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Fig. 1. Diagram of the ionization cell

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Abstract**Full Text****PHYSICAL CHEMISTRY****F. I. Vilesov, V. M. Zaitsev****PHOTOIONIZATION OF PHENYL DERIVATIVES OF GROUP 5 ELEMENTS***(Presented by Academician A. N. Terenin on January 26, 1963)*

The use of aromatic derivatives of elements in various fields of research, including the study of the consequences of nuclear transformations^{1,2}, required knowledge of the ionization potentials of these compounds, their stability in various excited states, etc. To obtain these data, the photoionization of triphenyl derivatives of Group 5 elements was studied in the gas phase on an apparatus described earlier³. The radiation source was a high-voltage hydrogen lamp. To monochromatize the radiation, a one-meter vacuum monochromator of normal incidence with a concave diffraction grating of 1200 lines/mm was used, concentrating light in the first order in the spectral region 1000–2000 Å. Since most of the compounds investigated have an insignificant vapor pressure at room temperature, the photoionization study was carried out in a specially constructed cell that could be heated to 200–250°. A diagram of the cell is shown in Fig. 1.

Fig. 1. Diagram of the ionization cell: 1 –clamping nut, 2 –spring washers, 3 –sealing washers, 4 –back wall, 5 –cell body, 6 –thrust washers, 7 –fluorite window, 8 –shield (fluoroplast-4), 9 –electrometer output, 10 –electrical-output insulator, 11 –kovar feedthrough, 12 –pumping.

The cell was made in the form of a hollow cylinder (diameter 400 mm, length 110 mm) of stainless steel 1Kh18N9T. All seals and insulators for the feedthroughs were made of fluoroplast-4. Crystals of the substances under investigation were placed directly in the cell. To obtain reliable measured photoionization currents (10^{-10} – 10^{-12} A), the cell was maintained at a temperature of 20–100°. During measurements, the vapors of the substance were continuously pumped out through a narrow channel in the kovar feedthrough (the electrometer output passes through this channel). Continuous renewal of the vapors ensured the necessary purity and a stable photoionization current, which was amplified by a “Kaktus” electrometer amplifier and recorded by an EPP-09 self-recording instrument. For the study of photoionization in the region 1800–1500 Å, a sapphire

Fig. 2. Curves of photoionization efficiency: 1 –triphenylamine, 2 – triphenylphosphine, 3 –triphenylarsine, 4 –triphenylstibine, 5 – triphenylbismuth. The curves are normalized to the ionization current at 1514 Å

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filter was used, which is transparent down to 1450 Å.

In the present work, the amount of absorbed radiation was not measured, and, to increase sensitivity, rather wide slits were used in the monochromator (the resolving power at the half-height of the hydrogen resonance line L_{α} 1216 Å was about 10 Å). This, as well as the specific properties of the compounds investigated, led to the fact that, for most compounds, no bends were found on the ionization curves, and the first ionization potentials reported by us in Table 1 correspond to the photoionization threshold.

The increase in the measurement error on going to heavier analogs is explained by the decrease in the quantum yield near the photoionization threshold.

Table 1

Ionization potentials of phenyl derivatives of Group 5, determined from the red limit of photoionization

No.	Compound	Ionization potential, eV	No.	Compound	Ionization potential, eV
1	Diphenylamine $(C_6H_5)_2NH$	7.25	4	Triphenylarsine $(C_6H_5)_3As$	7.34
2	Triphenylamine $(C_6H_5)_3N$	6.86	5	Triphenylstibine $(C_6H_5)_3Sb$	7.41
3	Triphenylphosphine $(C_6H_5)_3P$	7.36	6	Triphenylbismuth $(C_6H_5)_3Bi$	7.48

ionization. The errors reflect the scatter in determining the threshold for the appearance of ions when the experiment was repeated many times.

The ionization curves for the compounds studied (except diphenylamine) in the region 1500–1850 Å are shown in Fig. 2. All curves are normalized to the ionization current at 1514 Å. It is evident from the figure that, on passing to heavier analogs, a decrease is observed in the currents near the threshold of ion appearance, leading to the formation of “tails.”

Fig. 2. Curves of photoionization efficiency: 1 –triphenylamine, 2 –triphenylphosphine, 3 –triphenylarsine, 4 –triphenylstibine, 5 –triphenylbismuth. The curves are normalized to the ionization current at 1514 Å.

Fig. 3

Figure 3: Fig. 3

In experiments carried out at higher sensitivity, by increasing the vapor pressure when raising the temperature of the cell, a small (of the order of 0.1 eV) shift of the thresholds toward the long-wavelength region of the spectrum was observed for the compounds $(\text{C}_6\text{H}_5)_3\text{As}$, $(\text{C}_6\text{H}_5)_3\text{Sb}$, and $(\text{C}_6\text{H}_5)_3\text{Bi}$. For the same compounds, a decrease in the length of the “tails” and a shift toward longer wavelengths of the point of intersection of the extended rectilinear section of the ionization curve with the photon-energy axis were observed. Fig. 3 shows the initial portions of the ionization curves for $(\text{C}_6\text{H}_5)_3\text{As}$ at different temperatures. The scales of the curves were chosen so as to ensure parallelism of the rectilinear sections. In addition to the increase in sensitivity, the cause of the indicated phenomena is the transition of some molecules to excited vibrational levels as a result of thermal excitation and the resulting redistribution of the probability of ionization transitions to different vibrational levels of the ground state of the ion.

For the compounds $(\text{C}_6\text{H}_5)_3\text{P}$ and $(\text{C}_6\text{H}_5)_3\text{Bi}$, ionization-efficiency curves were also obtained in a broad spectral region (up to 11.7 eV). Fig. 4 presents the ionization curve for $(\text{C}_6\text{H}_5)_3\text{Bi}$. The curve obtained is characterized by a sharp increase in ion current at 8.8 eV, corresponding to the formation of an ion in a new excited state, as well as by the absence of a saturation current in the region studied.

Examination of the ionization curves shown in Fig. 2 indicates that the ionization efficiency near the threshold of ion appearance varies strongly within the group of substances studied.

This undoubtedly indicates a different degree of adiabaticity of

vibrational transition. According to the Franck–Condon principle, this should indicate significant differences in the internuclear distances in the molecules and in the corresponding ions within the class studied. The highest quantum yield near the ionization threshold is observed for the light analogues, i.e., upon their ionization the least rearrangement is required in going from the normal level of the molecule to the normal level of the ion. This makes it possible to regard the values of the ionization potentials given in Table 1 for $(\text{C}_6\text{H}_5)_3\text{N}$, $(\text{C}_6\text{H}_5)_3\text{P}$, and also $(\text{C}_6\text{H}_5)_2\text{NH}$ as close to adiabatic, and the remaining values as an upper estimate of the adiabatic potentials. This is also confirmed by the observed variations in the thresholds for the appearance of ions for different substances with increasing temperature.

Fig. 3. Effect of temperature on the course of the ionization curves in the case of triphenylarsine. The scale of the curve at 100° along the ordinate axis is reduced by a factor of 10.8.

Fig. 4

Figure 4: Fig. 4

As the data obtained show, in the case of aromatic amines there is a regular decrease in the ionization potentials when hydrogen atoms are replaced by phenyl radicals: C_6H_6 9.24 eV ⁽⁴⁾, $C_6H_5NH_2$ 7.70 eV ⁽⁵⁾, $(C_6H_5)_2NH$ 7.25 eV, $(C_6H_5)_3N$ 6.86 eV. Since in benzene the first ionization potential is due to the removal of one of the π -electrons, it was assumed that the first ionization potential of aniline is also due to detachment of a π -electron ⁽⁶⁾, whose binding energy to the molecular skeleton is considerably decreased as a result of the increased electron density in the ring. However, the further small decrease in ionization potentials, with an almost constant difference upon the introduction of successive benzene rings, rather indicates that ionization of aromatic amines occurs by detachment of one of the electrons of the unshared pair of the nitrogen atom. Such an ionization mechanism has been substantiated for ammonia and also for aliphatic amines ^(5,7,8).

Fig. 4. Ionization-efficiency curve of triphenylbismuth in the region 1550–1200 Å.

When considering the values of the ionization potentials in the series triphenylamine–triphenylbismuth (see Table 1), it is noteworthy that triphenylamine has the lowest potential, despite the fact that the ionization potential of the central atom in this series is greatest precisely for nitrogen. If one turns to the absorption spectra of the compounds studied in the near ultraviolet region ^(9,10), one can find a qualitative analogy with the data presented. Thus, the first absorption band of triphenylamine is strongly shifted to the red compared with the analogous bands of other triphenyl derivatives of Group 5. (The relationship between ionization potentials and absorption spectra has been established for many potential compounds ⁽¹¹⁾.)

It is known that, in their structure, the molecules of trisubstituted derivatives of group-5 elements are a trigonal pyramid ⁽¹²⁾. On the other hand, it has been shown that the ground state of MR_3^+ ions (in the case of ammonia and alkyl-substituted amines) is a planar formation ^(13,14). It seems probable that this regularity also holds for aromatic derivatives of group-5 elements. Then the adiabatic ionization potentials of the substances investigated will correspond to transitions from the ground states of nonplanar molecules to the ground states of planar ions, whereas the vertical potentials will correspond to transitions from nonplanar molecules to nonplanar ions. This may be the main reason for the small quantum yield near the ionization threshold, since the corresponding transition is “oblique.” The fact that, for triphenylamine, and also for diphenylamine, the adiabatic transition is relatively more direct agrees well with the more planar spatial structure of these molecules ^(15–17). The greater stability of the pyramidal form for the heavier analogs, as in the case of the hydrides of the elements of this group ⁽¹⁸⁾, can be explained by the occurrence of $p-d$

hybridization, since *d*-electrons are readily accessible in the phosphorus atom and in the heavier elements, but not in the nitrogen atom.

It may be noted that the magnitudes of the dipole moments of the compounds studied, as well as their ability to form certain complexes (^{19,20}), form a sequence of the type (N < P > As > Sb > Bi), which is similar to the change in the ionization potentials in this series.

The data obtained and their discussion show that the first ionization potentials of triphenyl derivatives of group-5 elements are due to the removal of one of the electrons of the lone pair of the central atom.

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

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