Two Photon Ionization of Benzene in Methanol and Cyclohexane Solution

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Irradiation of benzene with 15 ns flashes of 265 nm light caused ionization as evidenced by optical absorption measurements. In the case of dilute methanol solutions solvated electrons were formed. The yield depends on the intensity of the incident light I as $\varphi(e^-_{\text{solv}}) \propto I^{1.8}$. In the case of cyclohexane solution dimer radical cations were detected by their absorption between 600 and 1100 nm. O_2 enhances the yield of dimer cations because it scavenges electrons, thus impeding ion recombination.

Introduction

Multiphoton ionization of liquid benzene has been reported recently by several authors who inferred ion formation from photo currents generated upon irradiating benzene in an electrical conductivity cell with a UV light flash [1, 2]. Using incident light of $\lambda = 355$ nm (3.39 eV) the photoionization was ascribed to a three-photon process [2].

The present paper deals with optical absorption measurements in conjunction with laser flash photolysis using light of 265 nm (4.65 eV). In this case biphotonic absorption is expected to occur at sufficiently high incident intensities, because the extinction coefficient for the absorption of the second photon corresponding to the transition $^1E_{2g} \leftarrow {}^1B_{2u}$ at 265 nm is rather high, according to Nakajima et al. [3]: $\varepsilon = 4 \times 10^3$ l/mol cm. $^1B_{2u}$ denotes the excited singlet state, which is populated by absorption of the first photon with $\varepsilon = 7.5$ l/mol cm.

The present paper reports two kinds of experiments which were carried out during the search for ion formation. Thereby, account was taken of the fact that, in general, ions cannot be easily detected, because of rapidly occurring neutralization reactions. As will be shown below, two modes of ion stabilization were employed: (i) methanol was selected as a solvent for its capability of solvating electrons, (ii) O_2 was, purposely, kept present in cyclohexane solutions of benzene because of its high electron affinity.

Experimental Part

Irradiations were carried out in rectangular quartz cells (optical path length: 1 cm). Photolyzing light of 265 nm was generated by a Nd-YAG-laser system in conjunction with two frequency doublers. The duration of the flash was 15 ns. For absorption measurements in the wavelength range above 700 nm a photodiode (EG-G, FND-100) was used. Further details have been described elsewhere [4—6].

Experiments in Methanol

Upon irradiating Ar-saturated solutions of benzene in methanol (10 to 300 mM) with 15 ns flashes, the optical absorption spectrum of the solvated electron was formed during the flash. The spectrum is shown in Figure 1. For comparison the spectrum of e^-_{solv}, obtained during pulse radiolysis studies is presented in the insert (a). Therefore, it is concluded that ionization is accomplished from the state reached by two photon absorption referring to an energy of 9.3 eV, probably $^1E_{2g}$. Insert (b) shows an oscilloscope trace depicting the rapid formation of the electron absorption. The optical density measured at the end of the flash is plotted vs. the intensity of the incident light in Figure 2. This plot yields

$$\varphi(e^-_{\text{solv}}) \propto I^{1.8}; \quad (1)$$

$\varphi(e^-_{\text{solv}})$: quantum yield for the formation of solvated electrons .

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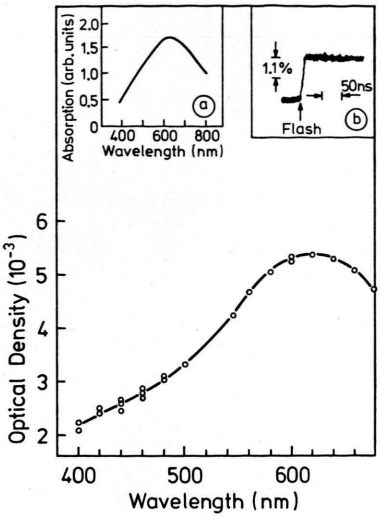

Fig. 1. Optical absorption spectrum obtained with an Argon-saturated solution of benzene in methanol (10 mM) 100 ns after the start of a 15 ns flash of 265 nm light. Insert (a): Spectrum of the solvated electron in methanol according to [7]. Insert (b): Oscilloscope trace depicting the formation of the absorption at $\lambda = 600$ nm.

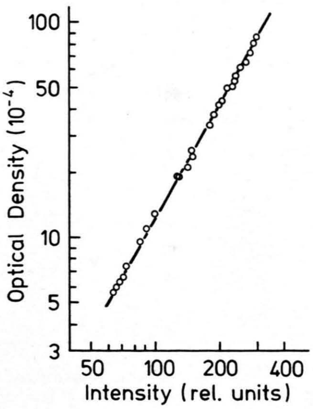

Fig. 2. Optical density at 700 nm recorded at the end of a 15 ns flash as a function of the incident intensity of 265 nm light. Benzene in Argon-saturated methanol (30 mM).

Experimente in Cyclohexane

Solutions of benzene in cyclohexane (8 mM) were irradiated with 15 ns flashes of 265 nm light both in the absence and in the presence of O_2. Curve I in Fig. 3 represents the absorption spectrum (having a pronounced maximum at 620 nm) observed with an Ar-saturated solution. It decays quite rapidly (see insert to Fig. 3, trace b) with a 1st order rate constant of 3.2×10^{7} s^{-1}. By referring to other work, this spectrum is assigned to the $S_3 \leftarrow S_1$ transition ($^1E_{1u} \leftarrow {}^1B_{2u}$) [3, 5].

Upon the decay of spectrum I in Fig. 3 a very weak longer-lived absorption remained in the wavelength range between 600 and 1100 nm, but the low signal to noise ratio did not allow to record the spectrum. This was, however, possible with an air-saturated solution (see spectrum II in Figure 3). As can be seen from the insert (a) in Fig. 3, the new absorption forms after the flash. The rate of formation decreased with decreasing benzene concentration. The new spectrum with its broad maximum at about 900 nm is assigned to the dimer radical cation of benzene B_2^{+}. The possibility of assigning spectrum II in Fig. 3 to singlet excimers of benzene can be discarded on the basis of the short lifetime of benzene excimers in cyclohexane solution ($\tau \approx 3 \times 10^{-8}$ s) [5]. The lifetime of the species corresponding to spectrum II in Fig. 3 is significantly longer (see oscilloscope trace (a) in Figure 3).

Badger and Brocklehurst [8] reported two bands due to B_2^{+} at 900 and at 470 nm as observed in a rigid matrix at low temperature. So far, a band at 470 nm could not be observed in the liquid phase at room temperature.

It appears that the band at 470 nm corresponds to a perpendicularly arranged radical cation B_2^{+} which is stable only in the rigid matrix. Upon warming up it converts readily to the sandwich-type structure, which does not absorb at 470 nm

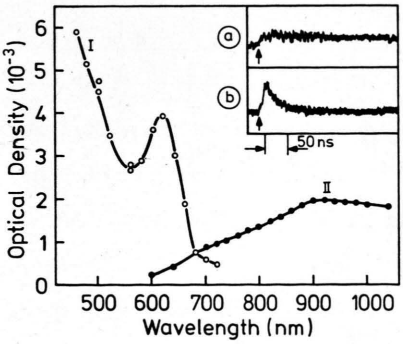

Fig. 3. Transient absorption spectra observed upon irradiating a cyclohexane solution containing 8×10^{-3} mol/l benzene at room temperature with a 15 ns flash of 265 nm light. Absorbed dose per flash: 2.2×10^{-5} einstein/l. — Spectrum I, obtained with an Ar-saturated solution at the end of the flash. — Spectrum II, obtained with an air-saturated solution 50 ns after the flash. — Inserts: (a) oscillogram recorded at 900 nm (aerated solution); (b) oscillogram recorded at 620 nm (deaerated solution).

[9]. The spectrum of B^+, the precursor of B_2^+ could not be observed in the present work. According to Shida [10], the absorption spectrum of B^+ extends from about 600 nm down to the UV range. Therefore, the absorption spectra of B^+ and B^* (excited benzene molecules) superimposed. Obviously, B^+ and B^* decay with similar rates in the present case. A detection of B^+ by its optical absorption appears, therefore, not feasible. Because the concentration of B^+ is much lower than that of B^*, the extinction of B^+ should also be much lower, if the extinction coefficients lie in the same order of magnitude.

Discussion

The present results are in accord with the following mechanism, where B denotes "benzene":

$$B \overset{265}{\rightarrow} B^* \quad ({}^1B_{2u})\,, \qquad (2)$$

$$B^* \overset{265}{\rightarrow} B^{**} \quad ({}^1E_{2g})\,, \qquad (3)$$

$$B^{**} \rightarrow (B^+ + e^-) \quad \text{geminate ion pair}\,, \qquad (4)$$

$$(B^+ + e^-) \rightarrow B^+ + e^- \quad \text{free ions}\,, \qquad (5)$$

$$B^+ + B \rightarrow B_2^+ \quad \text{dimer radical cation}\,. \qquad (6)$$

In methanol electrons are solvated:

$$e^- \xrightarrow[CH_3OH]{} e^-_{solv}\,. \qquad (7)$$

The rate of the neutralization reaction of e^-_{solv} with B^+ or ionic products formed from reactions of B^+ with the solvent is much lower than the rate of reactions (8) and (9):

$$\left.\begin{array}{ll} B^+ + e^- \rightarrow B^* & (8) \\ B_2^+ + e^- \rightarrow B^* + B & (9) \end{array}\right\} \text{volume combination of ions.}$$

In cyclohexane containing O_2, the latter reacts with electrons:

$$e^- + O_2 \rightarrow O_2^-\,. \qquad (10)$$

The rate of the combination reactions:

$$O_2^- + B^+ \rightarrow O_2 + B^* \qquad (11)$$

and

$$O_2^- + B_2^+ \rightarrow O_2 + B^* + B \qquad (12)$$

is much lower than the rate of reactions (8) and (9), because the mobility of e^- (0.24 $cm^2\,V^{-1}\,s^{-1}$) is much larger than that of O_2^- and B^+ ($< 10^{-3}\,cm^2 \cdot V^{-1}\,s^{-1}$) [11]. Doubts arising on the question as to whether spectrum II in Fig. 3 is to be assigned to radical anions of benzene can be discarded in so far as according to Holroyd [12] and Freeman et al. [13] thermalized electrons do not react with benzene in non-polar solvents, such as cyclohexane, at room temperature.

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