PHOTOIONIZATION OF AROMATIC COMPOUNDS IN BORIC ACID GLASS

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Summary

The two step photoionization of some aromatic compounds in boric acid glass (BA) at 20 °C has been studied. The spectrum of ionization action by the second photon was shown to coincide with the triplet–triplet absorption which implies that an autoionization mechanism is involved. Ionization potentials in BA are 2.4 eV lower than those in the gaseous phase. The dependences of photoionization quantum yields on the energy of exciting quanta are represented. Particular features of the behaviour of aromatic amines, such as deprotonation of the radical cation formed in BA, are discussed.

Introduction

Photoionization of aromatic compounds in BA was shown [1, 2] to occur via a two step mechanism with the triplet state involved. Photoionization of aromatic amines and their oxidized derivatives in various glassy solutions at 77 K is also known to occur by the same mechanism [3 - 5]. However the details of the ionization mechanism were not fully understood in spite of a number of investigations (*e.g.* see Joussot-Dubien's review [6]). The second photon is assumed [3, 4] to induce photoionization from the continuum, but autoionization could occur from the upper triplet states [5]. In this paper we report some new data on the photoionization mechanism, on the role of the upper triplet states in this process and on some spectral properties of aromatic cation radicals.

Experimental

The samples were prepared by dissolving aromatic compounds (10^{-3} M) in boric acid melts and casting them upon cooling. The samples were irradiated by 1 kW Hg or Xe arcs with appropriate glass and/or interference filters. Absorption spectra were obtained using a Unicam SP-800 spectrophotometer. Ferrioxalate actinometry was used in the light intensity measurements.

Photoionization mechanism

Upon UV irradiation the BA samples containing aromatic compounds become coloured because of the formation of cation radicals, recognized by their characteristic absorption spectra [1 - 6]. At sufficiently high concentrations of aromatics, however, other coloured products may also be formed, such as hydroradicals resulting from the attachment of atomic hydrogen to the aromatic molecule [7], so that special precautions were taken to exclude hydroradical formation.

The two step character of photoionization and the involvement of the first triplet state are now well established. Photoionization by absorption of a photon from the first triplet state may proceed in three different ways.

(1) Ionization of a charge transfer complex between an excited triplet and an unexcited solvent molecule.

(2) Autoionization from a highly excited triplet state.

(3) Ionization following excitation into the ionization continuum.

There is no evidence for the existence of charge transfer complexes in the triplet state since phosphorescence spectra of aromatic compounds embedded in BA do not display any apparent difference from those in other glassy matrices, *e.g.* frozen alcohols, hydrocarbons etc.

The occurrence of the autoionization process (2) may be shown by comparison of the ionization action spectrum $W(h\nu_2)$, *i.e.* the dependence of the ionization quantum efficiency of the second quantum upon the energy of this quantum, with the triplet–triplet (T–T) absorption spectrum. If autoionization is operative then $W(h\nu_2)$ should roughly follow the T–T absorption spectrum.

The dependence of the photoionization rate on the energy of the second quantum may be successfully observed for molecules which have a characteristic T–T spectrum within the spectral range where the second photon causes the photoionization. This requirement is met by the molecules of biphenyl and 4,4'-dimethoxybiphenyl. The samples were excited by two light sources: the first one was used for excitation in the S–S absorption band, and the wavelength of the second was varied within the T–T absorption band. The wavelength dependence $W(h\nu_2)$ together with the T–T spectra are given in Fig. 1.

The photoionization efficiency may be written as follows:

$$W = \frac{N_{cr}}{Q\,N_T} = \sigma\,\varphi \tag{1}$$

where φ is the quantum yield of cation radicals in the second absorption step, N_{cr} is the concentration of cation radical for the period of time t_1, Q is the number of photons of the second source for time t_1, σ is the cross section of light absorption leading to ionization and N_T is the concentration of triplet molecules. Values of N_{cr}, N_T and Q were experimentally determined. Triplet state concentrations N_T were the same in all experiments. In a single experimental run this was assumed to be constant since no more than 20% of molecules were ionized under our experimental conditions.
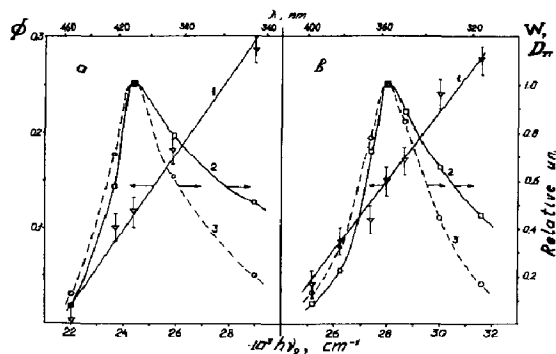
Fig. 1. Cation radical quantum yields (1), ionization action spectra (2) and T—T absorption spectra (3) for (a) 4,4'-dimethoxybiphenyl and (b) biphenyl in BA at 20 °C.
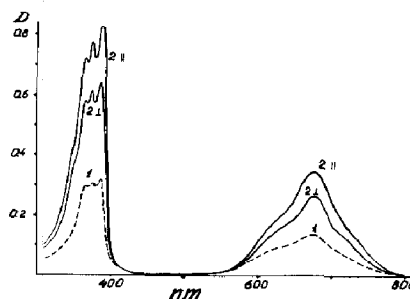
Fig. 2. Polarized absorption spectra of biphenyl cations in BA excited by (1) an unpolarized beam of wavelength 265 nm and (2) two sources: an unpolarized beam at 265 nm and a polarized beam at 365 nm.

It is seen from Fig. 1 that the action spectrum has a maximum coincident with the T–T absorption maximum. The ionization quantum yield is proportional to the photon energy; therefore, the presence of a maximum in the action spectrum may be accounted for only by the presence of a maximum in the cross section curve. Hence it may be concluded that highly excited triplet molecules are responsible for the photoionization process, i.e. autoionization is the dominant process for aromatics in BA at these excitation energies. If T–T absorption and ionization were mutually independent, then competition between them would have taken place and a minimum rather than a maximum of the function $W(h\nu_2)$ would have been observed. In spite of the fact that the quantum yield φ is rather high in the short wavelength region, there is no rise in the T–T absorption spectrum which would have been related to diffuse absorption into a continuum. This also supports the conclusion that autoionization is the predominant process.

Polarization experiments may also provide additional evidence for the participation of the upper triplet state in the photoionization process. No differences were observed in the rates of ionization induced by the second photon at various polarizations with respect to the first polarized light source. On the basis of these results it was concluded [3, 4] that the ionization occurs directly from excitation into the continuum, or into some state near the continuum. It should be noted that the N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) which was studied in these experiments [3, 4] may have a T–T absorption spectrum which consists of several bands of different polarization, which could lead to some ambiguities in the conclusions drawn. On the contrary, the polarization of the cation radical absorption spectra of amino- and oxybiphenyls has been found [5] upon ionization by two sources under conditions when only the second photon is polarized.

In our case the polarization of the absorption spectrum of biphenyl cation radicals was studied using two sources, the first emitting at 265 nm

was not polarized while the second at 365 nm was polarized. Under these experimental conditions a polarized absorption spectrum is observed (Fig. 2), but if the second irradiation is performed by non-polarized 365 nm light the absorption spectrum of the cation radical is not polarized. This implies the participation of the upper triplet state in the ionization process. The polarization of the cation radical absorption in the 400 and 680 nm regions coincides with that of T–T absorption in the 365 nm region and of the first S–S band of biphenyl, the latter being directed along the molecular axis. The following scheme for the ionization process was derived from the experimental data:

$$A \xrightarrow{h\nu_1} A_S \rightarrow A_T$$

$$A_T \xrightarrow{h\nu_2} A_T^*$$

$$A_T^* \xrightarrow{k_1} A^+ + e^-$$

$$A_T^* \xrightarrow{k_2} A_T \tag{2}$$

$$e^- + H^+ \xrightarrow{k_3} H$$

$$e^- + A^+ \xrightarrow{k_4} A$$

The quantum yield for the irreversible action radical formation process is given by

$$\varphi = \frac{k_1}{k_1 + k_2} \frac{k_3}{k_3 + k_4} \tag{3}$$

It is seen from Fig. 1 that the cation radical quantum yield increases with increasing ionizing quantum energy. Two lines of reasoning are possible.

(1) The autoionization rate k_1 is increased. This increase may be related to the enlargement of the excited orbital which should result in its becoming antibonding and in enhancement of electron interaction with the conduction zone and/or electron traps.

(2) The dependence of quantum yield on the excitation energy may in principle be related to changes in the second term in eqn. (3), *i.e.* by the process of electron stabilization. The electron stabilization rate k_3 is increased, while the recombination rate k_4 decreases with increasing distance between the electron and the parent ion. This distance is proportional to the excess of kinetic energy with which the electron is leaving the parent molecule, which is proportional to the photon energy. Both these situations seem to be important in condensed media.

Ionization potentials

From the data in Fig. 1 it seems to be possible to evaluate the threshold energy E_t to ionize triplet molecules and therefore to calculate ionization

TABLE 1

Ionization potentials of aromatic compounds in the gaseous phase (I_g) [8] and in BA (I_{BA}) and extinction coefficients for molecules (ϵ_0) and cation radicals (ϵ_{cr}) in BA at 20 °C

Compound	I_{BA} (eV)	I_g (eV)	$I_g - I_{BA}$ (eV)	Molecule		Cation radical			
				λ_0 (nm)	ϵ_0 (M⁻¹ cm⁻¹)	λ_1 (nm)	ϵ_{cr} (M⁻¹ cm⁻¹)	λ_2 (nm)	ϵ_{cr} (M⁻¹ cm⁻¹)
Biphenyl	5.90	8.23	2.33	250	18300	390	11700	680	6700
4-Oxybiphenyl	5.80	7.78	1.98	261	18800	360	13600	662	4100
4,4'-Dioxybiphenyl	5.78	–	–	265	20000	405	16000	780	9000
4-Methoxybiphenyl	–	–	–	264	29000	400	15200	690	5100
4,4'-Dimethoxybiphenyl	5.77	–	–	265	10800	418	20000	820	15200
p-Terphenyl	5.90	7.7	1.8	290	28600	430	23000	850	–
Quarterphenyl	–	–	–	302	41400	475	27000	–	–
Benzylbiphenyl	–	–	–	256	17000	375	13600	–	–
Naphthalene	5.7	8.12	2.42	–	–	–	–	–	–
Chrysene	5.32	7.72	2.40	320	13000	347	16000	480	9300
Phenanthrene	5.70	7.8	2.10	294	11600	405	9700	–	–
Fluoranthene	–	–	–	287	46800	508	5500	–	–
Triphenylene	5.70	8.09	2.39	286	14400	408	10000	700	5200
1,3,5-Triphenylbenzene	6.00	–	–	262	27000	400	11000	590	1700
2-Oxyfluorene	5.81	–	–	268	22200	387	26000	640	9000
Dibenzofuran	–	–	–	280	17200	362	12900	645	5400
2,3-Benzobiphenylene oxide	–	–	–	320	13800	455	3400	685	2000

potentials according to

$$I_{BA} = E_T + E_t \tag{4}$$

Ionization potentials obtained by this procedure are given in Table 1. It is seen that ionization potentials in BA are lowered by 2.3 - 2.4 eV compared with those for the gaseous phase. This is in accord with published data [6]. Electron polarization of the matrix evidently cannot account for the rather large decrease in BA ionization potentials with respect to alcoholic (1.4 eV) and hydrocarbon (0.9 eV) glasses [5, 9], and hence electron trapping by matrix protons should also be considered.

Spectral properties of cation radicals

Absorption spectra of cation radicals of aromatic compounds studied in the spectral region 200 - 800 nm are presented in Fig. 3. These spectra have two intense absorption bands in the near IR and near UV regions. Extinction coefficients of some cation radicals in BA, which were evaluated from a comparison of changes in the optical densities of the aromatic compound, and cation radical absorptions are also given in Table 1. These values were obtained assuming that the concentrations of the cation radical formed and the aromatic consumption are equal. The initial concentration was determined by dissolving a certain amount of the sample in ethanol and comparing its optical density with that of a solution of known concentration. The presence of boric acid in the liquid solution has no influence on the spectra and on the extinction coefficients of aromatic solutes. The data of Table 1 imply that extinction coefficients of cation radicals are the same order of magnitude as those of aromatic molecules.

Photoionization of aromatic amines in BA

Aromatic amines in BA are known to exist in the protonated state and that is why ionization in BA differs from the ionization process in neutral solvents. Photolysis of aromatic amines in BA as well as in phosphoric acid at 77 K [10] has the following particularities.

(1) Two step photoionization in mono- and diamino substituted benzenes and biphenyls is accompanied by deprotonation in one amino group. Irradiation of TMPD and benzidine in BA results in the appearance of absorption spectra characteristic of cation radicals of aniline and 4-aminobiphenyl, respectively.

(2) Deprotonation occurs after the absorption of the second quantum but not in the first triplet state, as was assumed for fluoroscein [11]. Our conclusion is supported by the following experimental data. First, the fluorescence, phosphorescence, T−T absorption spectra and phosphorescence lifetimes of amino substituted benzenes and biphenyls in BA are identical to
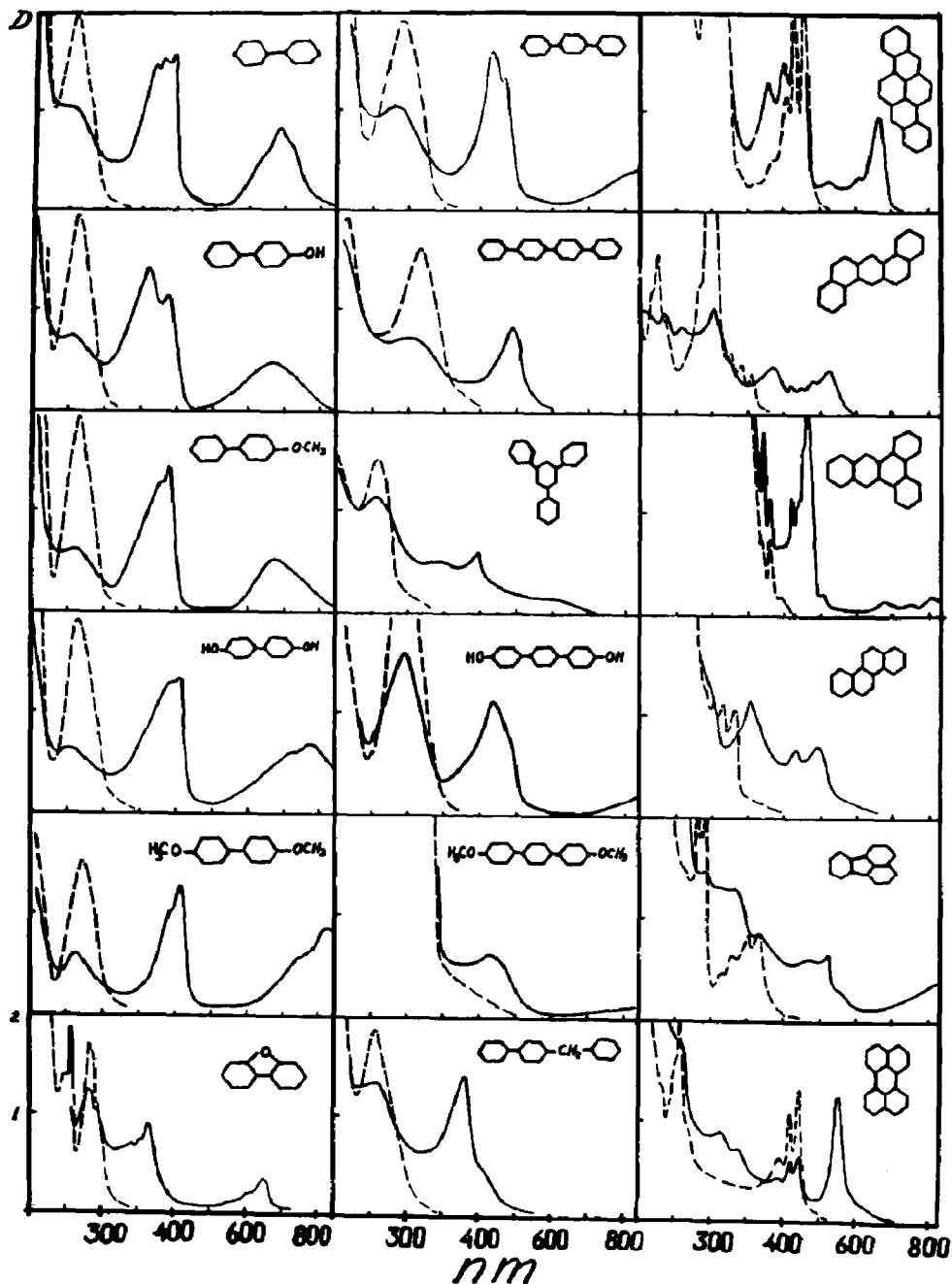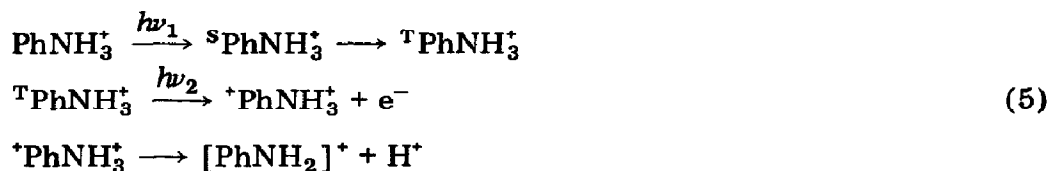
Fig. 3. Absorption spectra of aromatic molecules in BA at 20 °C before (broken curves) and after (solid curves) UV irradiation.

the corresponding characteristics of benzene or biphenyl. Secondly, the second quantum energy necessary for photoionization of the amine in BA is higher than the second quantum energy for the corresponding aromatic hydrocarbons. For the case of deprotonation in the first triplet state, the second quantum

energy should be lowered as compared with hydrocarbon molecules since amine ionization potentials are remarkably lower than those of aromatic hydrocarbons, while triplet state energies are the same. For instance, in benzidine the threshold energy of the second quantum is 3.4 eV, while in biphenyl it is 3.1 eV. This difference in ionization potentials in BA is evidently due to the fact that the second photon initially induces ionization of the aromatic hydrocarbon skeleton with two positive charges on the amino groups, and hence the deprotonation process seems to be secondary.

The photoionization of aromatic amines in BA may be represented as follows:

$$PhNH_3^+ \xrightarrow{h\nu_1} {}^S PhNH_3^{+*} \longrightarrow {}^T PhNH_3^{+*}$$

$$^T PhNH_3^+ \xrightarrow{h\nu_2} {}^+ PhNH_3^+ + e^- \qquad\qquad (5)$$

$$^+ PhNH_3^+ \longrightarrow [PhNH_2]^{+*} + H^+$$

Acknowledgment

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