Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965. Vol. 161, No. 5

PHYSICAL CHEMISTRY

M. E. AKOPYAN, F. I. VILESOV

MASS-SPECTROMETRIC STUDY OF THE PHOTOIONIZATION OF LOW-VOLATILITY ORGANIC COMPOUNDS

(Presented by Academician A. N. Terenin, 14 X 1964)

During the last 5 years, a mass-spectrometric method has been successfully used to study the processes of photoionization of complex organic molecules ([1],[2]). It should be noted, however, that, because of experimental difficulties, the choice of objects of investigation has been limited to volatile organic compounds.

In the present work, the first attempt has been made to extend the mass-spectrometric method for studying photoionization to low-volatility compounds. The paper presents and discusses the results of a study of the photoionization of anthracene, uracil, thymine, and certain amino acids (glycine, α- and β-alanine, β-phenylalanine).

The apparatus has been described previously ([2]). Most of the compounds studied decompose at temperatures above 200°, while at lower temperatures their vapor pressure is insufficient for introducing the sample into the ionization chamber by means of an inlet system with a buffer volume and a leak. Therefore, evaporation of the samples was carried out in the immediate vicinity of the photoionization region. A weighed portion of the substance under investigation (20-30 mg) was placed in a nickel crucible heated by a tungsten spiral. The temperature of the crucible was regulated by changing the heating current of the spiral. The ionization chamber was heated by the same spiral and by the cathode of the ion source. The ionization chamber had no slit forming an electron beam, so that electrons emitted by the cathode did not enter the ionization region. Heating of the ionization chamber reduces condensation in it of the vapors under investigation, which leads to more stable operation of the ion source.

The temperature of the crucible was chosen so that, over the course of 1.5–2 h, stable ion currents of the order of 10^{-16} A were obtained at a photon energy of 10.2 eV. The absence of decomposition was checked from the reproducibility of the mass spectra at different stages of heating.

Figure 1A shows the photoionization efficiency curve (p.i.e.) of anthracene.

Fig. 1

Figure 1: Fig. 1

The dashed arrows in the figure indicate the positions of filled one-electron molecular orbitals according to theoretical calculations (^{3}). The solid arrows show the positions of the same orbitals obtained from studies of the distribution of kinetic energies of electrons ejected in the external photoelectric effect from a solid layer of anthracene (^{4}). The threshold for the appearance of anthracene ions (7.40 ± 0.05 eV) corresponds to the removal of an electron from the highest of the filled molecular orbitals. The position of the threshold on the energy axis, within the experimental error, coincides with the adiabatic ionization potential (i.p.) of anthracene, 7.38 ± 0.03 eV (^{5}). The p.i.e. of anthracene has a number of breaks, which may be explained by processes of formation of excited molecular anthracene ions as a result of removal of electrons from inner molecular orbitals. The nature of the break at 12.1 ± 0.1 eV is unclear. The regularly reproducible maximum on the p.i.e. in the region 8.7–8.8 eV is apparently due to preionization processes. Processes of dissociative photoionization in the case of anthracene in the energy region up to

13 eV were not detected by us. In Fig. 1, B the ionization-efficiency curves of uracil are shown. Similar curves were obtained for thymine (5-methyluracil). The thresholds for the appearance of molecular ions are sharp and coincide with the adiabatic ionization potentials of the molecules (9.47 ± 0.03 eV for uracil and 8.94 ± 0.02 eV for thymine). The ionization-efficiency curves with formation of molecular ions have a not very pronounced, but reproducible, structure. The structure can be explained by the formation of excited molecular ions with appearance potentials of 10.2 ± 0.1 and 10.8 ± 0.1 eV in the photoionization of uracil, and 9.8 ± 0.2 and 10.8 ± 0.1 eV in the photoionization of thymine.

In the photoionization of both uracil and thymine, a process of dissociative photoionization was found, associated with the detachment of the neutral fragment CONH from the molecular ions. The appearance potentials of the corresponding ions from both molecules coincide (10.8 ± 0.1 eV). The process of CONH detachment was also observed under electron impact of cyclic amides (^{6}). In the photoionization of thymine at photon energies exceeding 12 eV, a process of formation of a fragment ion with $M/e = 54$ proceeds with high yield (appearance potential 11.5 ± 0.1 eV). The ions apparently are formed as a result of the reaction:

$$C_5N_2O_2H_6 \xrightarrow{h\nu} C_3NH_4^+ + C_2O_2NH_2 + e.$$

Fig. 1

Since methyl substitution leads to a significant (0.5 eV) change in the ionization potential of uracil, it should be assumed that the first ionization potentials of uracil and thymine are associated with removal of a π-electron of the C=C bond. This is also confirmed by the fact that the first I.P. of crotonaldehyde CH_3–CH=CH–CHO (9.73 ± 0.01 eV) should be assigned to removal of a π-electron, since the spectroscopically determined I.P. associated with removal of the p-electrons of the oxygen atom is noticeably higher (10.187 eV) (5). Then excited molecular ions of uracil and thymine may be formed as a result of removal, during photoionization, of electrons from other chromophoric groups.

Table 1

Molecule	I.P., eV	I.P., eV
	this work	literature
Glycine	9.00 ± 0.05	9.5 ± 0.2 (8)
α-alanine	8.65 ± 0.05	
β-alanine	8.80 ± 0.05	
β-phenylalanine	8.4 ± ?*	

* There is a long, low-intensity tail that can be traced down to 7.4 eV.

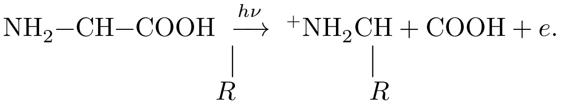
Thus, removal of the p-electrons of the oxygen atom can explain the formation of excited ions with an appearance potential of about 10 eV, while excitation at photon energies greater than 10.8 eV is apparently associated with removal of the lone-pair electrons of the N atom.

For photoionization of amino acids, a large role of dissociative photoionization processes is characteristic. Peaks of molecular ions were observed for all amino acids investigated, but their intensity was so small that it did not allow the ionization potentials of the amino acids to be determined reliably. Therefore, to determine the ionization potentials, the method of measuring the total photoionization current was used, without mass analysis. For this purpose a stainless-steel cuvette with a LiF window was used, capable of being heated to a temperature of 300°. The construction of the cuvette and the measurement procedure were analogous to those described earlier (7). The obtained values of the ionization potentials of the amino acids are given in Table 1.

In Fig. 1B, D are shown the total photoionization efficiency curves obtained by the method described above (curves 1) and the I.E.C. with the formation of fragment ions NH_2–CH_2^+ in the photoionization of β-alanine (2) and $NH_2(CH)C_6H_5CH_2^+$ (2) and $NH_2CHCOOH$ (3) in the photoionization of β-phenylalanine.

As is seen from Fig. 1, the ionization yield at the thresholds for formation of molecular ions is very small, which is also characteristic of some other compounds containing an amino group (for example, aliphatic amines (9)). The analogy indicates that photoionization of amino acids is associated with removal of one of the lone-pair electrons of the nitrogen atom. The small ionization yield near the threshold may be explained by a change, upon ionization, in the character of hybridization of the lone-pair electrons with the σ-bonding electrons, which leads to a change in interatomic distances. For example, there is spectroscopic evidence that ammonia in the ground state has the structure of a regular pyramid, whereas in the excited and ionized states it has a structure close to planar (10).

The character of the dissociative photoionization processes observed for amino acids confirms the conclusions made above. As in the case of aliphatic amines (11), the least energy is required by processes associated with rupture of the C—C bond located in the β-position to the amino group. In this case the fragment containing the nitrogen atom remains charged. Thus, in the photoionization of all the α-amino acids investigated, we observed the following process:



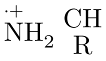
$$\mathrm{NH_2{-}}\underset{\substack{|\\ R}}{\mathrm{CH}}\mathrm{{-}COOH} \xrightarrow{h\nu} {}^{+}\mathrm{NH_2}\underset{\substack{|\\ R}}{\mathrm{CH}} + \mathrm{COOH} + e.$$

The appearance potentials (a.p.) of the corresponding ions are 9.6 $\pm$ 0.1 eV in the photoionization of glycine (R = H), 9.3 $\pm$ 0.1 eV in the photoionization of alanine ($R = CH_3$), and 9.1 $\pm$ 0.1 eV in the photoionization of phenylalanine ($R = C_6H_5CH_2$). In the photoionization of β-alanine, the process of rupture of the β—C—C bond is observed according to the reaction:

$$\mathrm{NH_2CH_2CH_2COOH} \xrightarrow{h\nu} \cdot\overset{+}{\mathrm{N}}\mathrm{H_2CH_2} + \mathrm{CH_2COOH} + \mathrm{e}$$

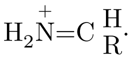
with an a.p. of the ions equal to 9.5 $\pm$ 0.1 eV.

Fragment ions



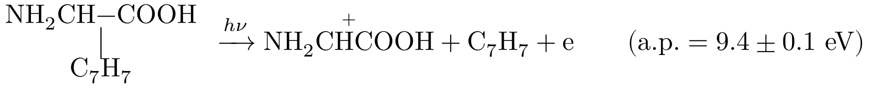
$$\overset{\cdot+}{\mathrm{N}}\mathrm{H_2}\,\genfrac{}{}{0pt}{}{\mathrm{CH}}{\mathrm{R}}$$

form intense peaks in the mass spectra of amino acids obtained upon ionization by high-energy electrons (10-17 eV) (8,11), which indicates their high stability. The stability of these ions may be associated with the existence of the stable structure

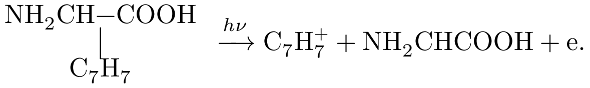


$$\mathrm{H_2}\overset{+}{\mathrm{N}}\mathrm{{=}C}\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{R}}.$$

In the photoionization of β-phenylalanine, rupture of the second β-C—C bond (detachment of the side group) was observed. However, the presence of a benzene ring in the side group leads to the charge being able to stabilize in either of the fragments formed:



$$\underset{\substack{| \\ C_7H_7}}{NH_2CH{-}COOH} \xrightarrow{h\nu} NH_2\overset{+}{CH}COOH + C_7H_7 + e \qquad (\text{a.p.} = 9.4 \pm 0.1\ \text{eV})$$



$$\underset{\substack{| \\ C_7H_7}}{NH_2CH{-}COOH} \xrightarrow{h\nu} C_7H_7^+ + NH_2CHCOOH + e.$$

The only rearrangement ion detected by us is likewise associated with stabilization of the charge on the side chain:

$$NH_2CH(C_7H_7)COOH \xrightarrow{h\nu} C_7H_8^+ + NHCHCOOH + e.$$

The photoionization efficiency curves of amino acids with formation of fragment ions reveal a structure coinciding with the structure of the curves of the total photoionization efficiency (Fig. 1, B, G). The p.i.e. curves with formation of molecular ions of amino acids, within the limits of experimental error (±20%), do not reveal such a structure. This indicates that the molecular ions of amino acids formed during photoionization in excited electronic states, like the ions in the ground state, almost completely decompose with formation of fragment ions.

A study of the energetics of photoionization processes confirms the general picture of amino-acid fragmentation in the formation of electron-impact mass spectra (8,12).

Physical Institute
of Leningrad State University
named after A. A. Zhdanov

Received
29 IX 1964

CITED LITERATURE

[1] H. Hurzeler, M. G. Inghram, J. D. Morrison, J. Chem. Phys., **28**, 76 (1958); B. Steiner, M. G. Inghram, C. F. Geese, J. Chem. Phys., **34**, 189 (1961); F. Elder, C. Giese et al., J. Chem. Phys., **36**, 3292 (1962); R. I. Schoen, J. Chem. Phys., **37**, 2032 (1962); M. E. Akopyan, F. I. Vilesov, A. N. Terenin, DAN, **140**, 1037 (1961).
[2] M. E. Akopyan, F. I. Vilesov, DAN, **158**, 1386 (1964).
[3] C. A. Coulson, Proc. Phys. Soc., **60**, 257 (1948); J. R. Platt, J. Chem. Phys., **17**, 484 (1949).
[4] F. I. Vilesov, A. A. Zagrubskii, D. Z. Garbuzov, Fiz. tverd. tela, **5**, 2000 (1963).

[5] F. I. Vilesov, UFN, **81**, 669 (1963).
[6] G. Spiteller, M. Spiteller-Friedman, Monatsh. Chem., **93**, 632 (1962); K. Heyns, H. Grützmacher, Ann. Chem., **669**, 189 (1963).
[7] F. I. Vilesov, V. M. Zaitsev, DAN, **154**, 886 (1964).
[8] G. Junk, H. Svec, J. Am. Chem. Soc., **85**, 639 (1963).
[9] K. Watanabe, J. R. Mottl, J. Chem. Phys., **26**, 1773 (1957).
[10] A. B. F. Duncan, Phys. Rev., **47**, 882 (1935), **50**, 700 (1936); D. E. Dougias, J. M. Hollas, Canad. J. Phys., **39**, 479 (1961); G. Herzberg, Ann. Rev. Phys. Chem., **9**, 315 (1958); C. A. Coulson, H. L. Strauss, Proc. Roy. Soc., **269A**, 443 (1962).
[11] H. Hurzeler, M. G. Inghram, J. D. Morrison, J. Chem. Phys., **28**, 76 (1958).
[12] K. Bieman, J. A. McCloskey, J. Am. Chem. Soc., **84**, 3192 (1962); K. Bieman, T. Seibl, F. Gapp, J. Am. Chem. Soc., **83**, 3795 (1961); K. Heyns, H. Grützmacher, Ann. Chem., **667**, 194 (1963).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.