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Examination of the formation process of pre-solvated and solvated electron in *n*-alcohol using femtosecond pulse radiolysis

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HIGHLIGHTS

- Formation time constants of the pre-solvated electrons in *n*-alcohols were determined.
- Formation time constants of the solvated electrons in *n*-alcohols were determined.
- Relation between pre-solvated electron formation kinetics and hydrogen bond kinetics.
- Relation between solvated electron formation kinetics and hydrogen bond kinetics.

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ABSTRACT

The formation process of pre-solvated and solvated electron in methanol (MeOH), ethanol (EtOH), *n*-butanol (BuOH), and *n*-octanol (OcOH) were investigated using a fs-pulse radiolysis technique by observing the pre-solvated electron at 1400 nm. The formation time constants of the pre-solvated electrons were determined to be 1.2, 2.2, 3.1, and 6.3 ps for MeOH, EtOH, BuOH, and OcOH, respectively. The formation time constants of the solvated electrons were determined to be 6.7, 13.6, 22.2, and 32.9 ps for MeOH, EtOH, BuOH, and OcOH, respectively. The formation dynamics and structure of the pre-solvated and solvated electrons in *n*-alcohols were discussed based on relation between the obtained time constant and dielectric relaxation time constant from the view point of kinetics. The observed formation time constants of the solvated electrons seemed to be strongly correlated with the second component of the dielectric relaxation time constants, which are related to single molecule motion. On the other hand, the observed formation time constants of the pre-solvated electrons seemed to be strongly correlated with the third component of the dielectric relaxation time constants, which are related to dynamics of hydrogen bonds.

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1. Introduction

Solvated electrons (Hart and Boag, 1962) in alcohols have been considered as an important reactive species in radiation chemistry. The rate constants for solutes (Watson and Roy, 1972) and yields of solvated electrons (Freeman, 1974) were studied using pulse radiolysis experiments. The ultrafast dynamics of the electrons has been considered for elucidation of the primary process of radiation chemistry. Precursors of the solvated electrons, which tend to have an absorption band around the near infrared region, were first

observed using nanosecond pulse radiolysis experiments at low temperature (Baxendale and Wardman, 1971). Picosecond pulse radiolysis experiments revealed that the formation time of the solvated electrons in alcohols were within a few picoseconds (Chase and Hunt, 1975; Kenney-Wallace and Jonah, 1976).

The ultrafast dynamics of a solvation process have been also studied by fs laser photolysis (Wang et al., 1980; Hirata and Mataga, 1991; Pepin et al., 1994; Walhout et al., 1995; Shi et al., 1995; Scheidt and Laenen, 2003; Migus et al., 1987; Goulet et al., 1999; Lampre et al., 2008; Bonin et al., 2007, 2008). The solvation process is often described using several models such as stepwise model (Shi et al., 1995; Migus et al., 1987), continuous sift model (Hirata and Mataga, 1991; Lampre et al., 2008), their hybrid model (Pepin et al., 1994; Goulet et al., 1999; Turi et al., 1997), multi-exponential model (Palit et al., 2014), and modified model of those (Bonin et al., 2007, 2008). In the stepwise model, the precursors of

Abbreviations: FWHM, full width at half maximum; MeOH, methanol; EtOH, ethanol; BuOH, butanol; OcOH, octanol; RF, radio frequency; UV, ultra violet; rms, root-mean-square; MSE, mean square error

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the solvated electrons were considered as several species such as the trapped electrons (Wang et al., 1980), the electronically excited state of corresponding solvated electrons (Shi et al., 1995), and partially solvated electrons (Hirata and Mataga, 1991). However, in the continuous shift model, the solvated electrons were formed because of the orientation of solvent molecules around the electrons, or the energy loss of electrons during the thermalization process (Lampre et al., 2008; Turi et al., 1997). The hybrid model in which the continuous shift model is combined with the stepwise model was proposed (Pepin et al., 1994; Goulet et al., 1999; Turi et al., 1997). However, the conclusive model is still under discussion. Both laser light pulse irradiation and irradiation of ionizing radiation can be used for ionization to examine solvation kinetics of the precursor of solvated electrons. The main difference between the two methods is the distance between the ejected electron and parent molecule: Ionizing radiation produces the pair with some distance, which is considered greater compared to that of photoionization. Therefore, the geminate ion recombination will begin from the separated condition of the electron and hole pair. This feature will be convenient to study the solvation processes of an electron, and to study reactivity of a pre-solvated electron.

Because of the development of a laser photocathode RF-gun linear accelerator (linac), the electron pulse width reduces from picosecond to femtosecond order. In addition, a mode-locked fs laser, which could be synchronized with the linac system have become useful analyzing light source. Recently, the systematical time resolution was achieved in the fs time region using the laser photocathode RF-gun linac combined with a magnetic bunch compressor in Osaka University (Yang et al., 2011, 2009). Improvement in the time resolution of our pulse radiolysis system enables us to observe both the solvated and pre-solvated electrons. In this study, the solvation processes in neat normal alcohols were studied using fs pulse radiolysis.

2. Experimental

2.1. Materials

Normal alcohols methanol (MeOH, 99.8%, Kishida chemical), ethanol (EtOH, 99.5%, Kishida chemical), *n*-butanol (BuOH, 95.5%, Merck), and *n*-octanol (OcOH, 98.0%, Kishida chemical) were used as received. All samples were bubbled by Ar gas in a quartz cuvette for more than 10 min to remove dissolved oxygen.

2.2. Pulse radiolysis measurement

The fs pulse radiolysis measurement system consisting of a photocathode RF gun electron linac with an excitation UV pulse light source for the photocathode (Nd:YLF ps laser, Pulrise IV, Time-Bandwidth, 262 nm, FWHM 5 ps), a magnetic bunch compressor, a timing synchronization system between the linac and the lasers, and a photo-detection system (Yang et al., 2011, 2009, 2006, 2006; Kan et al., 2008). The energy, charge, and duration of the electron pulse was 32 MeV, 1 nC/pulse, and 500 fs in rms, respectively. A Ti:Sapphire fs laser with a regenerative amplifier and optical parametric amplifier system (Tumani with Spitfire/TOPAS, Spectra Physics/Light Convseion) was used as an analyzing light source. The electron pulse was introduced to the sample in the quartz cuvette, and the analyzing light was also introduced coaxially to the sample. The analyzing light was delayed with an optical delay line. All the measurement of the alcohol samples were carried out in the quartz cuvette having an optical length of 2 and 5 mm. Dosimetry was performed on pure water (18 M Ω ion exchange water) at 700 nm.

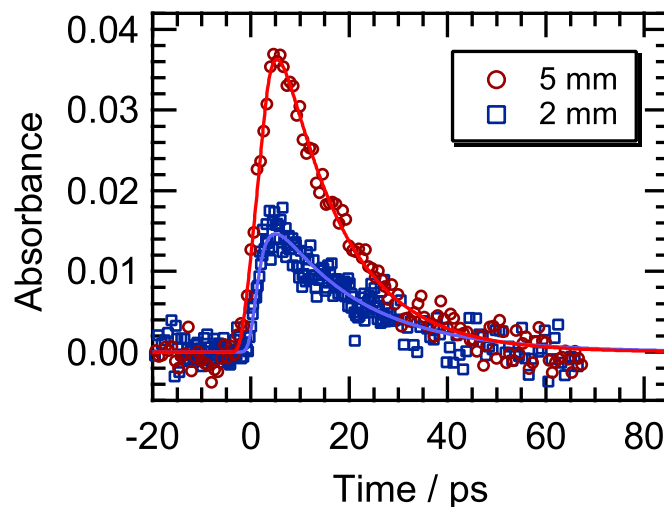


Fig. 1. Optical path length dependence on the time profiles of the pre-solvated electrons in EtOH, measured at 1400 nm. Optical path lengths of 2 mm (square) and 5 mm (circle).

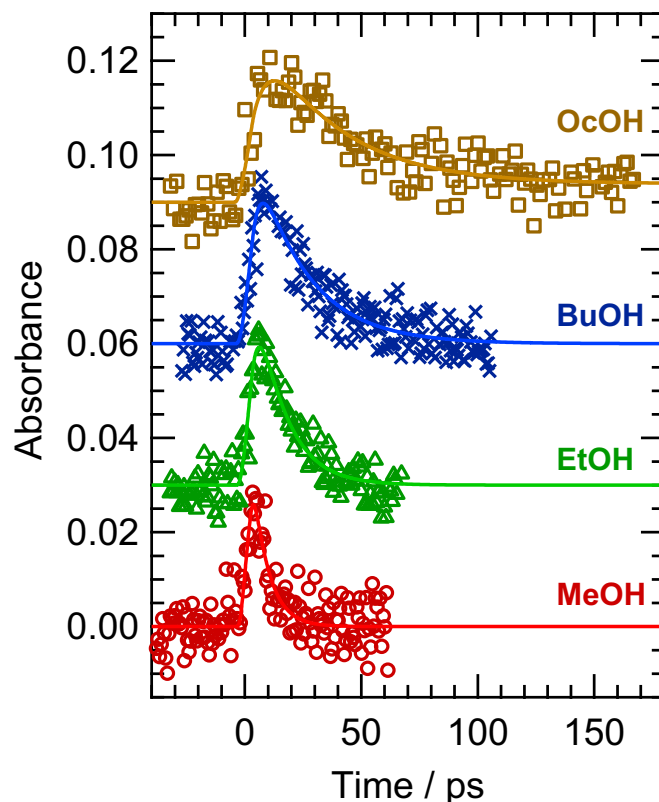


Fig. 2. The time profiles of the pre-solvated electrons in MeOH, EtOH, BuOH, and OcOH measured at 1400 nm. Experimental data points were plotted with markers and each solid line is the simulation result of the corresponding sample. All plots were plotted with offsets of 0.03 separation except for MeOH.

3. Results and discussion

The time profiles of the transient absorption of fs-pulse radiolysis on EtOH monitored at 1400 nm with an optical path length of 2 and 5 mm are shown in Fig. 1. At 1400 nm, only the pre-solvated electron in EtOH was supposed to be observed, and there was no contribution of the absorption because of the solvated electron (Baxendale and Wardman, 1971; Ferradini and Jay-Gerin, 1991). The typical dose was estimated to be 27 Gy/pulse from the measurement of a hydrated electron observed at 700 nm for the

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