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THE YIELD OF HYDRATED ELECTRONS AT 30 PICOSECONDS

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Direct measurements of the yield of hydrated electrons in aqueous solutions were carried out using a stroboscopic picosecond pulse radiolysis system. The yield 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.

Radiation chemistry of aqueous solutions has been reasonably explained by the spur diffusion model. This model was originally proposed by Samuel and Magee1) and is widely known in various forms now. The model adequately explains the dependence of experimental molecular product yields with solute concentrations and also LET effects.2,3) The initial yield of the hydrated electron (e^-_{aq}) 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 4.78.2) 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 ± 0.2 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 ± 0.2 at 100 ps using a single picosecond electron pulse. This significant disagreement prompted us to measure the $G(e^-_{aq})$ at 30 ps. The experiment was carried out using an SPR system6) 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. 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 a good linearity, the detection system consisted of an amplifier (ORTEC 451) and an A/D converter (NAIG 161) instead of a stretcher, a differential amplifier and an integrator.7) The optical absorption kinetic 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 irradiaion and then 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) with the shortest resolvable time of 10 ns and displayed on an X-Y recorder. The observed dose was 4.10 ± 0.3 krad/macro pulse as $\varepsilon_{633nm} = 1.44 \times 10^4\ M^{-1}cm^{-1}$ for e^-_{aq}.[4)] Figure 1 shows the SPR signals obtained in pure water and 0.5 M $HClO_4$. The dashed lines are computer simulated kinetic traces of e^-_{aq}. The decay of e^-_{aq} during the pulse, which brings about the decrease in the initial step height by a factor of 0.88[9)], was taken into account, and the correction for the density (1.03) was made in the case of 0.5 M $HClO_4$. The experimental kinetic traces of e^-_{aq} are best reproduced by adapting $G(e^-_{aq})_{30ps} = 4.8$ in both samples. Simulated traces with $G(e^-_{aq})_{30ps} = 4.0$ are also shown in Fig. 1 for comparison. From several experimental results, we concluded that $G(e^-_{aq})_{30ps} = 4.8 \pm 0.3$. These measurements do not depend on ε_{633nm} but on the shape of the electron macro pulse. When 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 $G(e^-_{aq})_{30ps} = 4.7 \pm 0.3$. It should be noted that the present experiments give a higher $G(e^-_{aq})$ value at 30 ps than that reported by Wolff et al.[4)] irrespective of the similar experimental conditions; however, $G(e^-_{aq})$ values close to those of the present study have been suggested in some steady state studies.[10,11)] Figure 2 shows the experimental values of $G(e^-_{aq})$ at various times after irradiation obtained by other workers[4,5,12,13)] as well as the typical theoretical time dependence of $G(e^-_{aq})$.[2)] Experimental values, except one by Wolff et al.,[4)] are higher by 0.3 than the theoretical ones in the time period from 3×10^{-11} to 10^{-8}. Nevertheless, both results show a quite similar time dependence, i.e., fast decay of hydrated electrons in spur reactions.

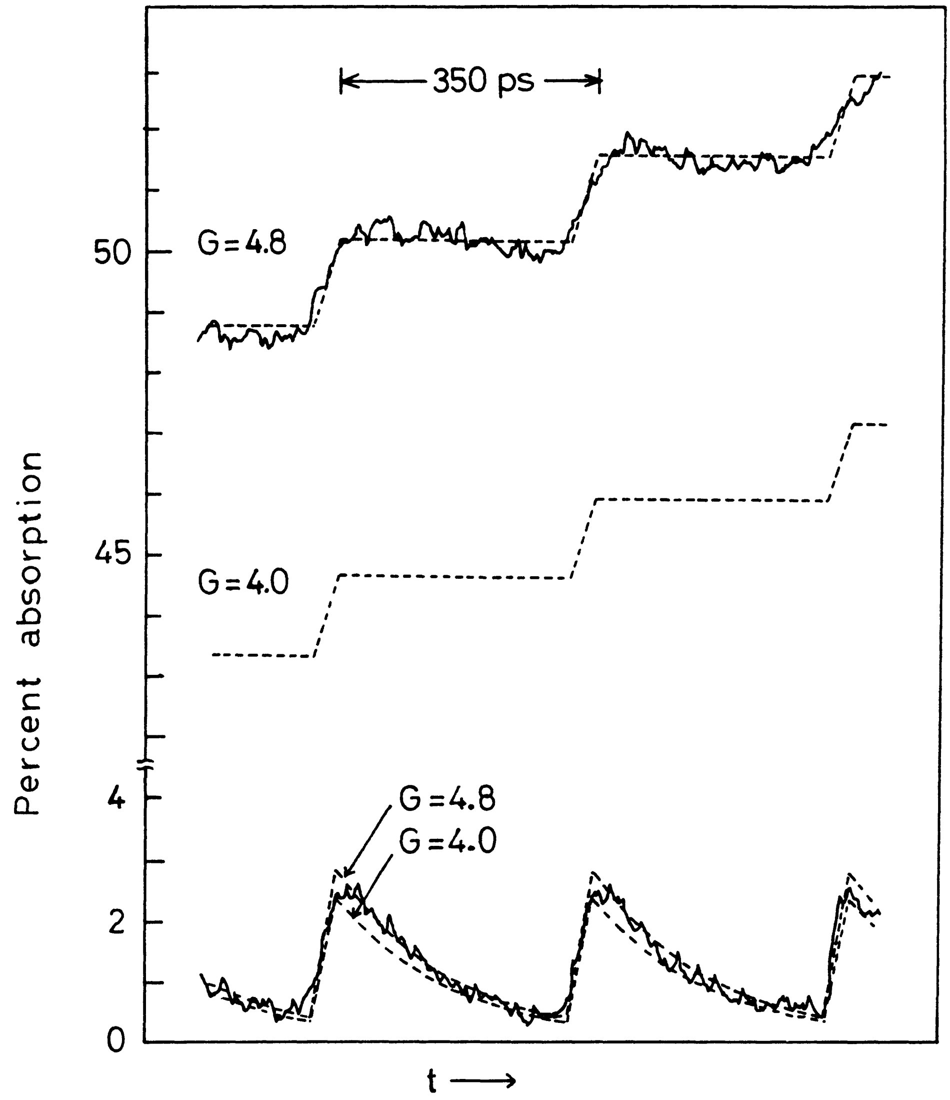

Fig. 1. The kinetic traces of e_{aq}^- observed in pure water (upper trace) and 0.5 M $HClO_4$ (lower trace) at 633 nm. The dashed lines are simulated traces with indicated $G(e_{aq}^-)_{30ps}$ values.

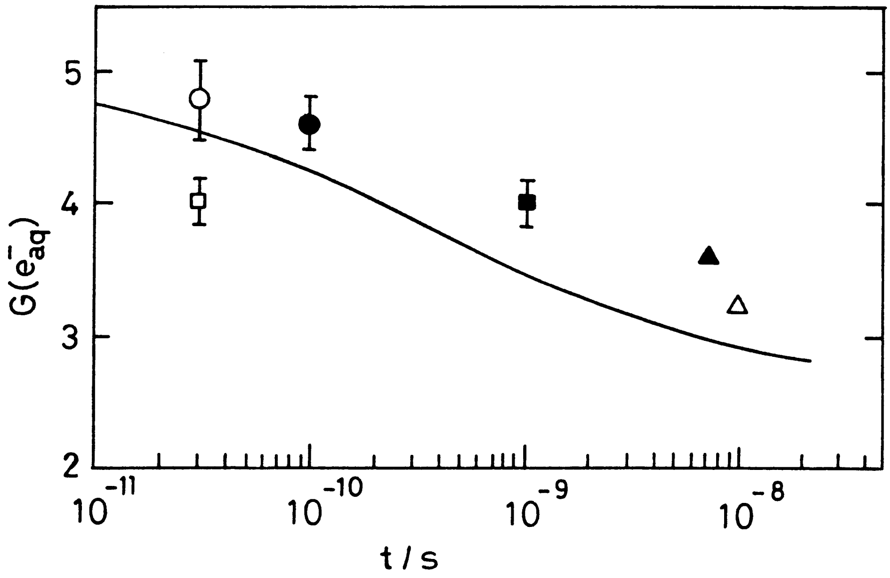

Fig. 2. Observed $G(e^-_{aq})$ values and theoretical time dependence of $G(e^-_{aq})$.
Experimental values; ○ (present work), □ (ref. 4),
●, ■ (ref. 5), ▲ (ref. 12), △ (ref. 13),
Theoretical curve$^{2)}$; solid curve.

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