Laser Flash Photolysis of Benzene. VI.[1] Photolysis in Aqueous Solution

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(Received July 21, 1982)

Three transient absorption spectra in aqueous solution were observed by irradiation of benzene with an excimer laser (KrF, 248 nm or ArF, 193 nm). A short-lived absorption with a peak at 275 nm is assigned to the $S_n \leftarrow S_1$ absorption. A long-lived absorption, which appears as a clear shoulder at 230 nm, stays longer than 500 ns and is not shortened by oxygen. This species is tentatively assigned to benzvalene, and the quantum yield is determined to be *ca.* 0.1. Solvated electron with a peak at 720 nm was formed *via* multiphoton processes at a power level of 60 mJ/cm² of an ArF laser. The $T_n \leftarrow T_1$ absorption was lower than our detection limit $(\Phi_T < 0.1)$.

Nanosecond laser photolysis has been successfully applied to benzene in cyclohexane and in the gas phase, and $S_n \leftarrow S_1$ absorptions, a $T_n \leftarrow T_1$ absorption, a vibrationally highly excited state, and mist formation were observed.[2-5] The first three observations brought detailed information on the properties of excited states and the last observations gave an interesting phenomenon of multiphoton photochemistry in the gas phase. Phenol was observed at quantum yield of 0.01 in the presence of O_2. Most recently we observed with gaseous benzene that the major deactivation process at 248 nm excitation was formation of highly excited vibrational states in the ground electronic manifold.[1] In order to investigate photochemistry of benzene in solution, we chose aqueous solution in this report because of the following reasons.

(1) The photochemistry of benzene in aqueous solution was investigated by Kaplan[6] and Stein[7,8] with steady-state irradiation and the conventional flash photolysis technique in the microsecond timescale. They reported that excitation of benzene to the $^1B_{2u}$ or $^1B_{1u}$ state in aerated aqueous solution gave the final photo-product **1**. Benzvalene has been postulated as an intermediate, which reacts with H_2O or O_2 to produce **1**. The quantum yield of total process is 0.07[6] or 0.18.[7] (Eqs. 1 and 2)

$$(1)$$

$$(2)$$

1
R = H or OH
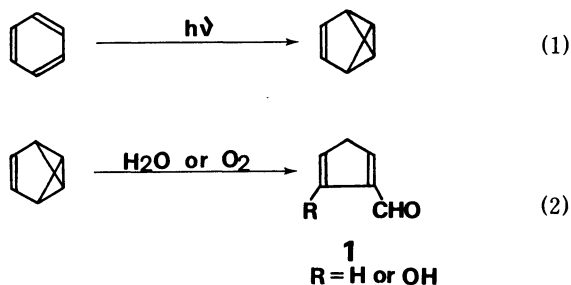
(2) Since the quantum yields of fluorescence and triplet formation are only 0.006[7] and 0.07,[9] respectively, the major process (0.75) is unknown in aqueous solution. Thus photochemical reaction leading to benzvalene as an unstable photoproduct is expected to occur. Internal conversion to the ground state must also be an important process. (3) Because of the low yield of triplet formation, some transient species other than the triplet benzene

could be observed in aqueous solution. It is essential to confirm Eq. 1 and to know the nature of the unknown processes.[10]

Experimental

Benzene in aerated aqueous solution (10^{-3} M, 1 M = 1 mol dm⁻³) in a $1 \times 1 \times 2.5$ cm³ quartz cell was excited by an excimer laser (KrF, 248 nm or ArF, 193 nm). The laser beam was not focused and had a cross section of 2.5×0.2 cm². The details of the flash photolysis apparatus have been described elsewhere.[2,3] Sample was renewed at every laser excitation because of an efficient formation of photoproducts. The absorbance of each wavelength at each laser shot was normalized at 230 nm by dual beam observation, one at 230 nm and the other at different wavelengths. Benzene (Merck, 99.9%), acetonitrile (Merck, Uvasol), methyl alcohol (Katayama Chemical, absorption spectrum grade), and oxygen (Nippon Sanso) were used without further purification. Water was distilled and passed through ion exchange resin (Toyo Aquarius GS-100T).

Results and Discussion

Figures 1 and 2 show three transient absorption spectra (A,B,C) of benzene in aqueous solution. The spectra of components A and C are taken immediately after excitation and the spectrum of component B is taken
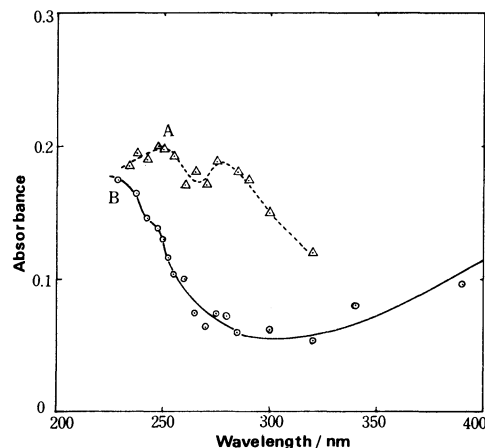
Fig. 1. Transient absorption spectra of benzene in aqueous solution by excitation at 193 nm (ArF). The spectrum A is taken immediately after excitation and the spectrum B is taken at 100 ns after excitation. Absorbance is normalized at 230 nm.
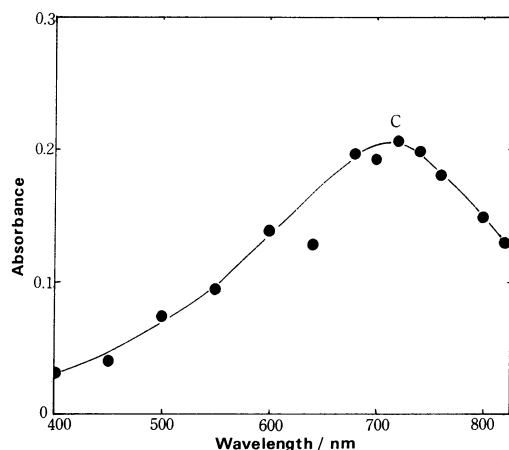
Fig. 2. Transient absorption spectrum of benzene in aqueous solution by excitation at 248 nm (KrF). The spectrum is taken immediately after excitation. Absorbance is normalized at 230 nm.
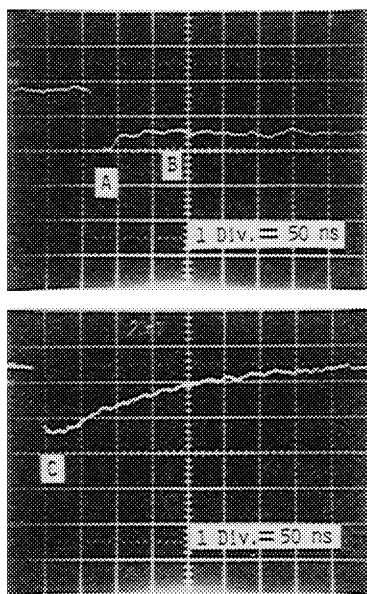

Fig. 3. Photolysis of benzene in water by excimer laser. (1) Excitation by ArF laser (193 nm), monitoring at 260 nm. (2) Excitation by KrF laser (248 nm), monitoring at 800 nm. The spectra of A (Fig. 1) and C (Fig. 2) are taken immediately after excitation, and the spectrum of B (Fig 1) is taken at 100 ns after laser excitation.

at 100 ns after laser excitation (Fig. 3). The spectra obtained by excitation at 248 nm (KrF) and at 193 nm (ArF) are similar to each other.

The broad absorption spectrum (C), between 400 nm and 850 nm, has a maximum absorbance at 720 nm. Both absorption peak position and the long-tailing character of the spectrum are in good agreement with that of solvated electron in water (hydrated electron).[11] The lifetime ($\approx$150 ns) of this transient absorption is reasonably explained by quenching of solvated electron by oxygen (Eq. 3).[12]

$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad (3)$$

In acetonitrile, methyl alcohol, or cyclohexane solutions, no absorption corresponding to the spectrum C is observed in the present power level. Because the laser power dependence of the formation of C is not linear even with 193 nm (6.4 eV) excitation, solvated electron is formed via ionization of benzene by multiphoton process. Integrated concentration of excited species is 4.2×10^{-4} M at a laser power of 60 mJ, while the concentration of solvated electron is estimated to be 1.5×10^{-5} M. About 7% of absorbed laser energy was utilized for formation of solvated electron. It should be noted that solvated electron is rather efficiently formed only in aqueous solution among the solvents we used.

The other transient absorptions, A and B, are obtained between 220 nm and 350 nm. The spectrum of component A, with a peak at 275 nm, is quite similar to that of the $S_n \leftarrow S_1$ absorption observed previously.[4] This component decays just after excitation and is not quenched by oxygen, because the fluorescence lifetime in water is too short (2 ns) to interact with oxygen.[13] These observations indicate that this spectrum is due to the $S_n \leftarrow S_1$ absorption. The absorbance at the 248 nm excitation is stronger than at the 193 nm excitation to some extent. This is reasonable because the fluorescence quantum yield decreases by excitation to the S_2 and/or S_3 electronic states.[8]

The component B, with a clear shoulder at 230 nm has a slightly weaker absorbance than the $S_n \leftarrow S_1$ absorption. This component does not decay during the period of observation ($\approx$500 ns) and is not quenched by oxygen saturated in water. These observations indicate that the absorption is not due to the $T_n \leftarrow T_1$ absorption. The latter should have an absorption peak at 235 nm and should be quenched by oxygen with a bimolecular rate constant of $\approx 6 \times 10^9$ M^{-1} s^{-1}.[2] The saturated concentration of oxygen in water is 0.3×10^{-3} M.[12] Thus, if the absorption were due to the triplet state, it should have decayed with a lifetime of $\approx$600 ns. It is reasonable that no $T_n \leftarrow T_1$ absorption is observed in our experiment, because the quantum yield of triplet formation is known to be only 0.07.[10]

The component B has a linear dependence on laser power at the 248 nm excitation, while the solvated electron is produced with a hyper-linear dependence. The situation is almost the same at the 193 nm excitation. The component B is suggested to be formed by one photon process. The absorption spectrum of benzvalene shows a shoulder at 230 nm in isohexane.[14] The component B has a similar absorption spectrum to benzvalene. Thus, we tentatively assign this transient to benzvalene.

If the component B is benzvalene, the quantum yield is estimated to be about 0.1 by calculating the concentration of excited species and the extinction coefficient of benzvalene. This value is close to the previous data.[6,7] The spectral shape, dynamic behavior, and other discussions on component B suggest that benzvalene is formed as an intermediate of product 1 in Eq. 2. We irradiated aqueous benzene solution with a KrF excimer laser and actually confirmed the final product 1 by UV absorption spectroscopy.

Judging from production of solvated electron, benzene

cation or dimer cation must also be formed. However we were unable to observe these species, which should appear at ≈550 nm or ≈900 nm. Benzene cation is known to react efficiently with water,[8,15] thus the transient concentration must be very low. The absorption of the product from benzene cation also seems to be too weak to be observed. It is less than our detection limit. Very recently Irion *et al.* photolized an aqueous benzene solution by excimer lasers. Phenol was observed with low quantum yield of 10^{-3} *via* multiphoton absorption.[16]

Photolysis of benzene in cyclohexane solution gave ring opening products, trienes.[2] As these compounds are postulated to be formed *via* triplet state,[2] it is reasonable that the absorption spectra of the ring opening products are not observed in aqueous solution because of low triplet yield.

In aqueous solution, high yield of solvated electron is observed, but in cyclohexane the yield of electron transfer process seems to be very small. We were not able to observe the dimer cation.

The quantum yield of processes other than fluorescence and triplet formation in aqueous solution is known to be about 0.92. In our present investigation with laser photolysis, we observed formation of a photoproduct, which is most likely to be benzvalene, with a quantum yield of *ca.* 0.1. We do not observe the high yield of other photoproducts or transients. The major process is suggested to be a nonradiative transition to the ground state.[1]

References

1) Part V of this series. N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, **77**, 6040 (1982).

2) N. Nakashima, M. Sumitani, I. Ohmine, and K. Yoshihara, *J. Chem. Phys.*, **72**, 2226 (1980).

3) N. Nakashima, H. Inoue, M. Sumitani, and K. Yoshihara, *J. Chem. Phys.*, **73**, 4693 (1980).

4) N. Nakashima, H. Inoue, M. Sumitani, and K. Yoshihara, *J. Chem. Phys.*, **73**, 5976 (1980).

5) N. Nakashima, and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **55**, 2783 (1982).

6) L. Kaplan, L. A. Wemdling, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **93**, 3819, 3821 (1971).

7) M. Luria and G. Stein, *J. Phys. Chem.*, **76**, 165 (1972).

8) Y. Ilan, M. Luria, and G. Stein, *J. Phys. Chem.*, **80**, 584 (1976).

9) R. B. Cundall, and L. C. Pereira, *Chem. Phys. Lett.*, **18**, 371 (1973).

10) N. Shimo, N. Nakashima, and K. Yoshihara, Proceedings of Symposium on Photochemistry 1981, Sapporo, 135 (1981).

11) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962); S. Tagawa, private communication.

12) J. P. Keene, *Nature*, **197**, 47 (1963).

13) M. Luria, M. Ofran, and G. Stein, *J. Phys. Chem.*, **78**, 1904 (1974).

14) I. E. D. Besten L. Kaplan, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **90**, 5868 (1968).

15) M. K. Eberhardt, *J. Am. Chem. Soc.*, **103**, 3876 (1981).

16) M. P. Irion, W. Fuss, and K.-L. Kompa, *Appl. Phys.*, **B27**, 191 (1982).