

## Picosecond Pulse radiolysis Study on Primary Processes of Radiation Chemistry

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### Abstract

The primary processes of the radiation chemistry were studied by a new picosecond pulse radiolysis system for the absorption spectroscopy at ISIR, Osaka University. The system was composed of a 38 MeV picosecond electron linac for the irradiation source and a femtosecond laser system for the analyzing light. The processes of geminate ion recombination in liquid alkanes was observed on the picosecond time-scale and was analyzed based on the diffusion theory.

### 1. History of Picosecond Pulse Radiolysis

Primary processes of radiation chemistry is very important to know the whole reaction processes induced by high energy radiation. Pulse radiolysis technique is one of the most powerful method to research the primary processes, because very fast reaction can be detected directly.

There are two methods, the time resolved emission and absorption spectroscopy, to measure the very fast reaction. The studies on excited states and energy transfer were done by using picosecond pulse radiolysis for emission spectroscopy<sup>1,2,3,4,5,6</sup> with a very fast response light detector such as a streak camera. In absorption spectroscopy, the streak camera<sup>7,8</sup> and very fast response detector<sup>9</sup> also were used. However, the experiment had the difficulty to make very intense analyzing light.

The stroboscopic method does not require the very fast light detector. The time resolution is mainly decided by the pulse width of the radiation source and the analyzing light. The several stroboscopic picosecond pulse radiolysis systems were

developed since the first stroboscopic picosecond pulse radiolysis by Hunt et al.<sup>10</sup> in 1970. Argonne group<sup>11</sup> developed the picosecond pulse radiolysis by using a single electron pulse from a L-band linac in 1980. Later so called twin-linac system<sup>12,13,14</sup> were developed at Tokyo univ. in 1985. In these systems, the Cherenkov light pulse produced by the high energy electron was used for the analyzing light. Although the primary processes of radiation chemistry were studied by using these pulse radiolysis, they were not good at the infrared spectroscopy, because of the low intensity of the Cherenkov light in the infrared region.

A picosecond pulse radiolysis system<sup>15,16</sup> by using the laser diode instead of the Cherenkov light was developed in 1991. The system enabled the absorption spectroscopy from visible to near infrared region. However, it was difficult to obtain

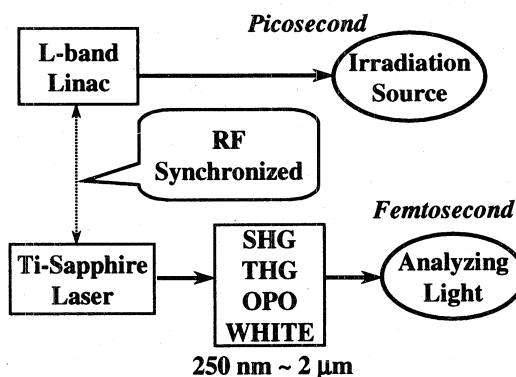


Fig.1 Concept of a new picosecond pulse radiolysis system.

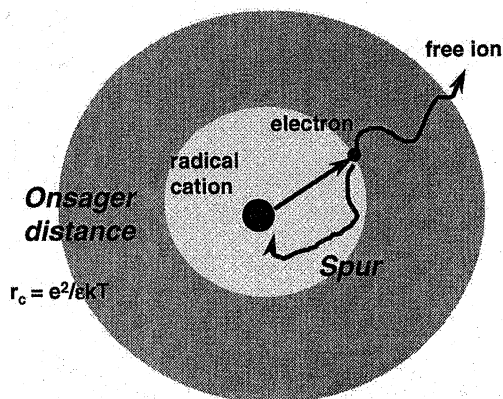


Fig.1 Block diagram of the new picosecond pulse radiolysis system.

complete spectra, because the laser diode was not tunable light source.

Recently, a new picosecond pulse radiolysis system has been developed in Osaka university. Figure 1 shows the concept of the new system. The femtosecond laser which is synchronized with the picosecond electron pulse is used for the analyzing light. The tunable laser pulse could cover the wide wavelength region from ultra violet to infrared by the non-linear optical effect. The study on the primary process of the radiation chemistry has been stated by using the new system.

## 2. Geminate Ion Recombination

The most important process of radiation chemistry in liquid alkanes is the geminate ion recombination<sup>17,18</sup> of alkane radical cations and electrons which are produced by the ionization. Figure 2 shows the behavior of the geminate process. After the thermalization of the electron emitted from the parent alkane by ionization, a parent radical cation and an electron diffuse under the Coulomb interaction. Most pairs recombined very quickly on the picosecond time-scale, due to the long-range Coulomb interaction in non-polar liquid. Small fraction of the geminate pairs escapes the recombination and becomes the free ion.

The geminate ion recombination is an inhomogeneous reaction and the kinetics is described by the diffusion theory under the Coulomb potential, so called, the Smoluchowski equation<sup>19,20</sup>, as follows.

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

where  $\omega$ ,  $D$ ,  $k$ , and  $V$  are the survival probability of the geminate pairs, the sum of the diffusion coefficients of the pairs, the Boltzmann constant, and the Coulomb potential, respectively. The equation shows the rapidity of the geminate ion recombination depends on the  $D$ .

The geminate ion recombination has been studied theoretically and experimentally by many researchers. However, it had been difficult for a long time to observe the geminate decays in neat alkanes by using pulse radiolysis, because the decays are so quick. Usually, the geminate decay of solute pairs instead of the alkane radical cations and electrons had been studied<sup>21</sup>, because the solute geminate decays were slow due to the large diffusion coefficients.

## 3. Primary processes of radiation chemistry of liquid alkanes

Figure 3 shows the typical time-dependent behavior of transient absorption of *n*-dodecane radical cations obtained in the picosecond pulse radiolysis liquid *n*-dodecane monitored at 830 nm<sup>22</sup>. The cation radicals formed within the time resolution of the system. The decay showed a typical geminate decay. The theoretical decay line was obtained by the Smoluchowski equation. In the analysis, the sum of the diffusion coefficients of  $6 \times 10^{-4} \text{ cm}^2/\text{s}$  for the electron and the radical cations and the exponential initial distribution with the initial separation of 6.6 nm were used. These parameters agreed with reported values<sup>15,16</sup>.

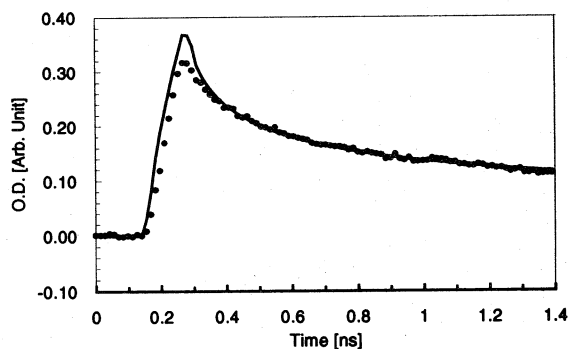


Fig. 3 Typical time-dependent behavior of transient absorption of *n*-dodecane radical cation obtained in the picosecond pulse radiolysis liquid *n*-dodecane monitored at 830 nm. (■ : experimental data, line : theoretical decay based on diffusion theory which is deconvoluted with the response function.)

**Table 1 Mobilities of electrons, characteristic lifetimes, initial spatial distributions and initial separation.**

Liquids	Mobilities (cm <sup>2</sup> /Vs)	lifetime (ps)	distributions	Initial separation (nm)
trans-decalin	0.013	35	exponential	6.1
methylcyclohexane	0.044	16	exponential	6.2
n-hexane	0.071	9.4	exponential	6.0
cis-decalin	0.10	5.6	exponential	5.6
cyclohexane	0.23	3.2	exponential	6.1
isooctane	5.3	0.43	exponential	9.3
neopentane	50	0.63	gaussian	13.2
TMS	100	0.31	gaussian	13.2

exponential  $R(r,r_0)=(1/r_0)\exp(-r/r_0)$

gaussian:  $R(r,r_0)=(4r^2/\pi^{0.5}r_0^3)\exp(-r/r_0)$

In other alkanes, such as cyclohexane and n-hexane, the decays of the electrons agree with the Smoluchowski equation. The mobilities of the electrons, the characteristic lifetimes, initial spatial distributions, and initial separation are summarized in Table 1<sup>21,23</sup>. The difference of the initial distribution depends on the slow down processes of electrons at ionization.

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