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PICOSECOND PULSE RADIOLYSIS OF LIQUID n-ALKANES

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Transient cationic species produced in irradiated liquid n-alkanes (heptane–decane) were observed by the stroboscopic picosecond pulse radiolysis technique at room temperature. The half life, buildup spectra and G ε were obtained and discussed.

Radical cations of higher alkanes have been observed in γ-irradiated CCl_4 or 3-methylpentane matrices at 77 K.[1] However, no RH^+ bands have been found in pure alkanes, presumably because of the fast recombination which occurs between cations and electrons after irradiation. Weak and fast decaying optical absorptions in several liquid alkanes were first observed by Mehnert et al.[2,3] in nanosecond pulse radiolysis experiments. In their low temperature pulse radiolysis studies, a faster absorption spike was observed and attributed to alkane cations non-homogeneously distributed. The present experiments were carried out to observe this faster decaying species in n-alkanes by means of picosecond pulse radiolysis at room temperature. The picosecond pulse radiolysis system which uses a 45 MeV, 11 ns electron pulse from an S-band LINAC at Hokkaido University was described in a previous paper.[4] The time resolution was about 30 ps. Samples of heptane, octane, nonane and decane (Wako Junyaku) were used as received.
They were circulated through a 2-cm optical cell by a pump. The spectra were obtained by fixing the movable mirrors at the position nearest to the electron beam. Figure 1 shows the typical kinetic traces of irradiated octane observed at 640 and 450 nm. The dashed lines are computer simulated kinetic traces, assuming that there is only a single exponentially decaying transient. The radiation dose was measured by the absorption of hydrated electrons in a 1 M $HClO_4$ solution using $G(e^-_{aq})_{30ps} = 4.8$.[5] Best fitting curves were obtained assuming the half life time to be 0.7 ns and the values of G ε to be 3.39×10^4 and 2.05×10^4 $M^{-1}cm^{-1}$ at 640 and 450 nm respectively. Figure 2 shows the kinetic traces observed in decane. Figures 3 and 4 show the buildup spectra observed in octane and nonane. The obtained half life time and absorption maxima were summarized in Table 1. These

Table 1. Half Life Time and Absorption Maxima Observed in n-Alkanes

	heptane	octane	nonane	decane
Half life time/ns	0.55	0.70	0.65	1.00
Absorption maxima/nm	560	600	550	>620

results suggest that the observed transient absorptions are attributed to alkane cation radicals.[1-3] The absorption maximum observed in nonane shifts about 150 nm towards the shorter wavelength as compared to 700 nm observed in CCl_4 at 77 K.[1] Since quantum mechanical calculations show that there are many excited states of higher alkane radical cations,[6] absorption of the excited cations is expected in the case of nonane.

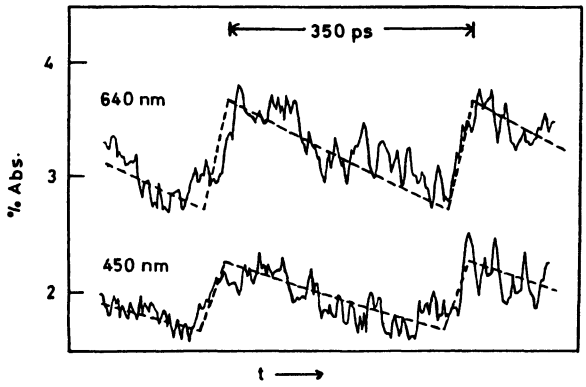

Fig. 1. Kinetic traces observed in octane. The dashed lines are simulated traces with $t_{1/2}$ = 0.7 ns.

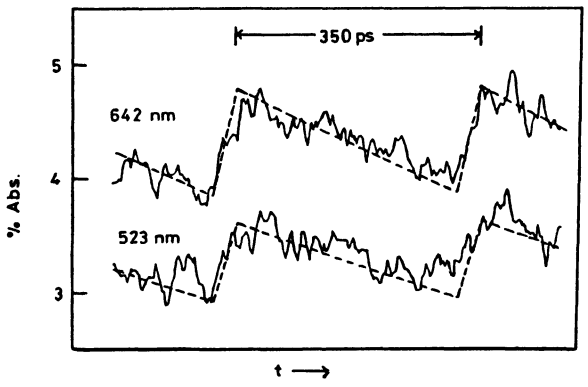

Fig. 2. Kinetic traces observed in decane. The dashed lines are simulated traces with $t_{1/2}$ = 0.65 ns.

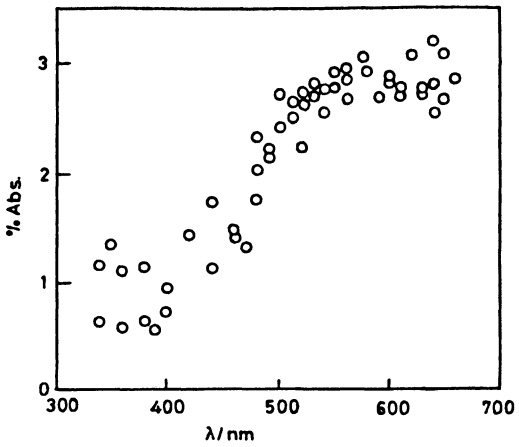

Fig. 3. Absorption spectrum in octane.

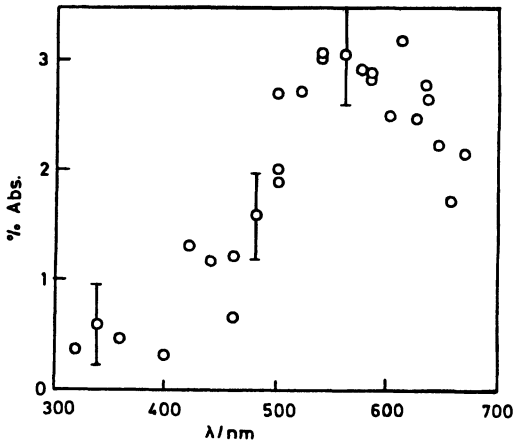

Fig. 4. Absorption spectrum in nonane.

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