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Optical Absorption Measurements of α-Hydronaphthyl Radical Produced in Naphthalene by Electron Beam Irradiation and Hydrogen Atom Bombardment

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Abstract—The optical absorption was measured of a naphthalene single crystal irradiated with electron beam and of naphthalene powder bombarded with hydrogen atom, both at room temperature. The optical bands at 380 mμ and 540 mμ observed for both samples, were attributed to α-hydronaphthyl radical by the comparison of annealing behaviors of optical absorption bands with that of the ESR signal of this radical.

1. Introduction

High energy radiation induces color centers[1] and ESR centers[1,2] in naphthalene single crystals.

In our previous paper[3] and the one by others,[1] the process of formation of ESR centers in naphthalene single crystals by irradiation has been elucidated as follows,

$$C_{10}H_8 + \text{High Energy Radiation} \rightarrow C_{10}H_7 + H \quad \text{(Low Temp.)} \quad (1)$$

$$C_{10}H_8 + H \rightarrow C_{10}H_9 \quad \text{(Room Temp.)} \quad (2)$$

As shown in Eq. (2), only α-hydronaphthyl radical is observed at room temperature by ESR.

Another method to produce radicals in naphthalene is hydrogen atom bombardment. With this method, two types of radical formation were reported by Cole and Heller[4] in some organic solids. One occurs in saturated organic compounds by the abstraction of a hydrogen atom from a host molecule and the other in some unsaturated hydrocarbons by the addition of a hydrogen atom to a double bond. In the case of naphthalene the possibility of production of $C_{10}H_7$ (naphthyl radical) or $C_{10}H_9$ (hydronaphthyl radical) by hydrogen atom bombardment was reported by them.[5] Recently, the production of cyclohexadienyl type radical by hydrogen atom addition to some benzene derivatives was reported by Campbell *et al.*[6]

In this paper, the optical absorption bands induced in solid naphthalene at room temperature both by electron beam irradiation and by hydrogen atom bombardment and their correlation with ESR signal were studied. The annealing behaviors of the optical absorption bands at 380 mμ and 540 mμ were found to be the same as that of the ESR signal, and the optical center for these bands is attributed to α-hydronaphthyl radical. These two optical absorption bands were also observed in hydrogen atom-bombarded naphthalene. Moreover, the ESR signal of hydrogen atom-bombarded naphthalene was almost identical with that of electron beam-irradiated. These results have led to the conclusion that α-hydronaphthyl radical is produced by hydrogen atom bombardment to naphthalene.

2. Experiment

Naphthalene single crystals were obtained by Bridgeman technique after purification by the zone melting method.

Electron beam irradiation was made with a 1.5 MeV Van de Graaff accelerator at room temperature to the total irradiation dose of 1×10^8 rad.

Powder of the crystals was bombarded by hydrogen atom in the chamber as shown in Fig. 1. Hydrogen gas passes through the discharge chamber of pyrex glass at a pressure of $1.0 \sim 3.0$ Torr. A discharge was initiated with capacitive type copper electrodes attached outside of the chamber and was maintained with a 200 Watt, 30 MHz microwave power generator. The discharged gas passed through a Venturi nozzle, which was used in order to impart high velocity to impinging hydrogen atoms, into the bombardment chamber, and reacted on naphthalene powder in a pyrex glass boat. The powder samples and the bombardment chamber were main-

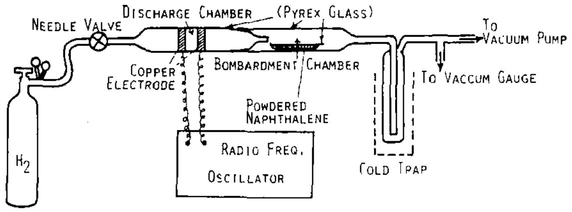

Figure 1. Experimental apparatus for the production of radicals in powdered naphthalene by means of hydrogen atom bombardment.

tained at room temperature. The diameter of the Venturi nozzle was about 1 mm and the influence of UV light was eliminated by the absorption of pyrex glass. Bombardment time ranged from 20 minutes to an hour. Hydrogen gas just after the discharge may be a proton but it is likely to recombine with an electron and become atomic hydrogen in the chamber or even in powder samples. This is the case of Eq. (2) in electron beam irradiated samples.

Optical absorption measurements were made at room temperature. Powdered samples were made into discs with KBr for the optical absorption measurements like those frequently used for infrared spectroscopy, so the wavelength of optical absorption bands could be determined fairly exactly.

ESR measurements were made at room temperature with a X-band spectrometer JES-3BX, which was operated at 9.4 GHz. The concentrations of spins were measured by using $CuSO_45H_2O$ crystal as a reference sample. The ESR signals both of electron beam-irradiated and of hydrogen atom-bombarded samples were likely to be saturated, so the microwave power was lowered so as to avoid saturation phenomena.

Annealing behaviors of optical absorption bands and the ESR center induced in naphthalene single crystals by 1.5 MeV electron beam irradiation were measured at room temperature after keeping the samples at each annealing temperature for 20 minutes.

3. Results

The optical absorption bands in naphthalene single crystals electron beam-irradiated at room temperature were found at 360, 380, 415, 440, 480, 510, and 540 mμ.

Figure 2 shows the isochronal annealing behavior of these optical absorption bands. The bands decrease with the increase of annealing temperature, and this tendency is clearly shown in Fig. 3. The annealing of the optical absorption bands at 380 mμ and 540 mμ goes quite parallel to that of the ESR signal of α-hydronaphthyl

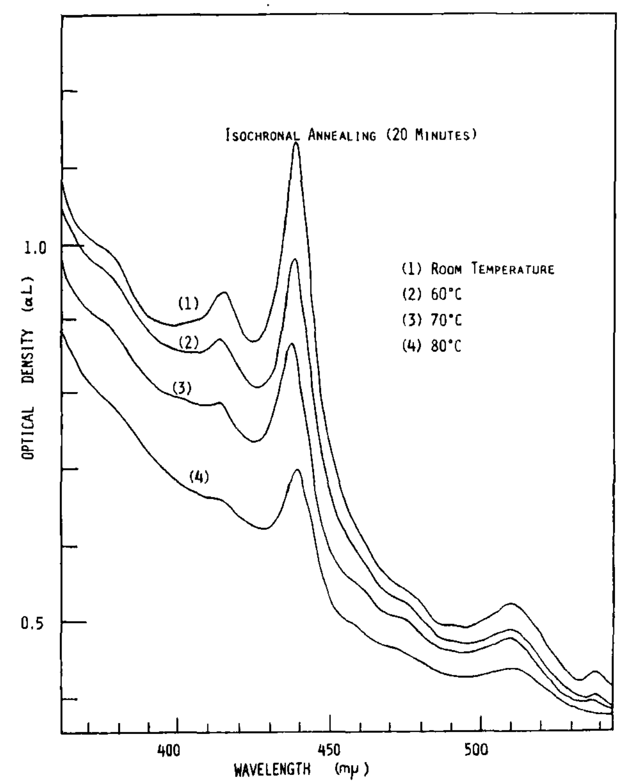

Figure 2. Optical absorption spectra of electron beam-irradiated naphthalene single crystal annealed for 20 minutes at each temperature.

radical. The band at 415 mμ and that at 440 mμ show annealing behaviors similar to each other, so do the optical absorption bands at 480 mμ and 510 mμ.

The isothermal annealing behavior of the optical absorption spectrum at room temperature is shown in Fig. 4. The optical absorption bands disappeared completely in the sample annealed for

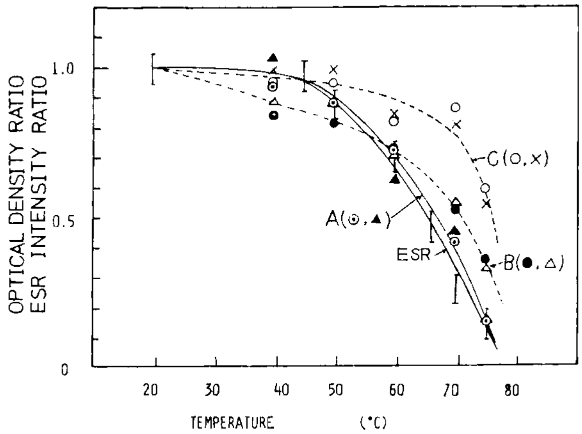

Figure 3. Isochronal annealing behavior of optical absorption bands and ESR center (α-hydronaphthyl radical) induced in naphthalene single crystal by 10^8 rad irradiation of 1.5 MeV electron beam at room temperature A(⊙380 mμ, ▲540 mμ), B(●415 mμ, △440 mμ), C(○480 mμ, ×510 mμ)

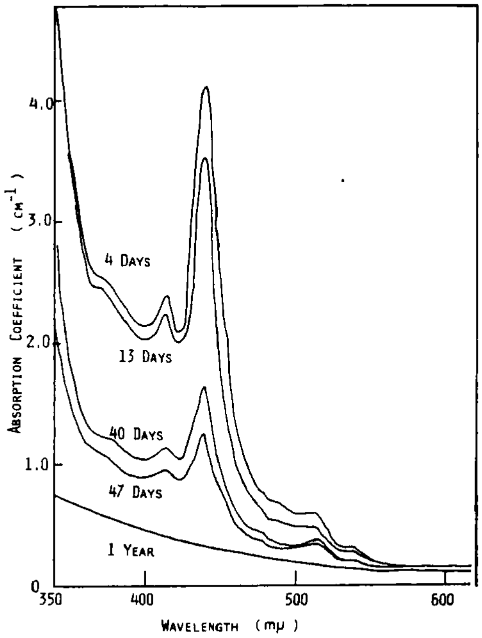

Figure 4. Optical absorption spectra of electron beam-irradiated naphthalene single crystal in isothermal annealing at room temperature (4 days–1 year).

a year at room temperature in vacuum. This suggests that permanent defects are not produced in naphthalene single crystals by irradiation with electrons of this energy range. This decay of absorption bands, as plotted in Fig. 5, suggests that three kinds of defects are produced, namely A(380 mμ, 540 mμ), B(415 mμ, 440 mμ), and C(480 mμ 510 mμ).

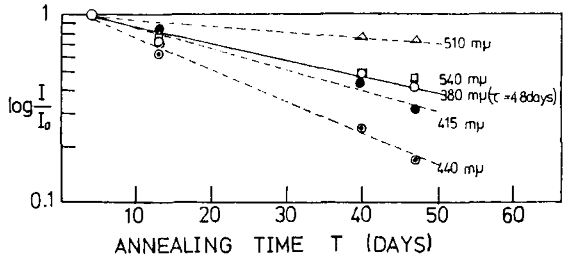

Figure 5. Isothermal annealing of optical absorption bands induced in naphthalene single crystal by 10^8 rad irradiation of 1.5 MeV electron beam at room temperature.

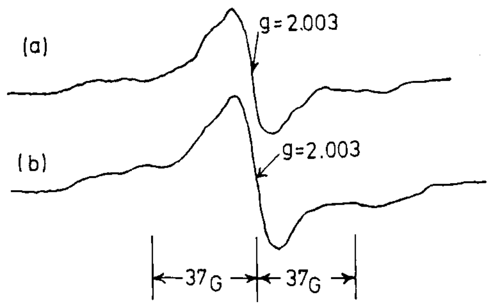

Figure 6. Electron spin resonance spectra of hydrogen atom bombarded (a) and electron beam-irradiated naphthalene powder (b).

Figure 6 shows the ESR spectra of naphthalene powder bombarded with hydrogen atom and that irradiated with 1.5 MeV electron beam, both at room temperature. The two spectra are quite similar, both with g-value of 2.003.

The optical absorption spectra of the same samples were obtained by KBr method and shown in Fig. 7. Hydrogen atom-bombarded sample has absorption bands at 360, 380, and 540 mμ, whereas those of electron beam-irradiated were found at 360, 380, 415, 440, 510, and 540 mμ, which were the same as those in electron beam-irradiated crystalline sample. The disc made of only KBr showed no apparent absorption bands in the measured wavelength range, neither did the disc of unirradiated naphthalene powder obtained with KBr method.

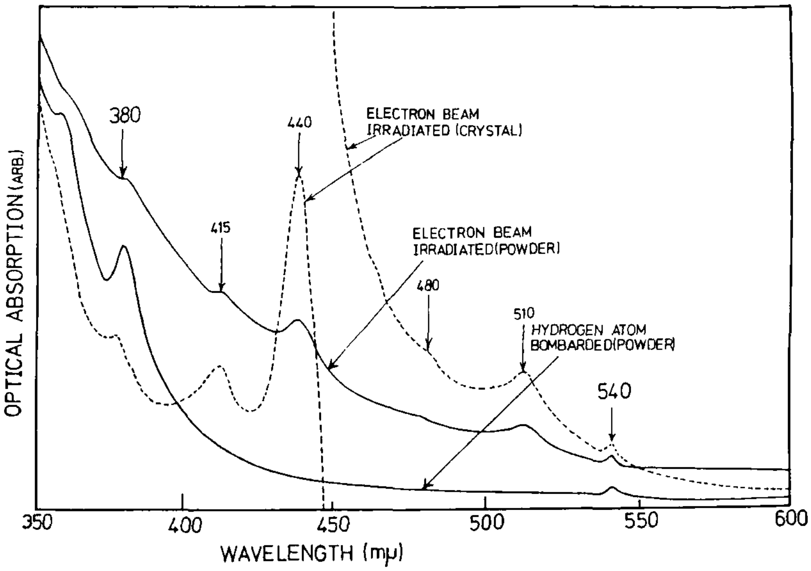

Figure 7. Optical absorption spectra of electron beam-irradiated and hydrogen atom-bombarded naphthalene.

4. Discussions

As shown in Fig. 3 and Fig. 5, the optical absorption bands of naphthalene single crystal irradiated with electron beam can be divided from their annealing behaviors, into three groups, A(380 mμ, 540 mμ), B(415 mμ, 440 mμ), and C(480 mμ, 510 mμ). The annealing behavior of group A is quite analogous to that of α-hydronaphthyl radical. The ESR spectrum of hydrogen atom-bombarded sample may be looked upon essentially as a triplet with the two outer absorptions significantly broadened, as shown in Fig. 6. As mentioned before, the spectrum is in good agreement with that of electron beam-irradiated sample in which at room temperature only hydronaphthyl radical is known to be produced as a paramagnetic center, naphthyl radical, on the other hand, unstable at room temperature.[3,7,8] These signals shown in Fig. 6 are essentially similar to that found by Leone and Koski,[9] who produced the radical in naphthalene in methanol by X-ray irradiation at 77 °K. Therefore, it is concluded that only α-hydronaphthyl radical is produced by hydrogen atom bombardment. The main triplet pattern of the α-hydronaphthyl radical arises from the coupling of the unpaired electron with the two α-hydrogens, with substructures arising

TABLE 1 Optical Absorption Bands Induced in Naphthalene Single Crystals by Irradiation

	Optical Absorption Bands (mμ)							
Experimental Result			380†	415	440	480	510	540†
Theoretical[1] Calculation	337†	352†	395†					537†

† Attributed to α-hydronaphthyl radical.

from the coupling with other hydrogen atoms in the molecule. The broadness of the signal is not due to the superpositions of some other radicals, but is due to the large anisotropy[9] of hyperfine couplings in α-hydronaphthyl radical. The hydrogen atom-bombarded sample has optical absorption bands at 380 mμ and 540 mμ, which correspond to the absorption in Group A in electron beam-irradiated sample. It is thus concluded that group A is caused by α-hydronaphthyl radical. As shown in Table 1, the wavelengths are in agreement with the theoretical predictions calculated by Hanazaki[1] with a SCF method using pseudo-π orbital of H_2 on position α of molecule. The ratio of the oscillator strength experimentally determined for various irradiation doses are shown in Table 2. The ratio of the oscillator strength of 540 mμ band to that of 380 mμ is about 0.2, whereas the calculated ratio is 0.5.[1]

As shown in Table 2, the ratio of the oscillator strength in each pair (A, B, or C) is almost constant with radiation dose, suggesting the production of three kinds of defects.

The isothermal annealing result of Fig. 8 suggests that α-hydronaphthyl radical decays exponentially with time in this annealing

TABLE 2 Oscillator Strength Ratio of Main Optical Absorption Bands in Electron Beam-irradiated Naphthalene Single Crystals with Various Irradiation Dose

	Optical Absorption Bands (mμ)					
	Group A		Group B		Group C	
Doses	380	540	440	415	510	480
10^8 rad	1	0.2	1	0.1	1	0.4
5×10^7 rad	1	0.3	1	0.1	1	0.6
10^7 rad	1	0.2	1	0.1	1	—

stage. Activation energy for the decay of α-hydronaphthyl radical was calculated from Arrhenius plots of the isochronal annealing result. If the initial intensity of absorption caused by the α-hydronaphthyl radical is designated by I_0, and the resultant absorption after heat treatment by I, the following relation holds:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \tag{3}$$

Now, if t_1 is small enough compared with the lifetime τ, and if the decay of α-hydronaphthyl radical is controlled by an activation energy E_a, then the relative rate constant k will be written as

$$\frac{I_0 - I}{I} = \frac{t_1}{\tau} = k = k_0 \exp\left(-\frac{E_a}{kT}\right). \tag{4}$$

The activation energies for the quenching of the ESR center and of the absorption bands can now be obtained using Eq. (4), and the results are tabulated in Table 3. The average value of the activation energy for the decay of α-hydronaphthyl radical, as obtained from ESR and the optical absorptions at 380 and 540 mμ, is 0.87 ± 0.06 eV.

It is reported by McGhie *et al.*[11] that the recombination of the radical produced in anthracene single crystal by irradiation is controlled by self-diffusion in anthracene. The activation energy for self-diffusion in naphthalene is 1.85 eV,[11] but for the sample in which dislocation content is high, self-diffusion along dislocation is dominant and the activation energy is lowered to 0.9 eV.[11] This value is in good agreement with 0.86 eV for the decay of the α-hydronaphthyl radical, suggesting that the decay of the radicals

TABLE 3 Activation Energies for the Decay of Optical Absorption Bands and ESR Center Produced in Electron Beam-irradiated Naphthalene

	ESR Center (Hydronaphthyl Radical)	Optical Absorption Band (mμ) 380	415	440	480	510	540
Activation energy for quenching (eV)	0.93	0.88	0.39	0.46	0.63	0.65	0.80
Group		(A)	(B)	(B)	(C)	(C)	(A)

would be controlled by self-diffusion. The subsequent recombination, the mechanism of which is unknown, would be associated with lower activation energy than that of self-diffusion.

5. Conclusions

The optical absorption bands at 380 and 540 mμ, produced in solid naphthalene either by electron beam irradiation or by hydrogen atom bombardment at room temperature are attributed to α-hydronaphthyl radical from the comparison of their annealing behaviors with that of the ESR signal.

The activation energy for the decay of α-hydronaphthyl radical is 0.87 ± 0.06 eV.

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