FEMTOSECOND PULSE RADIOLYSIS STUDY IN RADIATION CHEMISTRY USING A PHOTOCATHODE RF GUN LINAC

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Abstract

Femtosecond electron beam pulse radiolysis which has time resolution of 250 fs was achieved by a Photocathode RF gun LINAC in the ISIR, Osaka University. And geminate ion recombination (charged pair dynamics) in n-dodecane was studied. Kinetics of the Radical cation of n-dodecane was measured at 800 nm. As a result, existence of the excited-radical cation, and generation of the radical cation via relaxation from the excited-radical cation were suggested. New results were obtained in the field of the radiation chemistry by the photocathode RF gun.

INTRODUCTION

The electron beams generated by accelerators are used in various fields such as the industry, the medical care industry, the agriculture and the energy industry. It is necessary to elucidate the interaction between radiation and material, which yet are not completely understood, for developing the applied technology. Therefore more development of accelerator technology and higher quality electron beam is necessary. Photocathode RF gun is developing remarkably. Low emittance and high quality electron beam compared with a conventional thermal electron gun was generated by the photo-electric effect in photocathode RF gun. Electron beam was accelerated up to 4.2MeV by high gradient electric field over 100MV/m in the cavity.

It is thought that the interaction between radiation and materials begin in attosecond (10^{-18} s) time region. Pulse radiolysis system is developing day by day toward the elucidation of radiation induced chemical process from initial trigger of interaction between radiation and materials in attosecond time region. By change timing between the electron beam pulse and the analysis light pulse, pulse radiolysis is a powerful method to measure the time dependent behavior of the short life active spices generated by electron beam pulse in materials. Time resolution of pulse radiolysis is determined by electron pulse duration, light pulse duration, timing jitter and time difference in sample. Time resolution of pulse radiolysis was 800 fs by the L-band LINAC in the ISIR Osaka University with magnetic pulse compressor, and jitter compensation by the femtosecond streak camera. 100 fs electron beam pulse could be generated by non-linear compensation of pulse duration growth by electric field in accelerating tube. Time resolution of the pulse radiolysis was improved by generated 100 fs electron beam pulse. Measuring the intensity of analysis light and the absorbed signal light intensity by active spices generated by electron beam is obtained the light absorption. Changing in intensity and position of analysis light, and charge and position of electron beam become noise of optical absorption. There is a problem that measuring of small light absorption is became difficulty.

The alkanes have been studied well so far so that it was used as a solvent of the extraction agent in the nuclear fuel reprocessing. The geminate ion recombination is one of the most important primary processes, because the ionization process is about 90 % and the direct excitation is less than 10%. The initial intermediates species in n-alkane (RH) such as the excited radical cation ($RH^{\cdot+}$*) , the radical cation ($RH^{\cdot+}$), the electron (e^-), and the excited state (RH*), can be described as follows.

$$RH \;\wedge\wedge\wedge\rightarrow\; RH^{\cdot+}* + e^- \quad (1)$$

$$RH^{\cdot+}* \;\rightarrow\; RH^{\cdot+} \quad (2)$$

$$RH^{\cdot+} + e^- \;\rightarrow\; RH* \quad (3)$$

The geminate pair of the excited radical cation and the thermalized electron is generated by ionization (reaction (1)). The relaxation of the excited radical cation to the radical cation (reaction (2)) is very fast. So far the geminate pair of the radical cation and the electron has been studied as the starting point of the primary process. The simulation based on the diffusion theory can explain well the time dependent behavior of geminate ion pair after 50ps. There was a big unsolved problem that this simulation cannot explain that of before 50ps. Generation of alkyl radical is unsolved problem within 50ps.

In this study, to elucidate the initial process of radiation chemistry before 1ps, the femtosecond pulse radiolysis system was developed using the photocathode RF gun LINAC. To solve the problem on geminate ion recombination in alkan before 50ps, femtosecond pulse radiolysis measurement was carried out with carbon tetrachloride.

EXPERIMENTAL

The Photocathode RF gun LINAC in the ISIR Osaka University was consisted of the photocathode RF gun

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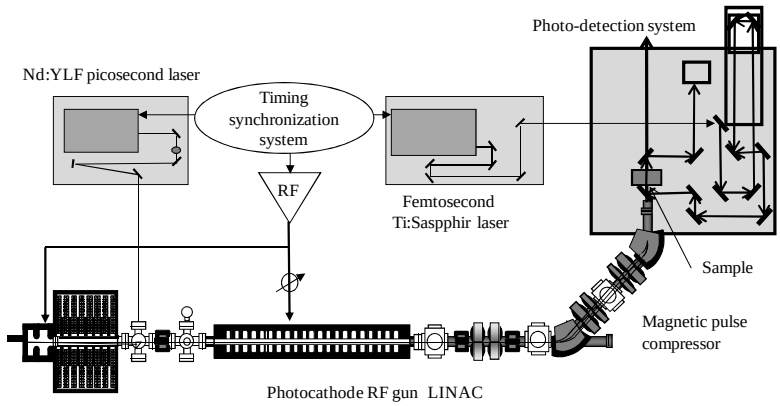

Figure 1: Femtosecond pulse radiolysis system by using the photocathode RF gun LINAC.

(BNL-type IV), the Nd:YLF picosecond laser, the solenoid magnet for emittance growth compensation, the 2 m traveling-wave accelerator tube and the magnetic pulse compressor. Fig.1 shows the femtosecond pulse radiolysis system which was consisted of the photocathode RF gun electron LINAC, the Ti:Sapphire femtosecond laser (Spectra-Physics KK) for the analyzing light, the timing synchronization system and the photo-detection system.

Both of the laser for electron generation and the laser for analysis light were installed on an optical table in a clean room. The measurement of small light absorption was enabled by stabilizing the environment of the clean room and the light path in measurement area. By focusing the generated low emittance electron beam in the sample, light absorption signal can be measured with using a sample cell of short optical path length. The double pulse method was used for the absorption measurement with high S/N ratio, and for the elimination of effects of vibration and long period fluctuation as for the drift.

Samples were irradiated by 32 MeV electron beam which has the charge of 1 nC/pulse, the repetition rate of 10 Hz, and the duration of 98 fs (r.m.s.) from the photocathode electron LINAC[1]. The wavelength, repetition and duration of the femtosecond laser were 800 nm, 79.333 MHz and 80 fs, respectively. The analyzing light was delayed by the optical delay line with 2μm accuracy. The developed pulse radiolysis system has time resolution of 240 fs, wavelength of 800 nm and measureable optical absorption of 0.005.

Anhydrous n-dodecane (n-$C_{12}H_{26}$) (Aldrich), carbon-tetrachloride (CCl_4) (Wako pure Chemical Industries, Ltd.) as an electron scavenger were used. All solutions which were bubbled by Ar gas (99.9999 %) were prepared in 2 mm and 5 mm spurasil sample-cells.

RESULTS AND DISCUSSIONS

Environment of the clean room was prepared for stabilizing the laser and the LINAC. Charge fluctuation in an electron beam pulse was 1.7%, and an influence on the optical density was estimated 0.0002. The change of the optical power of the Ti:Sapphire laser for analysis light was 0.9%, and the influence on the optical density was around 0.004. In the present, the cause of the biggest noise in the light absorption measurement was the changing of analysis light intensity.

The geminate ion recombination is described by the Smoluchowski equation based on the diffusion theory in the Coulomb potential as follows.

$$\frac{\partial w}{\partial t} = D\left(\nabla^2 w + \frac{1}{k_B T}\nabla w \nabla V(r)\right) \quad (4)$$

Where w, D, k_B, T and $V(r)$ mean the probability density of the geminate pair, the diffusion constant of the pair, the Boltzmann constant, the temperature and the Coulomb potential, respectively. The first term means the probability flow by the diffusion, and the second term means the flow in the Coulomb potential. Another method to solve the equation (4) is the Monte Carlo Simulation.

Microscopic Brownian motion in the Coulomb potential described in equation (5).

$$\Delta \boldsymbol{r} = \sqrt{6D\Delta t}\,\boldsymbol{n} + \mu \boldsymbol{E}\Delta t \quad (5)$$

Where $\boldsymbol{r}$, Δt, $\boldsymbol{n}$, μ, and $\boldsymbol{E}$ mean the distance of ion pairs, the time step, the random number, the mobility of ions, and the electric field by the Coulomb potential.

In this study, theoretical geminate kinetics was calculated by the Monte Carlo simulation, because the simulation is suitable for the complicated system considering reactions of the excited radical cation and scavengers.

On the Monte Carlo Simulation in this study, exponential function with average length of 6.6 nm was used for the initial distance distribution of geminate pair. Radical cations and electrons were recombined at the reaction radius of 0.5 nm. Mobility of the electron and the radical cation were 2.4×10^{-2} cm^2/Vs and 2.6×10^{-4} cm^2/Vs in n-dodecane. More details of the simulation will be reported in elsewhere.

Time-dependent behavior of the radical cation in n-dodecane was measured at 800 nm as a function of concentration of CCl_4 in the femtosecond pulse radiolysis. In case of existence of CCl_4, a strong electron scavenger, following reaction are added to reactions (1)~(3).

$$e^- + CCl_4 \rightarrow CCl_3^{\bullet} + Cl^- \quad (6)$$

The electron of geminate pair is converted to Cl^- by reaction (6). The time scale of the geminate ion

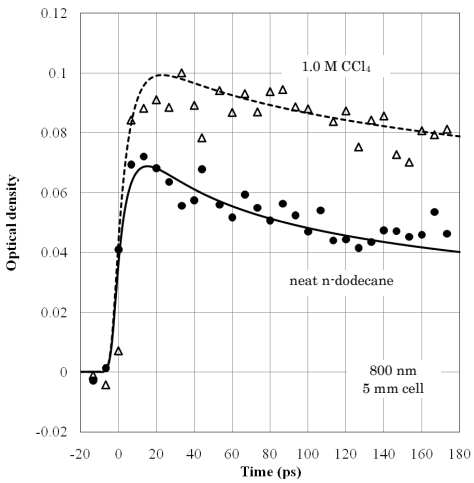

Figure 2: The time-dependent optical absorption of the radical cation monitored at 800 nm in the neat n-dodecane and the and the 1.0 M CCl_4 solution. Filled circle(●) and open triangle(△) mean experimental data and solid and dotted lines mean theoretical simulations.

recombination is delayed by the scavenging of Cl^- since the mobility of Cl^- is much smaller than that of the electron.

Fig.2 shows the time-dependent optical absorption of the radical cation monitored at 800 nm in neat n-dodecane and 1.0 M CCl_4 solution. By adding CCl_4, yields of the radical cation increased and slow formation process within several tens picosecond. Fig.3 also shows the time-dependent behavior of the radical cation measured in shorter time region. Even in the neat system, the slow formation process of the radical cation was observed. The observed formation process was not explained only by the reaction (3). It is necessary to consider the excited radical cation which is related to reactions (1), (2) and (7).

$$RH^{\cdot +}* + e^- \rightarrow RH** \qquad (7)$$

The time-dependent behavior in neat n-dodecane can be explained by the simulation when the relaxation time of

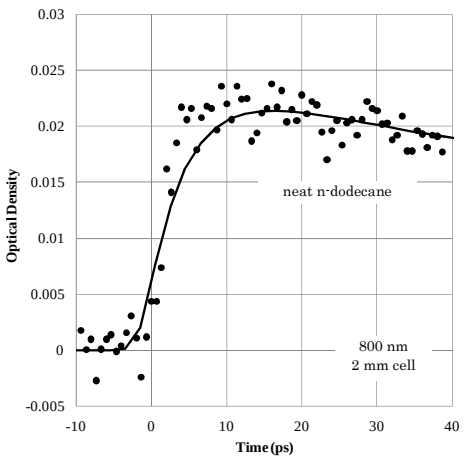

Figure 3: The time-dependent optical absorption of the radical cation monitored at 800 nm in the neat n-dodecane. Filled circle (●) mean experimental data and solid line means theoretical simulation.

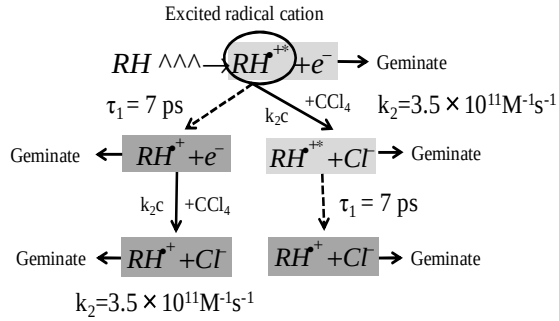

Figure 4: Reaction scheme of the geminate ion recombination considering the excited radical cation in the presence of CCl_4.

the excited radical cation is 7 ps. In the simulation, it was assumed that the excited radical cation was not observed at 800 nm.

Fig.4 shows the scheme of the geminate ion recombination considering the excited radical cation and the radical cation in the presence of CCl_4. The time-dependent behavior of radical cation agreed with the simulation result obtained in the scheme. The reaction rate constant of CCl_4 with electron (reaction (6)) was 3.5×10^{11} $dm^3mol^{-1}s^{-1}$. As the electron scavenging reaction is faster than the relaxation time of the excited radical cation in high concentrated solution, the geminate ion recombination of the excited radical cation (reaction (7)) was suppressed. Also, the geminate ion recombination of the radical cation was delayed by scavenging reaction. Therefore the yield of the radical cation is enhanced by adding the electron scavenger.

SUMMARY

The femtosecond pulse radiolysis system was developed in the ISIR, Osaka University. The 32 MeV electron beam pulse from the photocathode electron LINAC has the charge of 1 nC/pulse, the repetition rate of 10 Hz, and the duration of 98 fs (r.m.s.). The developed pulse radiolysis system has time resolution of 240 fs, wavelength of 800 nm and measureable optical absorption of 0.005. The geminate ion recombination in n-dodecane was studied by using the femtosecond pulse radiolysis. As a result, the experiment results were explained in the model that the radical cation is generated from the precursor. The precursor which has life time of 7 ps was suggested as the excited radical cation. The photocathode RF gun contributed to the field of the radiation chemistry by the femtosecond pulse radiolysis.

REFERENCES

[1] J. Yang, T. Kondoh, K. Kan, T. Kozawa, Y. Yoshida, S. Tagawa, Nuclear Instruments and Methods in Physics Research A 556(2006)52-56