Subpicosecond Pulse Radiolysis Study of Geminate Ion Recombination in Liquid Benzene

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Subpico- and picosecond pulse radiolyses were carried out to investigate geminate ion recombination in neat benzene. The fast decay of dimer radical cation corresponding to geminate ion recombination with an electron was directly observed for the first time. The characteristic lifetime and average initial distance between a thermalized electron and its parent cation were estimated to be 1.2 ps and 3.2 nm.

Radiation chemistry in benzene has been studied for many decades as a fundamental research on aromatic molecules. In a condensed phase, following the ionization by the low LET (linear energy transfer) radiation such as a high energy electron beam, ion pairs, called geminate ion pairs, are formed. A dimer radical cation (Bz_2^+), which has been well known as a stabilized form between a monomer cation (Bz^+) and a neutral molecule (Bz), is formed as follows,[1]

$$Bz^+ + Bz \rightleftarrows Bz_2^+. \qquad (1)$$

The recombination of a radical cation with a thermalized electron, called geminate ion recombination, occurs owing to their Coulomb potential and diffusion immediately after its ionization. A neutral excited state is mainly formed as a result of the ion recombination. Although the geminate ion recombination in a condensed phase such as alkane solutions has been investigated,[2–4] the geminate ion recombination in benzene has not been made clear because of its ultrafast (from femto- to picosecond-order) ion recombination. The researches on a radical cation of benzene in a condensed phase had been restricted to a diluted solution under low temperature conditions. In recent years, there have been some researches on benzene dimer radical cation in liquid phase using high time-resolved laser flash photolysis method.[5,6] However, the early processes dominated by the geminate recombination have remained unclear. In this study, the geminate ion recombination in neat benzene was investigated under room temperature by using high time-resolution pulse radiolysis method. We discuss the initial distribution of thermalized electrons and the time-dependent behavior of benzene dimer radical cation within 50 ps after exposure, which has never been observed.

Two types of pulse radiolysis systems were used in this study. In picosecond pulse radiolysis experiments, a 28 MeV L-band linac was used as an exposure source. The pulse width was 20 ps. The white-light continuum was used as a probe light, which was produced by focusing an amplified femtosecond laser pulse into a H_2O cell. The details of the system have been already described.[7] In subpicosecond pulse radiolysis experiments, electron pulses were compressed to less than 1 ps by a magnetic pulse compression method. A fundamental oscillation (790 nm) of Ti:Sapphire laser was used as a probe light. The details have been also described.[8] Absorbed doses in pico- and subpicoecond pulse radiolysis were 200 and 140 Gy/pulse, respectively. Spectral grade benzene (Kishida Co.) was passed through a silica-gel column and doubly distilled. The samples were saturated with argon in quarts cells with 0.2 cm (subpico-) or 2 cm (pico-) light-pass length. The experiments were done at room temperature.

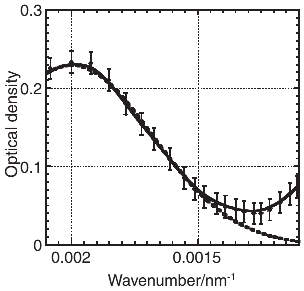

Figure 1. Transient absorption spectrum (solid line) in neat benzene at 100 ps after the exposure of 20 ps pulse. Dotted line denotes a Gaussian fit to the excimer band.

A picosecond pulse radiolysis experiment was carried out to obtain a spectrum of short lived intermediates, from which the contribution of two intermediates to the optical density monitored at 790 nm was estimated. A solid line with error bars in Figure 1 shows a transient absorption spectrum at 100 ps after the exposure, obtained by the picosecond pulse radiolysis of neat benzene. Absorption bands with maxima at 0.002 nm^{-1} (500 nm) and in near infrared (IR) region have already been identified as benzene excimer (Bz_2^*)[9,10] and a charge resonance (CR) band of Bz_2^+,[5,11,12] respectively. The excimer band was fitted to Gaussian function in order to estimate the ratio of optical density of the CR band to Bz_2^* at 0.0013 nm^{-1} (790 nm) (a dotted line in Figure 1). The result was well fitted at the wavenumber more than 0.0015 nm^{-1} (670 nm). The ratio was estimated at 1.9.

A bold line in Figure 2 shows an averaged kinetic trace observed by subpicosecond pulse radiolysis at 790 nm. The kinetic trace which shows an ultrafast decay due to geminate ion recombination of Bz_2^+, was obtained for the first time. The rise time at 790 nm agreed with the apparatus function. The full width at half maxima (FWHM) of apparatus function is 5.4 ps, which is mainly ascribed to the velocity difference in the sample cell between an electron beam and a probe light. This result is consistent with ultrafast laser pump and probe experiments which suggested a formation time of Bz_2^+ within 1 ps.[5,6]

The time-dependent behavior was analyzed by Smoluchowski equation.[3] It has been reported that the geminate ion recombination can be well described by Smoluchowski equation which is based on the diffusion theory,[13]

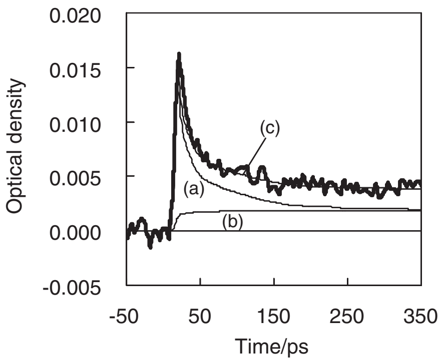

Figure 2. Kinetic traces observed in the subpicosecond pulse radiolysis (bold line) and kinetic trace of the theoretical at 790 nm (solid line) in neat benzene. Curve (a) represents time dependent behavior of $\mathrm{Bz_2}^+$ and (b) represents that of $\mathrm{Bz_2}^*$. Curve (c) is the sum of (a) and (b). Theoretical curves are convoluted by the instrumental function.

$$\frac{\partial w}{\partial t} = D\nabla\left(\nabla w + w\frac{1}{kT}\nabla V\right) \tag{2}$$

where w, D, V, k, and T are probability density of geminate ion pairs, a sum of diffusion coefficients, Coulomb potential, Boltzmann constant and the absolute temperature. The sum of diffusion coefficient is mainly determined by that of electrons, $2.8 \times 10^{-3}\,\mathrm{cm^2/s}$,[14] because electrons can move faster by two orders of magnitude than cation molecules. An exponential function was assumed as an initial distribution of thermalized electron. An average distance between a radical cation and a thermalized electron, r_0, of 3.2 nm was used.[15] The contribution of $\mathrm{Bz_2}^*$ to the absorption at 790 nm, which was previously estimated, was taken into account. The lifetime of $\mathrm{Bz_2}^*$, τ, of 18.2 ns.[9] was used. The decay time of $\mathrm{Bz_2}^+$ was tentatively used as formation time of $\mathrm{Bz_2}^*$, assuming a following reaction,[1]

$$\mathrm{Bz_2}^+ + \mathrm{e}^- \rightarrow \mathrm{Bz_2}^*. \tag{3}$$

With these parameters and the assumption, Eq 2 was calculated using Monte Carlo method. The sum (c) of decay curve of $\mathrm{Bz_2}^+$ (a) and formation curve of $\mathrm{Bz_2}^*$ (b) was shown in Figure 2. The fitting curve approximately agreed with the experimental data in the observed time region. The calculated decay of $\mathrm{Bz_2}^+$ indicated τ_g (the time when 43% of geminate pairs survived) is 1.2 ps. We suspect that a slight difference between the experimental and theoretical data within 50 ps after the pulse is due to the relaxation time of $\mathrm{Bz_2}^+$ formation or the influence of other ion pairs formed near one geminate ion pair (cross recombination).

The fast decay observed in this experiment has not been observed in any femtosecond laser photolysis experiments. The initial distribution of thermalized electron in the photolysis is considered to be smaller than the radiolysis because of lower excitation energy. Saik and Lipsky reported r_0 of 2.3 nm as the exponential distribution distance with 8.86 eV excitation.[16] Thus, faster geminate recombination by photoionization than by radiolysis is expected on account of the shorter r_0. The geminate ion recombination in neat liquid benzene by photoionization has been already discussed by other groups. Miyasaka et al. estimated the first-order lifetime of geminate ion pair in benzene at 10–30 ps indirectly by picosecond laser photolysis.[10] Inokuchi et al. directly obtained kinetic traces in near IR region by femtosecond laser photolysis.[5] The kinetic traces showed no distinct decay within 50 ps. They proposed slow geminate recombination in neat benzene in a time scale of 100 ps, which is different from our result. This difference is explained as follows. Assumed the initial distribution of 2.3 nm,[16] τ_g is decreased to 0.6 ps. In this case, geminate recombination is completed mainly within their apparatus resolution (<1 ps).

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References and Notes

1 B. Badger and B. Brocklehurst, *Nature*, **219**, 263 (1968).
2 S. Tagawa, N. Hayashi, Y. Yoshida, M. Washio, and Y. Tabata, *Radiat. Phys. Chem.*, **34**, 503 (1989); Y. Yoshida, S. Tagawa, M. Washio, H. Kobayashi, and Y. Tabata, *Radiat. Phys. Chem.*, **34**, 493 (1989).
3 A. Saeki, T. Kozawa, Y. Yoshida, and S. Tagawa, *Radiat. Phys. Chem.*, **60**, 319 (2001).
4 A. D. Trifunac, M. C. Saucer, and C. D. Jonah, *Chem. Phys. Lett.*, **113**, 316 (1985); M. C. Saucer and C. D. Jonah, *Radiat. Phys. Chem.*, **44**, 281 (1994).
5 Y. Inokuchi, Y. Naitoh, K. Ohashi, K. Saitow, K. Yoshihara, and N. Nishi, *Chem. Phys. Lett.*, **269**, 298 (1997).
6 W. Jarzeba, R. E. Schlief, and P. F. Barbara, *J. Phys. Chem.*, **98**, 9102 (1994).
7 Y. Yoshida, Y. Mizutani, T. Kozawa, A. Saeki, S. Seki, S. Tagawa, and K. Ushida, *Radiat. Phys. Chem.*, **60**, 313 (2001).
8 T. Kozawa, Y. Mizutani, M. Miki, T. Yamamoto, S. Suemine, Y. Yoshida, and S. Tagawa, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **429**, 471 (1999); T. Kozawa, A. Saeki, Y. Yoshida, and S. Tagawa, *Jpn. J. Appl. Phys.*, **41**, 4208 (2002).
9 R. Cooper and J. K. Thomas, *J. Chem. Phys.*, **49**, 5097 (1968); G. Beck and J. K. Thomas, *J. Phys. Chem.*, **25**, 3856 (1972).
10 H. Miyasaka, H. Masuhara, and N. Mataga, *J. Phys. Chem.*, **89**, 1631 (1985).
11 B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2582 (1969).
12 S. Tagawa, G. Beck, and W. Schnabel, *Z. Naturforsch*, **37a**, 982 (1982).
13 K. M. Hong and J. Noolandi, *J. Chem. Phys.*, **68**, 5163 (1978); K. M. Hong and J. Noolandi, *J. Chem. Phys.*, **69**, 5026 (1978).
14 N. Gee and G. R. Freeman, *Can. J. Chem.*, **70**, 1618 (1992).
15 The average distance of initial distribution was calculated on the basis of Onsager theory.[17] Used ratio of free ion yield to total ion yield (geminate ion + free ion) in benzene, $0.053/3.8 = 0.014$.[14]
16 V. O. Saik and S. Lipsky, *J. Phys. Chem.*, **98**, 11858 (1994).
17 S. Tagawa, in "CRC Handbook of Radiation Chemistry," ed. by Y. Tabata, Y. Ito, and S. Tagawa, CRC Press, Boca Raton (1991), Chap. 5, p 293; G. R. Freeman, in "Kinetics of Nonhomogeneous Processes," ed. by G. R. Freeman, Wiley Interscience, New York (1987), Chap. 2, p 19.