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A Stroboscopic Pulse Radiolysis System with a Time Resolution of Picoseconds

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Abstract

For the investigation of fast reactions, a stroboscopic pulse radiolysis system was constructed and tested successfully. The radiation source is a train of fine structure pulses from the 45 MeV S-band linear accelerator at Hokkaido University. The Cerenkov light flashes produced in the air by these fine structure pulses are suitably delayed and thus can be used to detect the absorption of transient species in the time region 35–350 psec. The averaging of the light signals and the movement of the movable mirrors of the optical delay system are carried out by an on-line minicomputer. Some preliminary results obtained in tests on aqueous systems by the use of this stroboscopic pulse radiolysis system are reported.

1. Introduction

As many chemical reactions induced by ionizing radiation involve short-lived intermediates, the formation or decay of these transient species has been investigated hitherto mainly by the pulse radiolysis technique. The time resolution of most pulse radiolysis systems has been limited to several nanoseconds due to the width of the available radiation pulses and the absence of a high speed optical detector. Two methods are known to improve the time resolution, the stroboscopic technique and a high speed optical detection system. The stroboscopic pulse radiolysis system was designed and built by Hunt and his coworkers¹⁾. Using 35 nsec pulses from an S-band linear accelerator (LINAC) and an ordinary optical detection system, they were able to study the reactions of solvated electrons²⁾, dry electrons and holes³⁾, and the solvation of electrons in alcohols in the time region 20–350 psec⁴⁾. Jonah applied this technique to a single picosecond pulse from an L-band LINAC⁵⁾ and was able to study similar aqueous systems for as long as 3.5 nsec after irradiation^{6,7)}. The distinct advantage of his method is that it removes the upper limitation of observation time (350 psec for an S-band LINAC and 770 psec for an L-band LINAC), which inevitably occurs as one works with a train of fine structure pulses.

A high speed optical detection system with picosecond time resolution makes it possible to study both emissions and absorptions. Beck and Thomas constructed a

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fast detection system utilizing a photodiode⁸⁾ and studied the formation kinetics of excited states in organic systems between 60–770 psec with a train of electron pulses from an L-band LINAC⁹⁾. Tagawa and his coworkers also studied emission kinetics in organic solvents with a streak camera having a time response of 10 psec and by using a single picosecond pulse from an S-band LINAC¹⁰⁾.

We have carried out preliminary experiments with a 45 MeV S-band LINAC without a subharmonic prebuncher. Although the stroboscopic method using a train of electron pulses is essentially accompanied by a long time limitation, as mentioned above, it is possible to obtain a good time resolution (~ 20 psec) with a conventional photomultiplier detection system¹⁾. This paper describes our picosecond pulse radiolysis system and some of the preliminary results obtained by it.

2. Experimental section

Our stroboscopic pulse radiolysis system was described previously in detail¹¹⁾. However, some modifications were needed before successful observations of the absorption signals could be made. In order to avoid γ -ray irradiation of the photomultiplier tube (Hamamatsu TV Co., R446UR), the analyzing light was detected in a separate room behind a shielding wall (3.5 m). And in order to decrease the amount of electronic noises from the krystron, the detection system, which contains a preamplifier, amplifier (ORTEC 451), A/D converter (NAIG D-161) and a minicomputer (TACC-1200M) was placed near the photomultiplier tube and 30 m away from

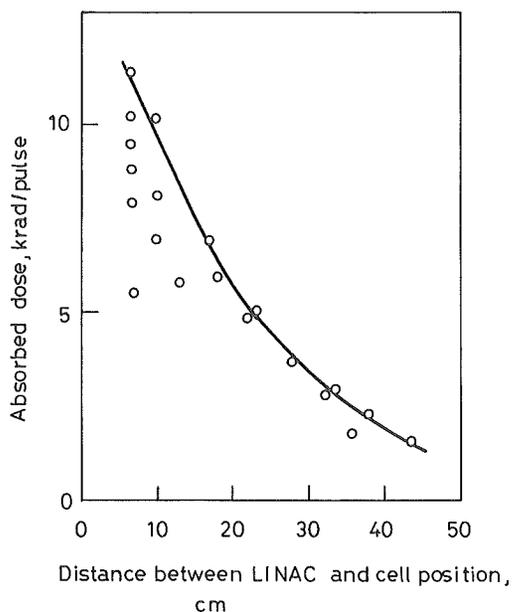


Figure 1. Absorbed dose of the 45 MeV electron pulse as a function of distance between the LINAC and the sample cell.

the LINAC control room. The dose of electron pulses decreased with the increase of the distance between the LINAC and the sample cell. Fig. 1 shows the doses measured at various distances with a conventional nanosecond pulse radiolysis system¹²⁾ using a KCNS dosimeter¹³⁾. Based on these results, we shortened the distance between the LINAC and the sample cell as much as possible. However, in order to produce the Čerenkov light flashes as analyzing lights, a 10 cm air path and another 7.5 cm were needed to accommodate the two thin mirrors and the lead beam chopper. The dose at 17.5 cm was about 6 krads per pulse with pulse width (FWHM) 17 nsec. Actually, this 17 nsec pulse consisted of 48 fine structure electron pulses with a time interval of 350 psec between them. The absorbed dose per fine structure pulse was about 120 rads, which was expected to produce an absorption signal of 2% at 600 nm for e^-_{aq} . Since a pulse fluctuation of $\pm 2.5\%$ is commonly observed for our LINAC, we considered that signal averaging techniques by a computer would be effective for reduction of the fluctuation.

Three types of light pulses were produced to reduce noise, and the absorption signal was extracted from the background light level by a rotating aluminum light chopper and lead beam chopper¹¹⁾. The LINAC was operated with line-locking at 50 Hz.

3. Results and Discussion

Hydrated electrons—Fig. 2 shows the typical formation and decay traces of the hydrated electron observed at 625 nm in solutions of 0.5–2 M HClO_4 . The reactions of the hydrated electron with various reactants have been studied extensively over the past twenty years¹⁴⁾. High concentrations of HClO_4 were used to reduce the lifetime of the hydrated electron to less than 350 psec. The bimolecular rate constant for reaction (1) has been reported as $2.0\text{--}2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at low H^+_{aq} concentrations¹⁴⁾



To estimate the rate constant, computer simulations were carried out since the rise above the base line was observed for the absorption signal in 0.5 M HClO_4 solution. In these calculations, it is assumed that a value of $\epsilon_{625\text{nm}}$ is $1.36 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for e^-_{aq} , and the decay of e^-_{aq} during the electron pulse is also taken into account. The dashed lines in fig. 2 were obtained when $\tau_{1/2}$ was 110 psec for 0.5 M, 57.5 psec for 1 M, 40 psec for 1.5 M and 29 psec for 2 M HClO_4 . The rate constant was calculated to be $(1.20 \pm 0.06) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which is in good agreement with the reported value of $(1.2 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ over the range 0.5–5.0 M H^+_{aq} ¹⁵⁾. The difference between the rate constants in the diluted and the concentrated solutions was attributed qualitatively to three factors, i. e., changes in ionic strength, incomplete relaxation of the ionic atmosphere before reaction and the time dependence of the rate constants¹⁶⁾.

The observed rise time (10–90 %) for the formation of the hydrated electron was about 35 psec. Since the formation time of e^-_{aq} has been shown to be less than 10 psec¹⁵⁾, this rise time was attributed mainly to the following two factors. One is

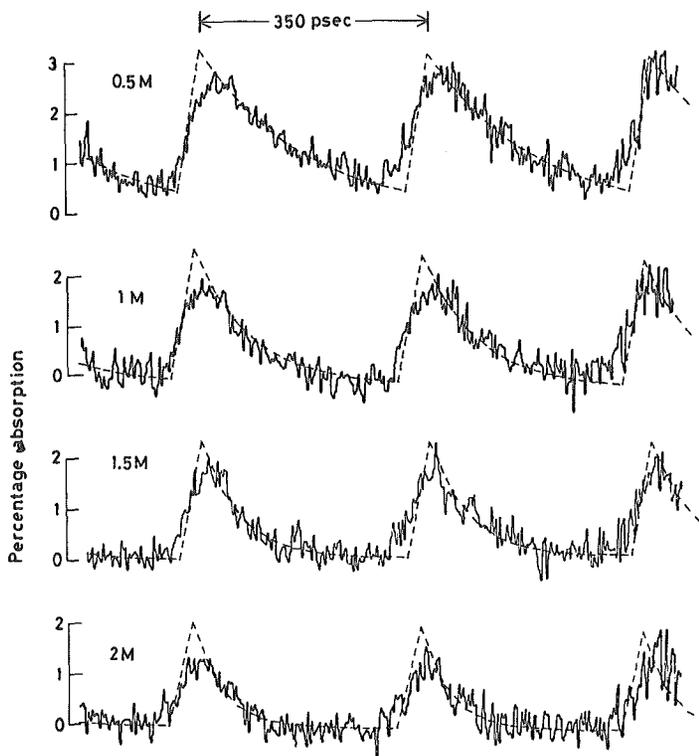


Figure 2. Formation and decay of e^-_{aq} in 0.5–2 M HClO, solutions as observed at 625 nm. The dashed lines are simulated traces.

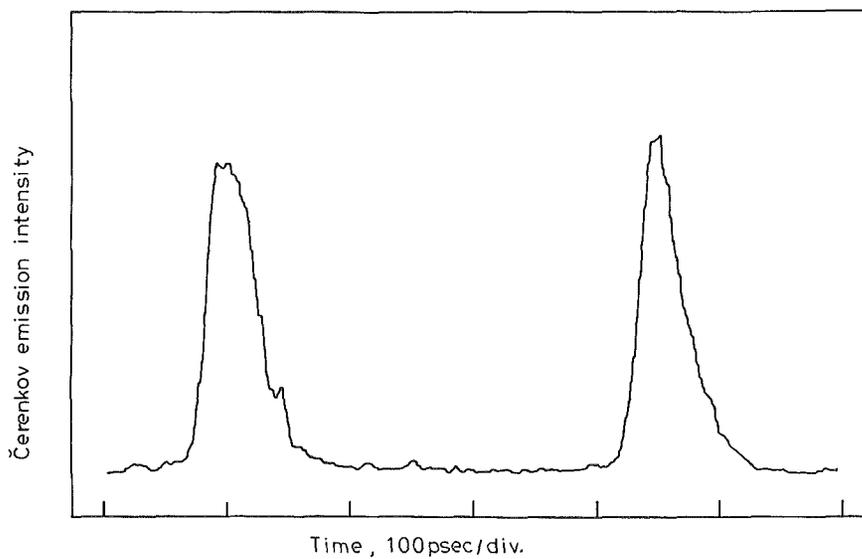


Figure 3. Fine structure pulses from the 45 MeV S-band LINAC. The Čerenkov light produced in air as observed with a streak camera system.

the width of the fine structure electron pulses. Fig. 3 illustrates some typical fine structure pulses. The width of the fine structure pulse observed with a streak camera system (Hamamatsu TV Co., HTV-C979X) having a rise time of 10 psec was observed to be approximately 39 psec (FWHM), which was longer than the rise time of e^-_{aq} . It is thought that the real pulse width is less than 30 psec. Another factor is the desynchronization of the pulses which is due to the difference between the velocities of high energy electrons and the analyzing light in water. The 45 MeV electron pulse moves with velocity close to that of light *in vacuo*, while the analyzing light moves slower with a velocity of c/n , where n is the index of refraction of light in the solution and c is the velocity of light *in vacuo*. The desynchronization of pulses is given by eq. (2)

$$\Delta t = (n-1) \frac{l}{c} \quad (2),$$

where l is the length of the cell. The time difference of a 2 cm path in water is 21 psec. A shorter optical path is desirable to achieve a fast rise time, although it will probably decrease the absorption signal.

It is well known that the product of G value (molecules/100 eV) of e^-_{aq} and the dose changes the signal intensity. The G value previously determined by Hunt and coworkers was 4.0 at 30 psec¹⁷⁾. Later a higher value of 4.6 at 100 psec was reported by Jonah and coworkers⁹⁾, and they also observed the fast decay of e^-_{aq} to be about 17% between 100 psec and 3 nsec. The substantial difference between the experimental results of these two groups in this particular case should be noted. If we use $G=4.0$, the dose per macro pulse will be 6.6 krad, which seems higher than that of the expected one from the data of fig. 1.

Fig. 4 shows the build-up of the absorption signal of e^-_{aq} during the decay of e^-_{aq} is suppressed in the observed time region. The major reactions of the hydrated electron in this case are as follows



Sodium hydroxide and ethanol were added to reduce $[\text{H}^+]$ and to scavenge the OH radical, respectively. The step heights (1.6%) corresponded to each fine structure pulse and were superimposed on the level of absorption (50–60%), which was due to the build-up of the signals. To analyze these data, one should consider the changes of G value and the extinction coefficient of e^-_{aq} which was varied by the added solutes. Actually, the half life time of e^-_{aq} changes the absorption level even if it is much longer than the observation time. For example, $\tau_{1/2}=100$ nsec caused a 1% adsorption decrease. The corrections of these three effects are too uncertain to obtain the formation and decay traces of e^-_{aq} per fine structure pulse by computer simulations.

Br^-_2 —Fig. 5 shows the kinetic traces for the formation of Br^-_2 at 360 nm in 0.5–2 M NaBr solutions. A fast and a slow component are shown. The contribution of the fast component showed increases with increased NaBr concentration. These

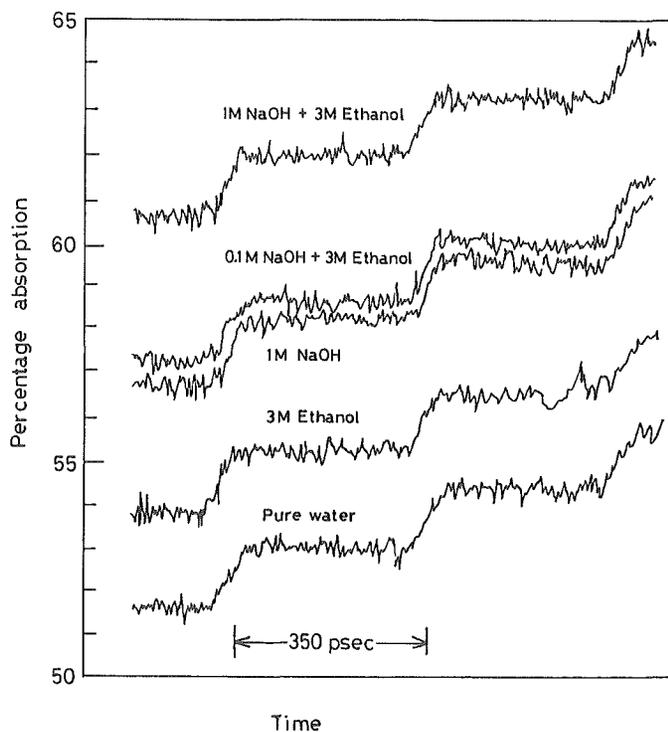


Figure 4. Formation and decay of e^-_{aq} in water, 3 M ethanol, 1 M NaOH, 0.1 M NaOH + 3 M ethanol and 1 M NaOH + 3 M ethanol as observed at 625 nm.

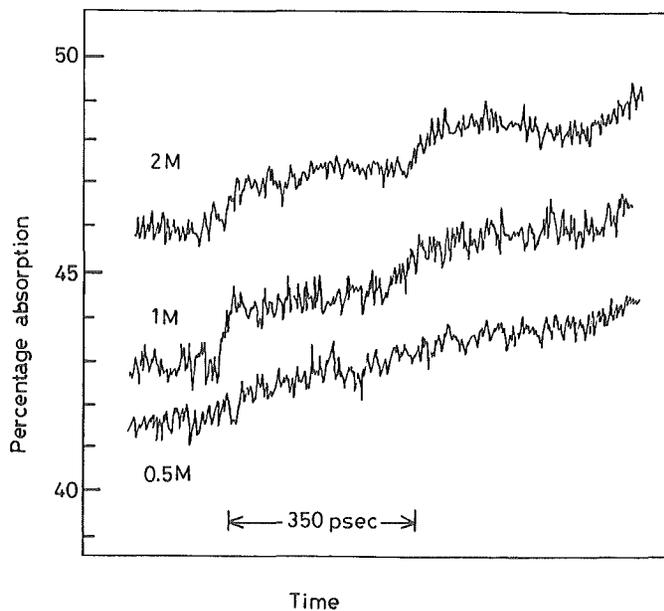


Figure 5. Formation of the absorption signal of Br_2 in 0.5–2 M NaBr at 360 nm.

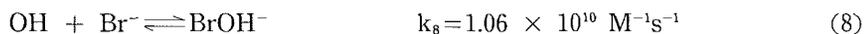
results are similar to those reported by Hunt and his coworkers¹⁸⁾, who suggested that the fast component is due to reactions of H_2O^+ as shown in eq. (6)



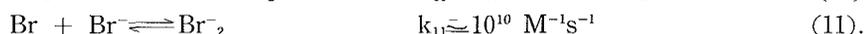
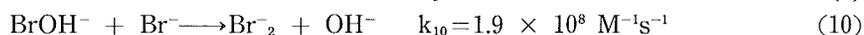
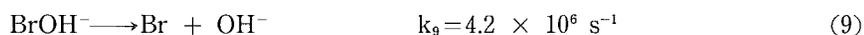
followed by the reaction



The slow component is explained by the reaction mechanism proposed by Zehavi and Rabani¹⁹⁾,



$$k_{-8} = 3.3 \times 10^7 \text{ s}^{-1}$$



$$k_{-11} < 10^3 \text{ s}^{-1}$$

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