

Primary process of scintillation mechanism studied by femtosecond laser-synchronized pulse radiolysis

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Abstract

In order to make clear primary processes of scintillation mechanism, the dynamics of radiation-induced reactions in a solute-solvent system were studied by femtosecond laser-synchronized pulse radiolysis with the time resolution of about 0.8 ps. The time-dependent behavior of solute cation and anion was analyzed by the Smoluchowski equation based on the diffusion theory.

1 INTRODUCTION

In a solute-solvent system such as liquid scintillator, solvent molecules are ionized by radiation, solvent cation radicals and electrons are formed. This ion pair recombine to form solvent excited states, or energy transfer occurs from solvent to solute. Solute excited states are formed by either energy transfer from solvent excited states or recombination of ion pairs. Scintillation is an emission phenomenon from solute excited states. The details have not been clarified, because these primary processes of scintillation mechanism are very fast. It is important to investigate the primary process of radiation chemistry in order to understand scintillation mechanism. The mechanism can be measured by using the laser-synchronized subpicosecond pulse radiolysis developed at Osaka University for the first time.

Pulse radiolysis technique is one of the most effective methods to investigate the primary processes of radiation chemistry. To measure the absorption or emission of short-lived intermediates (radicals, ions, excited states, etc.) directly leads to reveal reaction mechanism. We have attempted to elucidate the scintillation mechanism with solute-solvent system in the picosecond time range by using

the laser-synchronized subpicosecond pulse radiolysis.

2 EXPERIMENTAL

Three types of pulse radiolysis technique (nanosecond pulse radiolysis, picosecond white light pulse radiolysis, subpicosecond fundamental pulse radiolysis) were used for absorption spectroscopy. All the experiments were performed with 28 MeV L-band electron linear accelerator at the Radiation Laboratory of the Institute of Scientific and Industrial Research, Osaka University.

In the nanosecond pulse radiolysis, samples were irradiated with an 8 ns single electron pulse. A Xe lamp was used as an analyzing light. The time resolution is ca. 8 ns.

In the picosecond white light pulse radiolysis, samples were irradiated with a 20 ps single electron pulse. A white light continuum was used as an analyzing light. The white light continuum was obtained by focusing Ti-sapphire femtosecond laser into a water cell. The time resolution is ca. 20 ps.

In the subpicosecond fundamental pulse radiolysis, samples were irradiated with a 125 fs single electron pulse. Ti-sapphire femtosecond laser was used as an analyzing light. The time resolution is 800 ± 50 fs.

The details of three systems have been reported previously [1]-[3].

Biphenyl was dissolved into cyclohexane at the concentration of 0.1 M (mol dm⁻³). Solutions were degassed by Ar bubbling in high quality quartz cells with 1 cm or 2 mm optical path. 2 mm cell was used for the measurement of high time-resolution in subpicosecond pulse radiolysis experiments, because the thin cell is required to prevent the degradation of time resolution caused by the velocity difference

between laser and electron. Triethylamine was used as a cation scavenger and carbon tetrachloride was used as an anion scavenger.

3 RESULTS

3.1. Nanosecond pulse radiolysis experiment

Figure 1 shows the transient absorption spectra obtained in the nanosecond pulse radiolysis of biphenyl solution in cyclohexane. Several absorption bands were observed, and have been already reported [4]. The absorption band in the short wavelength region corresponds to biphenyl excited triplet states (360 nm), biphenyl cation radicals (380 nm), and biphenyl anion radicals (410 nm). In the long wavelength region, anion biphenyl radicals and biphenyl cation radicals have absorption bands around 660nm and 710nm, respectively.

It is easy to measure transient absorption in short wavelength region because of their large extinction coefficient. However, the absorption of biphenyl excited triplet states has an influence on absorption band in short wavelength region from the results of scavenger experiment. We have attempted to analyze the transient absorption at 660 nm in order to lessen the influence of absorption band of biphenyl excited triplet states.

3.2. Picosecond pulse radiolysis experiment and numerical analysis

In liquid irradiated by high energy electron beam, main phenomenon is ionization, which occurs in isolated spatial region (spur) along the trajectories of the radiation and the

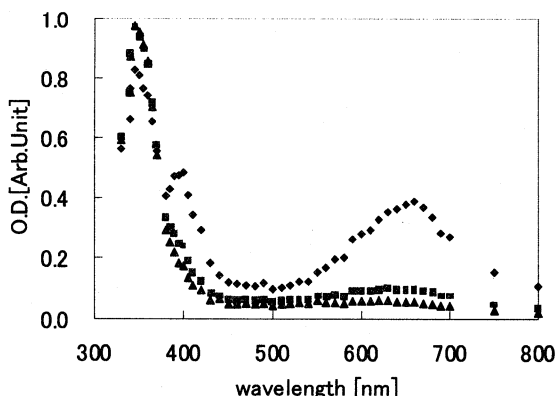


Fig. 1 Transient absorption spectra of intermediates obtained in the nanosecond pulse radiolysis of 0.1 M biphenyl solution in cyclohexane. ◆, ■, ● indicate optical density observed 8, 100 and 250 ns after pulse, respectively.

secondary electron. The electron produced by ionization is attracted by the Coulomb force of cation radical in the spur. In non-polar liquid, both the electron and the cation radical recombine. This reaction is called geminate ion recombination, which is one of the most important reactions of primary process of radiation chemistry. The time-dependent behavior of geminate ion recombination is theoretically described by the Smoluchowski equation based on diffusion theory. Smoluchowski equation is described as follows,

$$\frac{\partial W}{\partial t} = D\nabla^2 \left(\nabla W + W \frac{1}{kT} \nabla V \right) \quad (1)$$

where w , D , k , and V are the probability density function of the geminate ion pairs, the sum of the diffusion coefficients of the cation and the electron, the Boltzman constant, and the Coulomb potential, respectively.

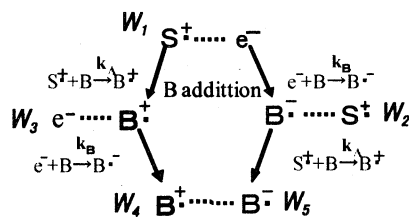


Fig2: Reaction schema in solute-solvent system, where S, B, k and W_i denote solvent, solute, reaction rate constant and survival probability.

In addition of solute into solvent, four ion pairs are formed, its reaction schema in solute-solvent system is shown in Fig.2. $W_1 \sim W_5$ in Fig.2 represent survival probability of each geminate ion pair, which can be calculated respectively by using diffusion coefficients and reaction rate constants of charge transfer [5]. With all the pairs considered, analyses were performed with Smoluchowski equation. The survival probability of solute anion is represented as the sum of W_2 , W_4 , and W_5 . Figure 3 shows the experimental and the theoretical behavior of intermediates of biphenyl solution in cyclohexane in the picosecond time region. In the analysis of experimental results at 660 nm, cyclohexane cation radicals, biphenyl cation radicals and biphenyl anion radicals were considered. The time-dependent behavior observed at 660nm, $A(t)$, was calculated as follows,

$$A(t) = X(\alpha W_{S^+} + \beta W_{B^+} + \gamma W_{B^-}) \quad (2)$$

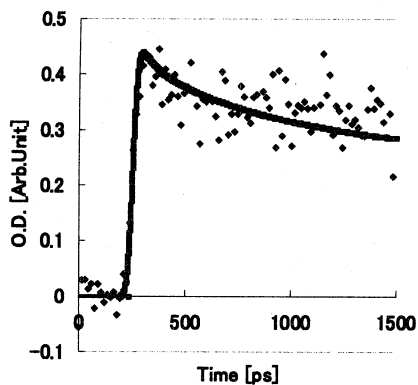


Fig. 3 Time-dependent behavior of transient absorption obtained in the picosecond pulse radiolysis of 0.1 M biphenyl solution in cyclohexane at 660 nm. The circles and dashed line indicate an experimental result and a theoretical result, respectively.

where X is a constant and W_{S^+} , W_{B^+} and W_{B^-} are the survival probability of cyclohexane cation radicals, biphenyl cation radicals and biphenyl anion radicals. The ratio of absorption coefficients α , β and γ , ($\alpha + \beta + \gamma = 1$), was decided as follows. The β and γ was decided from the ratio of transient absorption decreased by cation scavenger and anion scavenger in nano second pulse radiolysis. The value of α is decided so as to make the theoretical result fit the experimental result. In order to make the experimental result fit by using the value of β/γ , the α was decided. The value of α , β and γ is 0.5, 0.2 and 0.3, respectively. Theoretical calculation was in agreement with experimental result in the Fig. 3.

3.3. Subpicosecond pulse radiolysis experiment and numerical analysis

In order to confirm that the time-dependent behavior in the earlier time region is reproduced with Smoluchowski equation, the kinetics of geminate pair was studied by using fundamental subpicosecond pulse radiolysis at 790 nm. Figure 4 shows the time-dependent behavior of transient absorption obtained in picosecond pulse radiolysis of biphenyl solution in cyclohexane at 790 nm. The absorption decreased by adding both anion scavenger (carbon tetrachloride) and cation scavenger (triethylamine). Therefore, it is necessary to consider the overlap of intermediates in section. The ratio of absorption coefficients was decided again because of the difference of observed

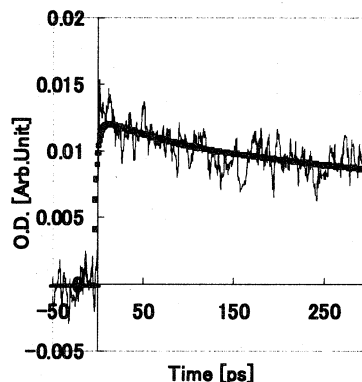


Fig. 4 Time-dependent behavior of transient absorption obtained in the picosecond pulse radiolysis of 0.1 M biphenyl solution in cyclohexane at 790 nm. The circles and dashed line indicate an experimental result and a theoretical result, respectively.

wavelength. The values of α , β and γ are 0.25, 0.25 and 0.5, respectively. Theoretical calculation was in agreement with experimental result at 790 nm in the Fig.4.

4 CONCLUSIONS

We studied kinetics of geminate processes in biphenyl-cyclohexane system at subpicosecond region with fundamental subpicosecond pulse radiolysis. Theoretical calculation was in agreement with experimental result in subpicosecond region.

By analyzing with Smoluchowski equation based on diffusion theory, the primary process of scintillation mechanism can be predicted in the other system.

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