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Yields of Solvated Electrons at 30 Picoseconds in Water and Alcohols

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Direct measurements of the yield of hydrated electrons in aqueous solutions and solvated electrons in alcohols were carried out using a stroboscopic picosecond pulse radiolysis system. The yield of solvated electrons was obtained by simultaneous consideration of the pulse shape and radiation doses. The yield at 30 ps after irradiation, $G(e_{aq}^-)_{30ps}$, was determined to be 4.8±0.3 products per 100 eV as compared to the $G(e_{aq}^-)_{100ns}$ of 2.7. Experimental values, including the present ones, are higher by 0.3 than the theoretical ones calculated using the spur diffusion model in the time period from 3×10^{-11} to 10^{-8} s. Nevertheless, both results show a quite similar time dependence, *i.e.*, fast decay of hydrated electrons in spur reactions. The *G*-values of solvated electrons at 30 ps were also determined in alcohols. The *G*-value of solvated electron is 3.4±0.3 in both methanol and ethanol, 2.0±0.3 in 1-propanol and 2.3±0.3 in ethylene glycol.

Hydrated electrons in aqueous solutions and solvated electrons in alcohols have been well known as one of the main products in radiation chemistry. Since the solvated electron reacts very rapidly in the spur in the time region from ps to ns, the experimental yield obtained depends on the time resolution of the apparatus. Radiation chemistry of aqueous solutions has been reasonably explained by the spur diffusion model.[1] This model was originally proposed by Samuel and Magee[2] and is now widely known in various forms. The model adequately explains the dependence of experimental molecular product yields with solute concentrations and also LET effects.[1,3] The initial yield of the hydrated electron before it escapes the spur is an extremely important parameter for the spur diffusion model. Calculations by Schwarz predict the initial yield of e_{aq}^- to be 4.78.[1] However, there is a substantial difference between the experimental *G*-values obtained in the time region 30—100 ps. Wolff *et al.*[4] reported $G(e_{aq}^-)=4.0\pm0.2$ at 30 ps by measurements using a stroboscopic picosecond pulse radiolysis (SPR) system with a train of fine structure electron pulses. Recently Jonah *et al.*[5] reported $G(e_{aq}^-)=4.6\pm0.2$ at 100 ps using a single picosecond electron pulse. This significant disagreement prompted us to measure the $G(e_{aq}^-)$ at 30 ps.

The yields of solvated electrons in several alcohols were also measured.

Experimental

The experiment was carried out using an SPR system with a time resolution of about 30 ps and the radiation source of a 45 MeV electron pulse from the S-band LINAC at Hokkaido University.[6] The optical apparatus of the SPR system was basically the same as that designed by Bronskill *et al.*,[7] and the Čerenkov light produced in a 10 cm air path was used as an analyzing light. To obtain good linearity, the detection system was equipped with an amplifier (ORTEC 451) and A/D converter (NAIG 161) instead of a stretcher, a differential amplifier and an integrator.[7] The optical absorption signals of e_{aq}^- were observed at 633 nm in pure water and 0.5 M† $HClO_4$. The cell used had a 2 cm optical path length and two circular apertures of 3 mm at its front and rear. The pure water in 1 dm^3 reservoir was bubbled with pure argon before and during irradiation and circulated through the cell by a pump. The yield of e_{aq}^- at 30 ps was obtained by simulations considering the pulse shape and radiation doses. The shape of the macro pulse was measured by monitoring the Čerenkov light with a photomultiplier (HAMAMATSU TV R446UR) and a 500 MHz oscilloscope (TEXTRONIX 7904), and it could be approximated to a Gaussian with a half width of 11 ns. The dose was measured by the absorption signal of e_{aq}^- in pure water at 100 ns assuming $G(e_{aq}^-)=2.7$.[8] The dose measurement was carried out by a conventional nanosecond pulse radiolysis technique using the SPR system, which allows a He-Ne laser (633 nm) to pass through the irradiation volume of the sample. The output of the photomultiplier was fed into a transient digitizer (IWATSU DM901) having the shortest resolvable time of 10 ns, and then displayed on an X-Y recorder. The observed dose was 4.3±0.3 krad/macro pulse as $\varepsilon_{633nm}=1.44\times10^4\ M^{-1}\,cm^{-1}$ for e_{aq}^-.[4] Aqueous solutions were prepared with triply distilled water. Alcohols were guaranteed reagents (Wako Junyaku) and were used without purifications.

Results and Discussion

Figure 1 shows the SPR signal of decay of e_{aq}^- observed at 633 nm in 0.5 M $HClO_4$. The dashed line and dotted line are computer simulated kinetic traces of e_{aq}^-. Since the observation time was limited up to 350 ps after each fine structure pulse, high acid concentrations were used to prevent the significant buildup of absorption signal from one fine structure pulse to the next.

The bimolecular rate constant for the scavenging reaction of e_{aq}^- has been measured as $(1.2\pm0.2)\times10^{10}\ M^{-1}\,s^{-1}$ for $[H_{aq}^+]$ from 0.5—5.0 M.[9] Therefore, the half lifetime of e_{aq}^-

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† 1 M=1 mol dm^{-3}.

$$e^-_{aq} + H^+_{aq} \xrightarrow{k_2} H\cdot \qquad (1)$$

in 0.5 M $HClO_4$ solutions is expected to be 120 ps. By this reason, the decay of e^-_{aq} during the pulse, which brought about a decrease in the initial step height by a factor of 0.88,[9] was taken into account, and correction for the density (1.03) of solutions was also made in the simulation.

The experimental kinetic trace of e^-_{aq} was best reproduced by adapting $G(e^-_{aq})_{30\,ps}=4.8$. A simulated trace with $G(e^-_{aq})_{30\,ps}=4.0$[4] is also shown in Fig. 1 (dotted line) for comparison. From several experimental results, we concluded that $G(e^-_{aq})_{30\,ps}=4.8\pm0.3$.[10]

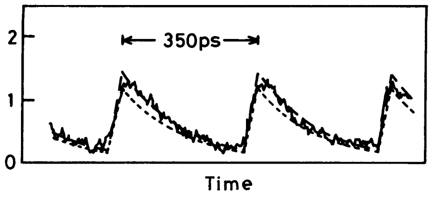

Fig. 1. The kinetic trace of e^-_{aq} observed at 633 nm in 0.5 M $HClO_4$. The dashed and dotted lines are simulated traces with $G(e^-_{aq})_{30\,ps}$ as 4.8 and 4.0 respectively. The dose was 4.3 krad/macro pulse and the half life time was 120 ps.

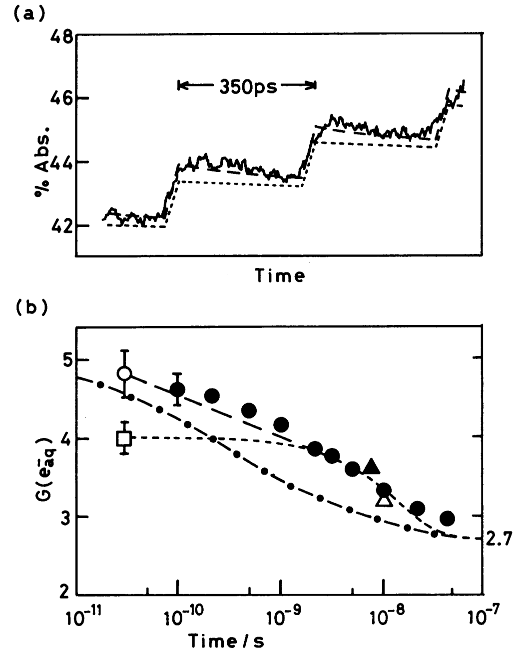

Fig. 2. (a) The kinetic trace of e^-_{aq} observed at 633 nm in pure water. The dashed and dotted lines are simulated traces with time dependences given in (b).
(b) The time dependences of $G(e^-_{aq})$ in pure water. (○),[10] (□),[4] (●),[5] (▲),[13] and (△)[14] are experimental values.
(—·—·—) is the theoretical time dependence of $G(e^-_{aq})$ by Schwarz.[1]

The error of $G(e^-_{aq})_{30\,ps}$ depends directly on the error of radiation dose measurements, while it depends on the shape of the electron macro pulse only slightly. If the shorter pulse width of 10 ns was used to simulate instead of the 11 ns that was actually observed, the best fit was obtained with $G(e^-_{aq})_{30\,ps}=4.7\pm0.3$. It should be noted that the present experiments give a higher $G(e^-_{aq})_{30\,ps}$ value than that reported by Wolff *et al.*[4] irrespective of the similar experimental conditions; however, $G(e^-_{aq})$ values close to those of present studies have been suggested in some steady state studies.[11,12]

The solid line in Fig. 2a shows the kinetic trace of e^-_{aq} observed in pure water. The dashed line and the dotted line are computer simulated kinetic traces. In the case of pure water, the half lifetime of e^-_{aq} ($T_{1/2}>10$ ns) is much longer than the interval of fine structure pulses (350 ps). Therefore the observed step signals correspond to each fine structure pulse are superimposed on the level of absorption which is due to the buildup of the signals. To analyze the experimental data, two kinds of time dependence of $G(e^-_{aq})$ were considered. The dashed line in Fig. 2b is given by fitting to experimental data[4,5,13,14] which include the present experimental value, $G(e^-_{aq})_{30\,ps}=4.8$ and can be expressed by equations;

$$\begin{aligned} G(e^-_{aq}) &= -0.53 \log t - 0.77 \\ &\text{for } 3\times10^{-11} < t < 2.7\times10^{-9}\,\text{s} \\ &= 1.3\exp(-t/1.4\times10^{-8}) + 2.7 \\ &\text{for } t > 2.7\times10^{-9}\,\text{s}. \end{aligned} \qquad (2)$$

On the other hand, if we take the lower $G(e^-_{aq})$ value at 30 ps which had been reported by Wolff *et al.*[4] as 4.0, the time dependence of $G(e^-_{aq})$ which is shown by the dotted line in Fig. 2b can be given by

$$G(e^-_{aq}) = 1.3\exp(-t/1.4\times10^{-8}) + 2.7. \qquad (3)$$

Corresponding simulation traces are shown in Fig. 2a and it is clear that the time dependence of $G(e^-_{aq})$ which contains $G(e^-_{aq})_{30\,ps}=4.8$ gives a satisfactory fitted trace.

In Fig. 2b, the typical theoretical time dependence of $G(e^-_{aq})$ calculated by Schwarz[1] is also shown for comparison. Experimental values, except one by Wolff *et al.*,[4] exhibit quite similar time dependence to the theoretical one, while they are higher by 0.3 than the theoretical one in the time period from 3×10^{-11} to 10^{-8} s. This may suggest that the spur diffusion model is not adequate in its present form.

Recently, Trumbore *et al.*[15] have improved the spur diffusion model and reported excellent agreement between calculated and experimental e^-_{aq} decay kinetics in pure water over a wide time range (10^{-11}—10^{-5} s).

Figire 3 shows the kinetic traces of decay of solvated

Table 1. MEASURED DOSES AND OTHER PARAMETERS USED FOR KINETIC SIMULATIONS OF THE DECAY OF SOLVATED ELECTRONS IN ALCOHOLS

	Methanol	Ethanol	1-Propanol	Ethylene glycol
Dose per macro pulse/krad	2.7	4.0	4.0	3.0
Wavelength/nm	630	700	700	580
Extinction coefficient/M^{-1} cm^{-1}	10200[16]	9300[16]	12800[17]	14000[17]
Half life time/ns	0.5	0.5	0.5	0.5
$G(e^-_{sol})_{30\,ps}$	3.4±0.3	3.4±0.3	2.0±0.3	2.3±0.3

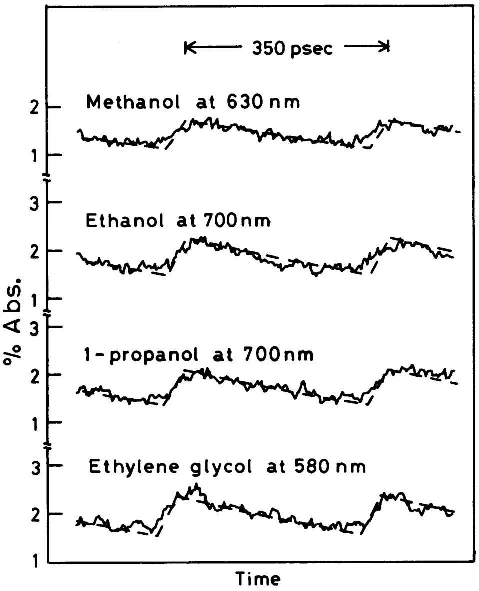

Fig. 3. Kinetic traces of solvated electrons in methanol (630 nm), ethanol (700 nm), 1-propanol (700 nm), and ethylene glycol (580 nm) in 0.10–0.15 M H_2SO_4 solutions. Dashed lines are simulated traces with parameters given in Table 1.

electrons in various alcohols at room temperature. Since in alcohols fast decaying infrared absorption was observed and attributed to the electrons in shallow traps,[18] 0.10—0.15 M H_2SO_4 was added to eliminate their contribution to the absorption of the normal solvated electron. The dashed lines are computer simulated kinetic traces which were calculated by adapting measured doses and other parameters given in Table 1. After several experimental runs, $G(e^-_{sol})_{30ps}$ values were determined to be 3.4±0.3 in both methanol and ethanol, 2.0±0.3 in 1-propanol and 2.3±0.3 in ethylene glycol.

It is expected that the radiolysis of alcohols should exhibit similar spur decay, but the spur diffusion model has not yet been applied to alcohols. The present $G(e^-_{sol})_{30ps}$ values should be useful in theoretical treatment of the spur model of alcohols.

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References

1) H. A. Schwarz, *J. Phys. Chem.*, **73**, 1928 (1969).

2) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

3) A. Appleby and J. L. Magee, *J. Phys. Chem.*, **73**, 1937 (1969).

4) R. K. Wolff, M. J. Bronskill, J. E. Aldrich, and J. W. Hunt, *J. Phys. Chem.*, **77**, 1350 (1973).

5) C. D. Jonah, M. S. Matheson, J. R. Miller, and E. J. Hart, *J. Phys. Chem.*, **80**, 1267 (1976).

6) T. Sumiyoshi, S. Sawamura, Y. Koshikawa, and M. Katayama, *Bull. Chem. Soc. Jpn.*, **55**, 2341 (1982).

7) M. J. Bronskill, W. B. Taylor, R. K. Wolff, and J. W. Hunt, *Rev. Sci. Instrum.*, **41**, 333 (1970).

8) E. J. Hart and M. Anbar, "The Hydrated Electron" Wiley-Interscience, New York (1970).

9) M. J. Bronskill, R. K. Wolff, and J. W. Hunt, *J. Chem. Phys.*, **53**, 4201 (1970).

10) T. Sumiyoshi and M. Katayama, *Chem. Lett.*, 1887 (1982).

11) T. I. Balkas, J. H. Fendler, and R. H. Schuler, *J. Phys. Chem.*, **74**, 4497 (1970).

12) W. H. Hamill, *J. Phys. Chem.*, **73**, 1341 (1969).

13) G. V. Buxton, *Proc. R. Soc. London, Ser. A*, **328**, 9 (1972).

14) J. K. Thomas and R. V. Bensasson, *J. Chem. Phys.*, **46**, 4147 (1967).

15) C. N. Trumbore, W. Youngblade, and D. R. Short, *J. Phys. Chem.*, **88**, 5057 (1984).

16) K. N. Jha, G. L. Bolton, and G. R. Freeman, *J. Phys. Chem.*, **76**, 3876 (1972).

17) M. C. Sauer, Jr., S. Arai, and L. M. Dorfman, *J. Chem. Phys.*, **42**, 708 (1965).

18) K. Y. Lam and J. W. Hunt, *J. Phys. Chem.*, **78**, 2414 (1974).