carry out additional analysis by photoionization thresholds and thus to identify even different isomers.

Fig. 3. Mass spectra of radicals upon photodissociation of benzylamine.

Figure 3: Fig. 3. Mass spectra of radicals upon photodissociation of benzylamine.

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* The magnet was kindly provided by Prof. N. I. Ionov, to whom we express our deep gratitude for his friendly assistance.

Our study of photodissociation was carried out as follows. First, the mass spectrum of the vapors of the substance under investigation was recorded at high electron energy without optical excitation. Then the electron energy was reduced to the value at which all peaks due to radicals disappeared, and irradiation with a hydrogen lamp was switched on. In this case, peaks of radicals appeared in the mass spectrum, formed by photodissociation of molecules followed by their ionization by electron impact. Figures 2 and 3 show the corresponding spectra obtained for vapors of ammonia, hydrazine, aniline, and benzylamine.

Ammonia. In Fig. 2 (spectrum 1) two peaks with masses 17 and 16 are visible, which correspond to the ions NH_3^+ and NH_2^+, respectively; consequently, along with photoionization of the molecule there is a process of its photodissociation according to the scheme

$$\mathrm{NH_3} + h\nu \rightarrow \mathrm{NH_2} + \mathrm{H}.$$

Hydrazine. In the case of hydrazine (Fig. 2, spectrum 2), an intense peak corresponding to the radical NH_2-NH is observed, and weak peaks corresponding to the radicals NH_2 and NH_2-N, which indicates a greater probability of detachment of a hydrogen atom than of the molecule breaking in half at the weaker $N-N$ bond (^{3}).

The photodissociation of ammonia and hydrazine was previously investigated in the work of Neuimin and Terenin (^{2}), where it was shown that the processes

$$\mathrm{NH_3} + h\nu_{\mathrm{B}} \rightarrow \mathrm{NH_2^*} + \mathrm{H} \rightarrow \mathrm{NH_2} + \mathrm{H} + h\nu_{\phi},$$

$$\mathrm{NH_2} - \mathrm{NH_2} + h\nu_{\mathrm{B}} \rightarrow \mathrm{NH_2^*} + \mathrm{NH_2} \rightarrow \mathrm{NH_2} + \mathrm{NH_2} + h\nu_{\phi}.$$

take place. It was noted that the fluorescence of the NH_2 radical in the case of hydrazine is considerably weaker than in the case of ammonia, which agrees with the mass spectra of hydrazine obtained in the present work.

Benzylamine. From Fig. 3 it is seen that there is an intense peak with mass number 106, corresponding to the ion $C_6H_5-CH_2-NH^+$, formed, evidently, upon photodissociation according to the scheme:

$$\mathrm{C_6H_5} - \mathrm{CH_2} - \mathrm{NH_2} + h\nu \rightarrow \mathrm{C_6H_5} - \mathrm{CH_2} - \mathrm{NH} + \mathrm{H}.$$

In addition, there are weaker peaks with masses 16 and 91, which are due to the ionized radicals $C_6H_5-CH_2$ and NH_2, obtained, evidently, upon photolysis of benzylamine according to the scheme:

$$\mathrm{C_6H_5} - \mathrm{CH_2} - \mathrm{NH_2} + h\nu \rightarrow \mathrm{C_6H_5} - \mathrm{CH_2} + \mathrm{NH_2}.$$

Aniline. In the study of aniline vapors, photodissociation of it into any radicals was not detected. We made repeated attempts, following the example of work (2), to obtain the fluorescence spectrum of the NH_2^+ radical upon irradiation of benzylamine and aniline vapors with the light of a powerful hydrogen lamp through a LiF window. However, no positive result was obtained. The absence of photodissociation with excitation of the NH_2 radical can be explained by the fact that the benzene ring, having a large number of vibrational degrees of freedom, draws off the excess energy absorbed by the $C-NH_2$ bond, and also deactivates the excited NH_2 particle. Such withdrawal of energy is especially significant in the case of the aniline molecule, in which the NH_2 group is directly connected with the benzene ring. The presence of the NH_2 radical in the mass spectrum of benzylamine testifies to the cleavage of the NH_2 radical occurring here, which is connected with the fact that the CH_2 group is, as is known, insulating and hinders the direct transfer of energy from NH_2 and the $C-NH_2$ bond into the benzene ring. With sufficiently powerful irradiation, it is possible in benzylamine vapors to observe the appearance of the excited NH_2 radical from its fluorescence spectrum.

Moreover, this point of view agrees well with the small quantum yield of photoionization near the threshold for these molecules (3-5%) in comparison with molecules of other compounds (30-50%).

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named after A. A. Zhdanov

Received
30 V 1958

CITED LITERATURE

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