A Photoconductivity Study of Trapped Ionic Species in γ-Irradiated Ethylcyclohexane Glass at 77 K

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A photoconductivity study has been made of trapped ionic species in γ-irradiated ethylcyclohexane glass at 77 K. The photocurrent peak initially increases with an increase in the dose, reaches a maximum, and then decreases with a further increase in the dose. The experimental results indicate that the photocurrent *vs.* dose curve is probably affected by the radiolysis products. The photocurrents of γ-irradiated ethylcyclohexane–cyclopentane and 3-methylpentane glasses were also measured in the presence of biphenyl. It has been observed that electrons can be transferred almost reversibly between the biphenyl molecules and solvent traps. An analysis of the experimental data shows that only a very small fraction of the trapped electrons are responsible for the observed photoconductivity. A procedure is developed for estimating the lifetime of mobile electrons in glassy matrices.

Since the investigation of ionic processes became one of the main subjects in radiation chemistry, a great many efforts have been made to investigate the properties of trapped ionic species in glassy matrices by the techniques of ESR and optical absorption spectroscopy.

Electrical conductivity techniques have, on the other hand, been used mostly in the radiolysis of liquids. They are particularly useful, since even those ionic species can be measured which are not observable by means of ESR and optical absorption spectroscopy. In previous studies, photoconductivity studies have brought information on the energy levels of trapped electrons in the glassy matrices of MTHF,[1] 3-methylhexane,[2] and alkaline ice,[3] while thermal conductivity studies have been made on the thermal behavior of trapped ionic species in the glassy matrices of 3-methylpentane,[4,5] and of TEA[6] after γ-irradiation. The present paper will report on the photoconductivity of trapped ionic species in glassy hydrocarbon matrices.

Experimental

Materials and Sample Preparation. The ethylcyclohexane (ECH), cyclopentane (CP), and biphenyl were Tokyo Kagaku Seiki standard pure and were used as received. The Aldrich 3-methylpentane (3MP) was purified by passing it through an activated silica gel column.

The sample preparation was carried out by distilling the proper solvent, dried over calcium hydride *in vacuo*, into a conductivity cell.

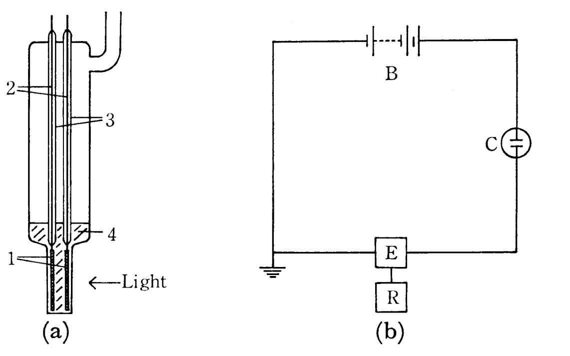

Fig. 1. (a) Schematic view of the conductivity cell: (1) stainless mesh electrode; (2) tungsten rod; (3) glass shield; (4) preparated sample.
(b) Electrical circuit: (B) applied voltage source; (C) cell; (E) electrometer; (R) recorder.

Photoconductivity Apparatus. The photoconductivity cell is of a rectangular type with suprasil windows, as is shown in Fig. 1a. The electrodes of stainless steel mesh are separated from each other with a quartz ring spacer 1 mm thick.

The electric circuit is shown schematically in Fig. 1b. A series of 90 V dry batteries were used as the voltage supply. The electric current was measured with a Toa Electronics Ltd. PM-18C electrometer and recorded with a Toa Electronics Ltd. EPR-2T recorder. The lower limit of the measurable current value was of the order of 10^{-12} A.

The light sources for photobleaching were a Toshiba 500 W lamp for the IR region and a Toshiba medium-pressure mercury lamp for the UV region.

Results and Discussion

Photoconductivity of ECH Glasses. A typical photocurrent profile of the γ-irradiated and IR bleached ECH glass at 77 K is shown in Fig. 2. The photocurrent

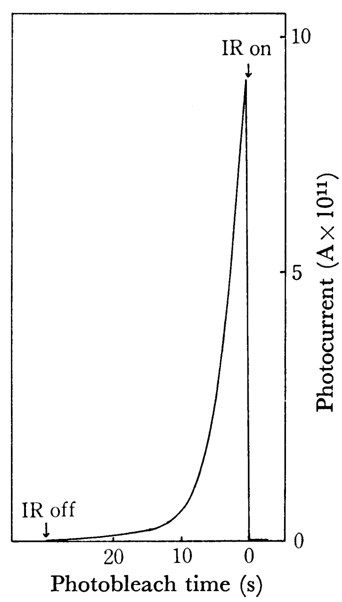

Fig. 2. Typical photocurrent profile for γ-irradiated (2×10^{19} eV/g) ECH glass at 77 K with an applied electric field of 4.5 kV/cm.

rises instantaneously within the response time of the apparatus and decays at a rate which differs slightly from one hydrocarbon matrix to another. The magnitude of the photocurrent per cm^2 is given by the following equation;

$$I = en\mu\tau E \tag{1}$$

where e is the electronic change, n is the number density of current carriers photoexited into the conduction band per second, μ is the mobility of the current carriers, τ is the average lifetime of the carriers, and E is the applied field. Since μ and τ are normaly independent of the applied field, Eq. (1) indicates that the photocurrent is linearly proportional to the applied field; this is called Ohm's law. The observed voltage-dependence of the initial photocurrent on the ECH glass was almost linearly proportional to the applied field up to 5.4×10^3 V/cm. The measurement of the photocurrent was carried out in this ohmic region.

Dose Dependence of the Photocurrent. The dose dependence of trapped electrons in γ-irradiated hydrocarbon glasses at 77 K has been previously investigated by ESR[7] and IR[8] absorption techniques. Those studies indicate that the yields of trapped electrons reach a maximum at a dose of from 1 to 2 Mrads.

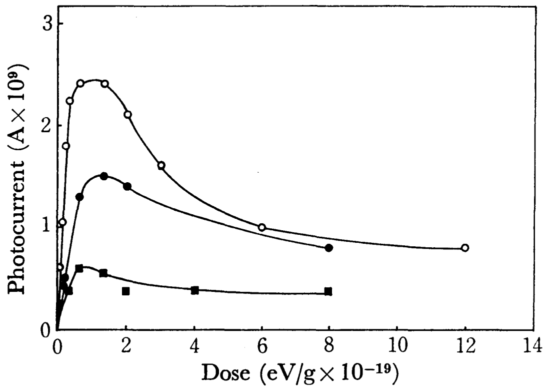

Fig. 3. Dose dependence of initial photocurrent for ECH glass at 77 K: ○, fresh sample; ●, the same sample preirradiated with a dose of 2.57×10^{20} eV/g; ■, the same sample preirradiated with a dose of 3.81×10^{20} eV/g.

The photocurrent peak *vs.* dose curves on ECH glasses at 77 K are shown in Fig. 3. The curves show two characteristic dose dependences: (a) they have a maximum value at a dose of about 0.1 Mrad, much lower than the 1 Mrad reported for 3 MP;[7] (b) they suffer from the effect of preirradiation, *i.e.*, the photocurrents diminish in intensity each time a sample is repeatedly melted, freezed, and irradiated after the previous experiment. The (b) result indicates the influence of some impurities formed by the γ-irradiation. This may be supported by the following experiment. The photocurrent-dose curve for ECH glass containing 0.04% biphenyl is shown in Fig. 4.[12] This curve is close in the shape and magnitude of the current to those for samples preirradiated with high doses (Fig. 3). The plateau of the current in an ECH–biphenyl system starts at about the same dose as that at the maximum current in pure ECH, as is shown in Fig. 3. However, the impurities formed by radiolysis are yet unknown. Treatment with concentrated sulfuric acid could not eliminate them.

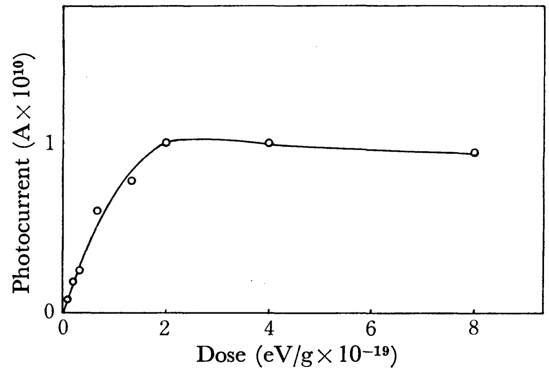

Fig. 4. Dose dependence of initial photocurrent for ECH glass containing 0.04% biphenyl at 77 K.

The appearance of the photocurrent maximum mentioned in the (a) result is at present a well-known phenomenon except that the dose at the maximum is much lower than that in the literature.[7,8] The decrease in the yield of trapped electrons with an increase in the dose has been interpreted in terms of the reactions of trapped electrons with trapped positive ions and radicals.[7] The (a) result may be explained by this hypothesis, but the influence of molecular products other than radicals and ionic species may also be significant, because the value of the maximum current is lowered every time the γ-irradiation is repeated.

The photocurrent profile in Fig. 2 may be represented as follows Eq. (1);

$$A = \int I\mathrm{d}t = n_\mathrm{t}e\mu\tau E = n_\mathrm{t}ew \tag{2}$$

where A is the area under the photocurrent curve, n_t $(=\int n\mathrm{d}t)$ is the total number of electrons per unit of volume released by bleaching, and w is the average distance of carrier movement.

The electrons contribute to the photocurrent when they are trapped far from parent ions where the Coulomb potential is very weak. Then, n_t can be expressed as follows;

$$n_\mathrm{t} = G^\mathrm{p}_\mathrm{fi}\frac{D}{100}V \tag{3}$$

where G^p_fi is the yield per 100 eV of the electrons mentioned above, D is the dose (eV/g), and V is the volume between the electrodes.

In the region of a linear current-dose relation for the fresh sample (Fig. 3), the following numerical relation was obtained from Eqs. (2) and (3), with V taken as 0.1 cm^3 and D as 5×10^{18} eV/g;

$$5.7\times10^{-9} = G^\mathrm{p}_\mathrm{fi}\times0.8\times10^{-3}\times w \tag{4}$$

If all of the free electrons are assumed to travel over the distance between the electrodes, w becomes 0.1 cm and G^p_fi is calculated as 7.1×10^{-5}. It should be noted that this value is at the lower limit for G^p_fi.

By further putting $\mu=0.1$ cm^2/V·s[9] and $E=4.5\times10^3$ V/cm into $\mu\tau E=w$, τ is obtained as 2.2×10^{-4} s. However, flash photobleaching is necessary for the measurement of the precise value of τ, which will be carried out in a subsequent work.

Photoconductivity of Hydrocarbon Glasses in the Presence of Biphehyl. ECH glass has some cracks at 77 K, but an ECH–cyclopentane (CP) mixture (50 : 50 in volume) forms a very transparent glass. However, the photocurrent shows the same value as that for pure ECH.

ECH–CP glass containing 0.04% biphenyl yields both trapped electrons and biphenyl anions under γ-irradiation.

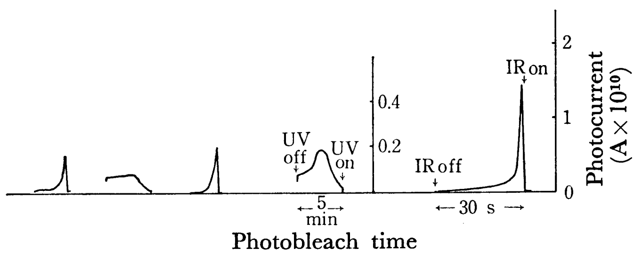

Fig. 5. Photocurrent profile for ECH–CP (50: 50 in volume) glass containing 0.04% biphenyl illuminated alternately with IR and UV light.

The photoconductivity profile of the sample illuminated alternately with IR light with λ>900 nm and UV light with λ<340 nm is shown in Fig. 5. The profile indicates that electrons can be transferred back and forth between the matrix and biphenyl molecules with little loss due to neutralization with positive ions. 3MP glass containing 0.04% biphenyl illuminated alternately with IR light and UV light showed the same photocurrent profile as the ECH–CP glass containing 0.04% biphenyl in Fig. 5. The results are the same as those found for MTHF[10] and 3MP[11] glasses spectroscopically.

The number of electrons photobleached is almost equal in each bleaching cycle except for the first cycle. The decrease in the photocurrent in the first cycle is presumably to be attributed to the recombination of electrons with positive ions in the neighborhood. The following relation may be deduced from Eq. (2);

$$\frac{A_2}{A_1} = \frac{n_t e\mu\tau_2 E}{n_t e\mu\tau_1 E} \tag{5}$$

where the subscripts 1 and 2 stand for the bleached electrons from the solvent traps and those from the biphenyl anions respectively.

The A_2/A_1 ratio obtained from the bleaching profile is equal to the ratio of the lifetimes of the electrons, τ_2/τ_1, in the conduction state; it is 1.1×10^2.

The value of 1.1×10^2 for τ_2/τ_1 implies that the electrons detached from biphenyl anions have a mean free path, $\bar{l}$, 1.1×10^2 times as large as that for the electrons from the solvent traps, since the lifetime is represented as $\tau=\bar{l}/\mu E$. It is conceivable that this difference in lifetime is due to the difference between the average energy of electrons optically released from the biphenyl anions and that of electrons released from the solvent traps.

Photoconductivity due to Carbanions. As has been stated above, only a very small fraction of the trapped electrons are responsible for the observed photoconductivity. A major fraction of them may be captured by impurities and/or radicals and neutralized by cations. As is the case with the biphenyl anions in the above section, electrons can be photoionized from carbanions by UV light shorter than 340 nm, as is shown in Fig. 6. Such a phenomenon has already been seen by Willard *et al.* on 3MP and 3EP glass by means of optical absorption spectroscopy.[7]

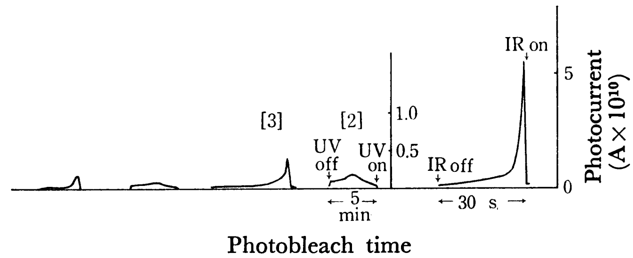

Fig. 6. Photocurrent profile for ECH–CP (50: 50 in volume) illuminated alternately with IR and UV light.

The photocurrent areas, [2] and [3], in Fig. 6 are almost equal. This might idicate that the solvent radicals have nearly the same trapping rate for mobile electrons as the solvent traps under the present experimental conditions.

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