The Photobleaching of Trapped Electrons and the Electron Capture of Radicals in γ-Irradiated Hydrocarbon Matrices at 77 K

Yo-ichi Ishikawa, Ko-ichi Oka, and Shin Sato

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The rate of the photobleaching of the trapped electrons in the 3-methylhexane and methylcyclohexane matrices at 77 K was measured by means of ESR as a function of the concentration of the 3-methylhexyl or methylcyclohexyl radicals present in the matrices. The quantum yield of the photobleaching at the wavelength of 1300 nm increased with the increase in the radical concentration. The stable products such as olefins formed during the γ-irradiation did not affect the quantum efficiency. These results support the suggestion made by Willard *et al.* that the 3-methylhexyl and methylcyclohexyl radicals capture the electrons released from the trapping sites by the irradiation of the infrared light. A comparison showed that the radicals are comparable with sulfur hexafluoride in electron capture.

The γ-irradiation of hydrocarbon glasses produces trapped electrons, radicals, and cations.[1] The increase in the radical concentration is approximately linear during the first 4×10^{20} eV g^{-1}. After *ca.* 2×10^{21} eV g^{-1} of continuous irradiation, the yield of radicals reaches a steady state.[2] On the other hand, the yield of trapped electrons has its maximum value at the point where the yield of radicals becomes saturated, and it drops to zero when the yield of radicals reaches the steady state.[3]

After complete bleaching with IR light, the irradiation of UV light at 375 nm can regenerate the trapped electrons.[4-7] This experiment suggests the following reversible reaction;

$$R + e_t^- \underset{UV}{\overset{IR}{\rightleftharpoons}} R^-$$

although the reformed trapped electrons are much fewer than originally. In the pulse radiolysis of a solution of alkali metal cations in tetrahydrofuran, the rate constant of the reaction between tetrahydrofuran radicals and mobile electrons has been reported to be 6×10^{10} mol^{-1} s^{-1}.[8]

The present study attempted to measure the rate of the electron capture of the radicals produced in the γ-irradiated, glassy 3-methylhexane (3-MHX) and methylcyclohexane (MCH) matrices. If this rate is very large, the electron capture by radicals has to be taken into account in the interpretation of the dose dependence of the formation of trapped electrons, as Willard *et al.* have mentioned.[4]

Experimental

The details of the ESR instrument, the method for the purification of 3-MHX, the set-up for photobleaching, and the actinometry of the IR light were reported in a previous paper.[9]

The MCH, purchased from the Tokyo Kasei Kogyo Co., Ltd., was degassed by freeze-thaw cycles and stored with sodium-potassium alloy. The 1-pentene, supplied by Tokyo Kasei Kogyo, was used without further purification.

A constant volume of hydrocarbons, 0.32 ml for 3-MHX and 0.25 ml for MCH, was sealed in a Suprasil quartz tube in a mercury-free vacuum system. The γ-irradiation of the samples was done at a dose rate of $0.53—0.44\times10^6$ R hr^{-1} at 77 K in the dark.

In order to obtain various concentrations of the matrix radicals, we used the following technique. The sample is γ-irradiated for various intervals, 5—150 min; we can thus obtain the trapped electrons and the 3-methylhexyl or methylcyclohexyl radicals. When this sample is irradiated with IR and visible light from a tungsten lamp (375 W) for an appropriate time interval, the trapped electrons disappear and only the matrix radicals remain. In some cases, a medium-pressure mercury lamp was used without any filter to bleach radical anions completely. This sample is again γ-irradiated for 5 min in the case of 3-MHX and for 30 min in the case of MCH. Then, we can obtain trapped electrons in the matrix, together with various concentrations of matrix radicals.

Results

Radical Concentration. For the estimation of the concentration of the trapped electrons in the 3-MHX and MCH glassy matrices, we assumed $G(e_t^-)=0.87$ for 3-MHX and 0.38 for MCH.[10] The concentration of the radicals was estimated by comparing the integrated areas of the spectrum of the radicals with those of standard samples (DPPH and Ultramarine blue). Values of G(3-MHX radicals)$=4.3\pm0.5$ and G(MCH radicals)$=4.0\pm0.5$ were obtained. When the concentration of the trapped electrons is measured by ESR, attention has to be paid to the saturation effect. Therefore, we made a calibration curve and measured the ESR spectra, usually at a constant low power of microwaves, 0.08 mW.

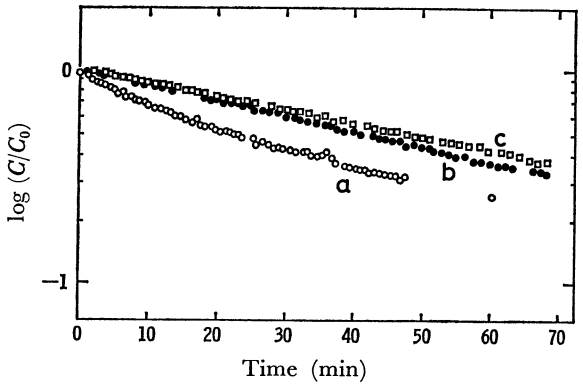

Fig. 1. Semilogarithmic plot for the decay of trapped electrons in the γ-irradiated 3-MHX glass during photobleaching at 1300 nm. The γ-irradiation dose were a) 0.27, b) 4.8, and c) 6.4×10^{19} eV g^{-1}.

Photobleaching in the Case of 3-MHX. Figure 1 shows a typical decay plot for the trapped electrons in the 3-MHX matrix during the irradiation of the IR light at 1300 nm. Apparently the decay rate is larger for a smaller initial amount of the trapped electrons. However, this is due to the non-uniformity of the light intensity in the sample tube.[9] When the concentration of the trapped electrons is high, the light absorption in the tube is not homogeneous and the apparent decay rate decreases, although the quantum yield for the decay is not affected. The details have been discussed in the previous paper.[9] Consequently, in order to study the effect of the radicals on the decay rate, we have to start with a low concentration of trapped electrons in the presence of various concentrations of the radicals.

In order to check the effect of radicals on the microwave-power-saturation phenomenon of the trapped electrons' spectrum, we made four samples containing various concentrations of the radicals in the matrix. The procedure for the preparation was described in the experimental section. Then, these samples were γ-irradiated with a constant dose of 2.57×10^{18} eV g^{-1}, and the yields of the trapped electrons were measured. Figure 2 shows the results. Here, each plot was obtained by extrapolating the microwave power to zero. The microwave-power-saturation character for the trapped electrons in 3-MHX is shown in Fig. 3. As we used the ESR instrument under fast and non-adiabatic conditions,[11] the saturation factor, Z, may be given by the following equation:[12]

$$Z = (1+2\gamma H_1^2 T_1/\pi H_m)^{-1}$$

Here, γ is the gyromagnetic ratio, H_1 is the component of the rotating magnetic field perpendicular to the direction of the external magnetic field, T_1 is the spin-lattice relaxation time, and H_m is the width of

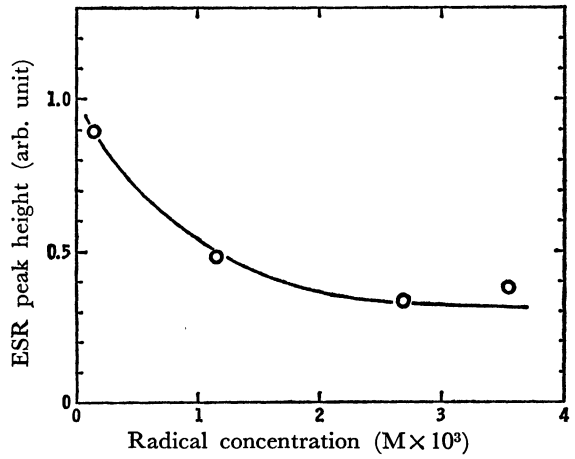

Fig. 2. The yield of trapped electrons in the γ-irradiated 3-MHX glass in the presence of various concentrations of radicals. The γ-irradiation dose for the production of trapped electrons was 0.26×10^{19} eV g^{-1}.

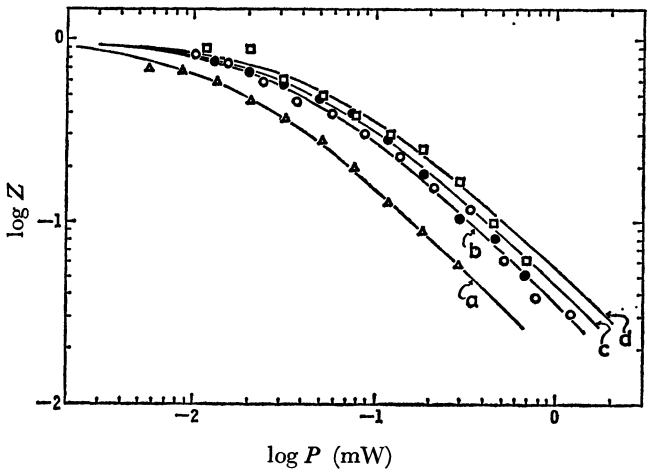

Fig. 3. Experimental values and theoretical curves for microwave-power saturation of trapped electrons in the 3-MHX glass at 77 K. P is microwave power in mW. The radical concentrations are a) 0.14, b) 1.2, c) 2.7, and d) 3.5×10^{-3} mol l^{-1}.

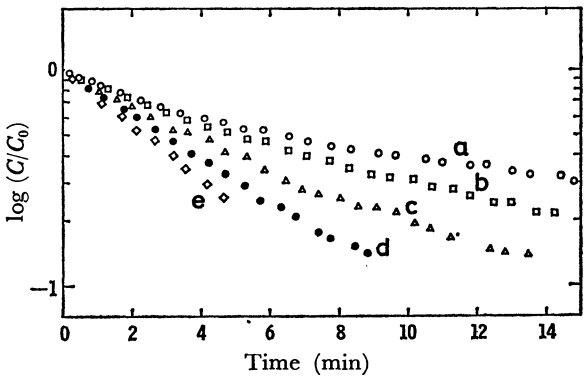

Fig. 4. Semilogarithmic plot for the decay of trapped electrons in the γ-irradiated 3-MHX during photobleaching at 1300 nm. The radical concentrations are a) 0.15, b) 1.2, c) 1.8, d) 2.9, and e) 3.7×10^{-3} mol l^{-1}.

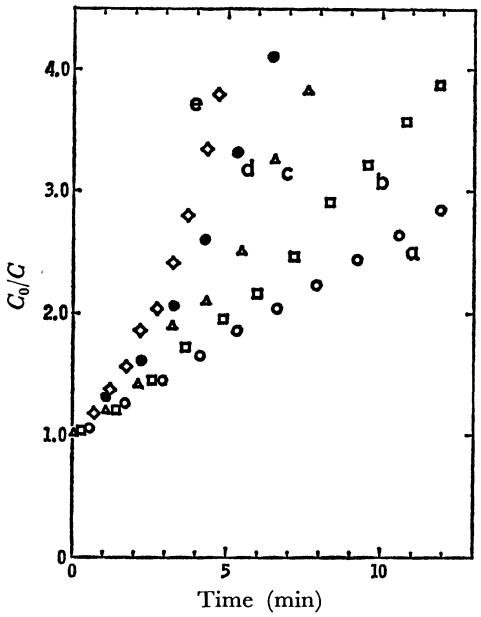

Fig. 5. The second-order decay plot for the trapped electrons in the γ-irradiated 3-MHX. The radical concentrations are a) 0.15, b) 1.2, c) 1.8, d) 2.9, and e) 3.7×10^{-3} mol l^{-1}.

the modulating magnetic field. As Fig. 3 shows, the experimental values coincide with the theoretical curves.

The results of the decay of the trapped electrons during photobleaching with various 3-MHX radical concentrations are shown in Fig. 4. Figure 5 is the second-order decay plot of the same results. Obviously the decay rate increases with the increase in the radical concentration. Moreover, when the radical concentration is small, the decay rate is of the second-order, and as the concentration increases, the decay rate becomes first-order.

In order to check the effect of the stable compounds produced by the pre-irradiation, the decay rate was measured by using samples which had been annealed to room temperature after the pre-irradiation (Fig. 6). The decay rate decreased slightly with the pre-irradiation. The stable products are some olefins and paraffins, and perhaps only olefins affect the decay rate of trapped electrons. Figure 7 shows the decay rate of the trapped electrons in the 3-MHX matrix in the presence of various concentrations of 1-pentene. These results show that the stable products do not make the decay of trapped electrons fast, but, rather, make it a little slow.

In order to obtain a completely neutralized system, we used the UV light from a mercury medium-pressure

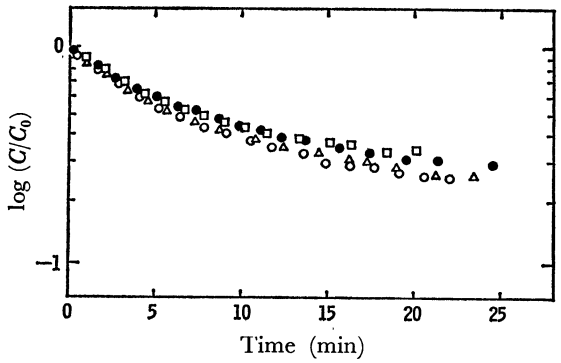

Fig. 6. Effect of thermal annealing on the decay of the trapped electrons by photobleaching. The dose for the production of trapped electrons is 0.27×10^{19} eV g^{-1} after annealing. The dose of the initial γ-irradiation are 0 (○), 2.2 (△), 5.2 (●), and 6.8 $\times10^{19}$ eV g^{-1} (□).

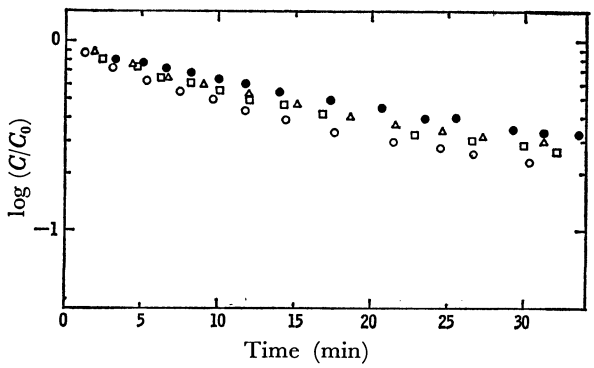

Fig. 7. The effect of the addition of 1-pentene on the decay of the trapped electrons by photobleaching. The concentrations of 1-pentene are 0(○), 5×10^{-3} (□), 6×10^{-2} (△), and 1.1×10^{-1} mol l^{-1} (●).

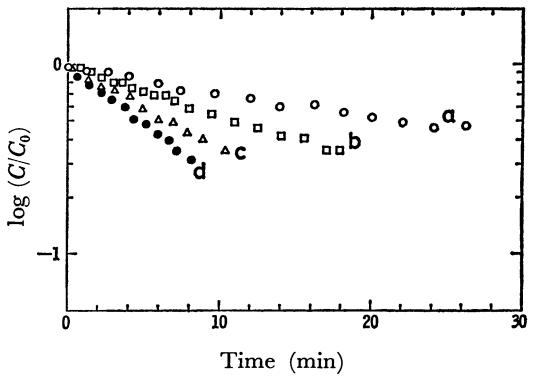

Fig. 8. The effect of UV photobleach on the decay of the trapped electrons by photobleaching at 1300 nm. The radical concentrations are a) 0.13, b) 1.7, c) 2.5, and d) 3.4×10^{-3} mol l^{-1}.

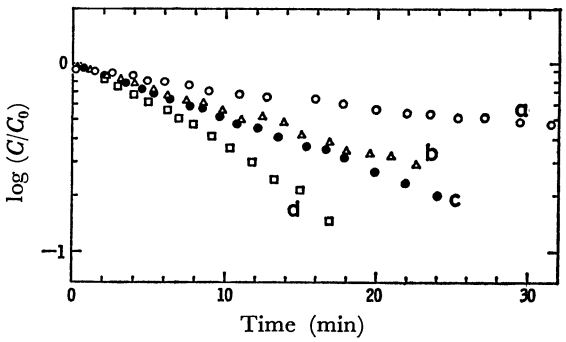

Fig. 9. Semilogarithmic plot for the decay of trapped electrons in the γ-irradiated MCH during photobleaching at 1300 nm. The dose for the production of the trapped electrons is 1.37×10^{19} eV g^{-1}. The radical concentrations are a) 0.84, b) 2.5, c) 3.3, and d) 4.1×10^{-3} mol l^{-1}.

lamp in addition to bleaching with the tungsten lamp. If all the matrix cations do not recombine with electrons by photobleaching with the tungsten lamp, the decay rate depends not only on the concentration of the radicals, but also on that of matrix cations. Irradiation with both the tungsten and the medium-pressure mercury lamps will make all the electrons recombine with cations. The peak of the absorption of the 3-methylpentyl radical anions has been reported to be at 375 nm.[4] The 3-MHX radical anions have a similar absorption spectrum. Figure 8 shows the decay curves for the trapped electrons, along with the samples thus obtained. The results are the same as those shown in Fig. 4. That is, in the present experiment, the electrons photobleached with the tungsten lamp seem to recombine completely with cations.

Photobleaching in the Case of MCH. The results are shown in Fig. 9. There was a small difference in the electron-scavenging ability, but the general tendency was almost the same between the 3-MHX and MCH matrices.

Discussion

We may draw the following conclusions from the experimental results: 1) In the matrices γ-irradiated

at 77 K, there is something which can capture the electrons released from trapping sites by the irradiation of IR light. 2) From the experiments of the thermal annealing and the addition of 1-pentene, the stable products cannot be the cause of the electron capture. 3) From the experiment of UV bleaching, the matrix cations also are not the cause of the change in the decay rate. Finally, we may conclude that the matrix radicals can capture the electrons released from the trapping sites by the irradiation of IR light.

Under a constant illumination of the IR light, the decay rate of the trapped electrons may be expressed in this form:

$$-\frac{\mathrm{d}(\log C)}{\mathrm{d}t} = \varepsilon\Phi I\overline{Q} \qquad \text{(I)}$$

Here, C denotes the concentration of the trapped electrons; ε, the molar extinction coefficient; Φ, the quantum yield by which the released electrons react with substances in the matrix and do not give the trapped electrons any more, and I, the light intensity. $\overline{Q}$ is a correction factor depending upon the optical density of the substance which absorbs the light and upon the shape of the sample tube. The details of the calculation for $\overline{Q}$ and the actinometry have been reported in the previous paper.[9] By using $\varepsilon_{3\text{-MHX}} = 2.04\times10^4\ \mathrm{cm^{-1}\,l\,mol^{-1}}$ and $\varepsilon_{\mathrm{MCH}} = 2.40\times10^4\ \mathrm{cm^{-1}\,l\,mol^{-1}}$ at 1300 nm,[13] we have calculated the quantum efficiency as a function of the relative concentration of the trapped electrons. The results for 3-MHX are summarized in Fig. 10.

When the trapped electrons are released from the trapping sites by the illumination of IR light, they undergo the following three reactions: 1) Recombination with the parent cations. Since the electrons ejected by γ-irradiation are trapped around their parent cations, there should be a certain distribution for the position of the trapped electrons from their parent cations. When they are released, the electrons trapped close to their parent cations will react faster than those trapped distantly. 2) Retrapping by the trapping sites. 3) Reactions with the radicals in the matrix. The trapping sites and the radicals may be distributed homogeneously in the matrix.

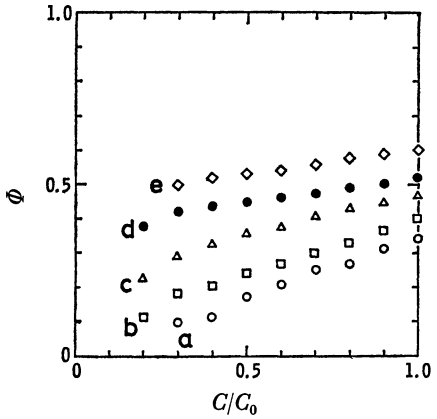

Fig. 10. The relation between the quantum yield Φ and the relative amount of the trapped electrons in the 3-MHX glass. The radical concentrations are a) 0.15, b) 1.2, c) 1.8, d) 2.9, and e) 3.7×10^{-3} mol $\mathrm{l^{-1}}$.

The reaction mechanism under consideration may be described as follows:

$$\mathrm{M} \rightsquigarrow \mathrm{M^+},\ \mathrm{R},\ \mathrm{e_t^-} \qquad (1)$$

$$\mathrm{e_t^-} + h\nu \xrightarrow{\sigma} \mathrm{e_m^-} \qquad (2)$$

$$\mathrm{e_m^-} + \mathrm{T.S.} \longrightarrow \mathrm{e_t^-} \qquad (3)$$

$$\mathrm{e_m^-} + \mathrm{M^+} \longrightarrow \mathrm{M} \qquad (4)$$

$$\mathrm{e_m^-} + \mathrm{R} \longrightarrow \mathrm{R^-} \qquad (5)$$

where M is the matrix molecule; R, the matrix radical; $\mathrm{e_m^-}$, the mobile electron, and T.S., the trapping site. σ is the quantum efficiency for the photo-liberation of trapped electrons from the trapping sites. The quantum yield for the photobleaching, then, may be equated in this form:

$$\Phi = \sigma\frac{k_4W+k_5[\mathrm{R}]}{k_3S_t+k_4W+k_5[\mathrm{R}]} \qquad \text{(II)}$$

Here, W is a function depending on the concentration of the cations and on the distribution of the trapped electrons. S_t is the concentration of trapping sites. With the progress of photobleaching, the spatial distribution of the trapped electrons will be changed. Consequently, W is also a function of the irradiation time.

From Eq. (II), assuming $\sigma=1$,[9] we can obtain the following equation:

$$\frac{1}{1/\Phi_i-1} = \frac{k_4W_i}{k_3S_t} + \frac{k_5}{k_3S_t}[\mathrm{R}] \qquad \text{(III)}$$

Here, the subscript, i, attached to Φ and W means $t=0$. The left-hand side of Eq. (III) is plotted in Fig. 11 as a function of the concentration of matrix radicals. From the slopes of these plots, we could obtain:

$$k_5/k_3S_t = (0.29\pm0.06)\times10^3\ \mathrm{mol^{-1}\,l}$$

for 3-MHX and

$$k_5/k_3S_t = (0.14\pm0.06)\times10^3\ \mathrm{mol^{-1}\,l}$$

for MCH.

When sulfur hexafluoride was used as an electron scavenger in 3-MHX,[9] the following ratio was reported:

$$k_6/k_3S_t = 1.2\times10^3\ \mathrm{mol^{-1}\,l}$$

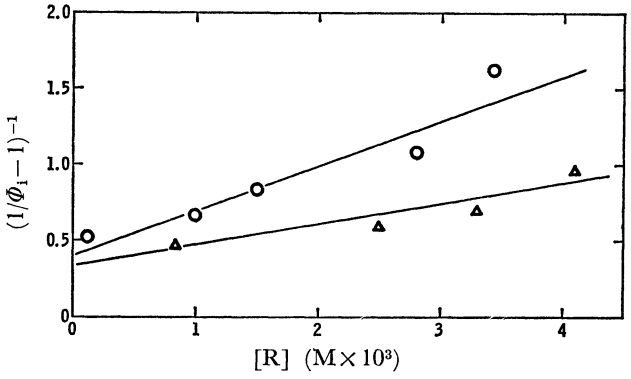

Fig. 11. The relation between $1/(1/\Phi_i-1)$ and the radical concentration [R]. ○ for 3-MHX and △ for MCH.

Here, k_6 is the rate constant of the reaction:

$$e_m^- + SF_6 \longrightarrow SF_6^- \quad (6)$$

These values suggest that the radicals under consideration have an ability comparable with sulfur hexafluoride in the electron capture in the glassy hydrocarbon at 77 K.

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