An Optical Absorption Study of Trapped Electrons in γ-Irradiated 3-Methylhexane-2,2,4-Trimethylpentane-2,2-Dimethylbutane Mixture Glasses at 77 K

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An optical absorption study was made on trapped electrons in γ-irradiated 3-methylhexane–2,2,4-trimethylpentane–2,2-dimethylbutane glasses at 77 K. The absorption maximum of trapped electron spectra shifts to longer wavelengths and the trapped electron yield decreases with decreasing 3-methylhexane concentration. The observed spectral shifts were interpreted through a semicontinuum model calculation.

Excess electrons generated by ionizing radiation in polar and nonpolar matrices have been extensively studied by various experimental methods. Studies on electron mobilities in nonpolar hydrocarbon liquids have revealed that electron mobilities range over three orders of magnitude depending on the hydrocarbon liquids,[1] which reflects the strength of interaction between an excess electron and the medium. Measurements of the quasi-free electron state energy V_0 have also shown that the V_0 value differs considerably among hydrocarbons in the liquid state[2,3] as well as in the glassy state.[4] On the basis of the results from these two types of experiment, hydrocarbons can roughly be classified into two types: type I in which electron mobilities are high (>10 cm^2 V^{-1} s^{-1}) and the V_0 values are low, and type II in which electron mobilities are low (<1 cm^2 V^{-1} s^{-1}) and the V_0 values are high. It is well known that excess electrons in the type I hydrocarbons are not localized, whereas those in the type II hydrocarbons are localized. On the other hand, it is known that optical absorption spectra of trapped electrons (e_t^-) in hydrocarbon glasses at 77 K are similar to each other.[5] This may be due to the fact that hydrocarbon matrices studied so far belong to type II. Thus, it is of interest to investigate how the optical absorption spectrum of e_t^- would change if we could choose as matrices the hydrocarbons which do not belong to type II. Values of V_0 of the type I hydrocarbons, 2,2,4-trimethylpentane (224TMP) and 2,2-dimethylbutane (22DMB), and the type II hydrocarbons at 77 and 295 K are listed in the upper, middle and bottom portions in Table 1, respectively. The electron mobilities ($10 \gtrsim \mu_e \gtrsim 1$ cm^2 V^{-1} s^{-1}) and V_0 values in 224TMP and 22DMB lie between those in the type I hydrocarbons and those in the type II hydrocarbons. We have found that a mixture of 224TMP and 22DMB makes a clear glass at 77 K. We report here absorption spectra and yields of e_t^- in the mixed systems of 3-methylhexane(3MHx)–224TMP–22DMB. We used a mixture of 224TMP and 22DMB in 1 : 1 volume ratio (at room temperature), which will be designated as (224TMP–22DMB) in what follows.

Table 1. Quasi-free electron state energies in some hydrocarbons

	V_0 at 77 K/eV	V_0 at 295 K/eV
Neopentane	0.33[a]	−0.38[c]
224TMP	0.57[a]	−0.17[c]
22DMB	0.59[a]	−0.26[c]
Hexane	0.98[a]	0.1[c]
MCH	1.00[a]	0.08[d]
3MP	0.86[b]	0.01[c]

a) Ref. 4. b) Ref. 4. Value estimated relative to V_0 of MCH. c) Ref. 2 a). d) Ref. 2 b).

Experimental

3-Methylhexane (Tokyo Kasei, extra pure) and 2,2,4-trimethylpentane and 2,2-dimethylbutane (Tokyo Kagaku Seiki, standard pure) were degassed and then purified *in vacuo* three times using molecular sieves 13X which were heated at 550 K *in vacuo* for 12 h before use. The hydrocarbons were taken into a volumetric flask *in vacuo*, and vacuum distilled into optical cells. Samples were sealed off a vacuum line. The optical cells were made of Suprasil quartz and the optical path length was ≈2 mm. γ-Irradiation was made with ^{60}Co γ-rays to a dose of 1.0×10^5 rad. Optical absorption spectra were taken on a Hitachi 323 spectrophotometer. γ-Irradiation and optical absorption measurements were carried out at 77 K.

Results and Discussion

Optical Absorption Spectra. No optical absorption was observable for the γ-irradiated (224TMP–22DMB) samples in the wavelength range from 340 to 2000 nm over the dose range from 0.1 to 1.8 M rad. Thus, it is concluded that electrons cannot be stably trapped in the (224TMP–22DMB) glass at 77 K. The optical absorption spectrum of e_t^- in a 3MHx–(224TMP–22DMB) mixture glass has an absorption maximum at a wavelength longer than that in neat 3MHx glass. The e_t^- spectrum in a 0.5 electron fraction (e.f.) 3MHx–

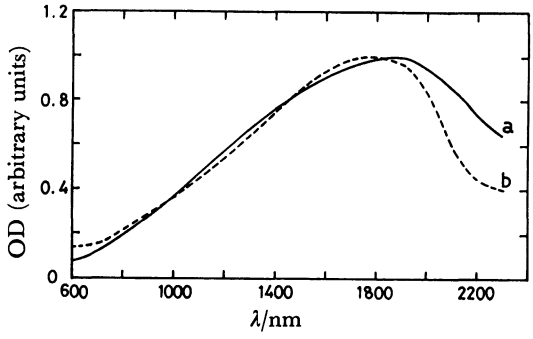

Fig. 1. Optical absorption spectrum of e_t^- in (a) 0.5 e.f. 3MHx–(224TMP–22DMB) and (b) 3MHx.

Table 2. Comparison of the observed wavelengths at the absorption maxima and the calculated wavelengths of the 1s→2p transition in 3MHx–(224TMP–22DMB) systems

[3MHx], e.f.	λ_{max}(obsd)/nm	$\lambda_{1s\rightarrow 2p}$(calcd)/nm
0.2	—	2030
0.4	1950	1780
0.5	1900	1720
0.6	1880	1670
0.8	1800	1570
1.0	1780	1500

(224TMP–22DMB) glass is shown in Fig. 1 together with that in neat 3MHx. Both spectra in Fig. 1 are normalized to the same peak height. It is seen in Fig. 1 that the spectrum in 0.5 e.f. 3MHx–(224TMP–22DMB) system has λ_{max} at 1900 nm (curve a), whereas that in neat 3MHx has λ_{max} at 1780 nm (curve b), and that the half-width of spectrum a is somewhat wider than that of spectrum b. The values of λ_{max} for e_t^- in 3MHx–(224TMP–22DMB) systems are listed in Table 2 as a function of e.f. of 3MHx.

Semicontinuum Model Calculation of the Optical Transition. In the present calculation we assumed four 3MHx molecules in a first solvation layer, which were arranged in such a way that the center of e_t^- and the midpoints of each C–C bond in the main chain of 3MHx lie on a straight line. The medium beyond the first solvation layer was treated as a continuous dielectric medium. The total energy for the ith state is given by Eq. 1,

$$E_t(i) = E_k(i) + E_e^s(i) + E_m^s(i) + E_e^l(i) + E_m^l(i) + E_q(i) + E_v + E_{HH}, \quad (1)$$

where E_K is the kinetic energy of the excess electron; E_e^s and E_m^s are short-range electronic and medium rearrangement energies, respectively; E_e^l and E_m^l are long-range electronic and medium rearrangement energies, respectively; E_q is the short-range repulsive interaction energy between the excess electron and the medium electrons; E_V is the energy required to form a cavity in the medium; and E_{HH} is the repulsive interaction energy between the hydrogen atoms in the different methyl groups nearest to the center of the cavity in which the electron is localized. Detailed expressions for each term in Eq. 1 are given in Ref. 6. The 1s→2p transition energy is then calculated using hydrogenic 1s and 2p wave-functions as Eq. 2. The physical parameters for the mixtures, A_{mix}, were estimated assuming a simple relation, $A_{mix}=\sum_i \chi_i A_i$, where χ_i and A_i are the mole fraction and the physical parameter value for hydrocarbon component i, respectively. The V_0 values for 224TMP and 22DMB were taken from Table 1. The V_0 value for 3MHx at 77 K is not available. Since V_0 values for the type II hydrocarbons at 77 K in Table 1 are close to 1.0 eV although it is somewhat lower for 3MP, we have assumed that V_0 for 3MHx is 1.0 eV at 77 K. Using these V_0 values the short-range repulsive interaction between the excess electron and the medium electrons was incorporated in the calculation. The values of 1s→2p transition energy in wavelength units are listed in Table 2. The calculated $\lambda_{1s\rightarrow 2p}$ is in semiquantitative agreement with the observed λ_{max}. The calculation accounts for a red shift in λ_{max} of e_t^- in 3MHx–(224TMP–22DMB) systems with decreasing concentration of 3MHx. This trend is unchanged even if different molecular arrangements in the first solvation layer are assumed. Such a shift is ascribed to the lower V_0 values for (224TMP–22DMB) compared with that for 3MHx.

$$h\nu_{1s\rightarrow 2p} = E_t(2p) - E_t(1s) \quad (2)$$

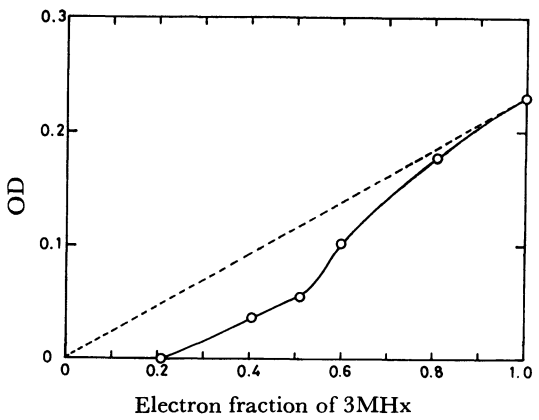

Fig. 2. Optical densities of e_t^- in 3MHx–(224TMP–22DMB) systems *vs.* electron fraction of 3MHx.

The Yield of Trapped Electrons. Trapped electrons in 3MHx decay quite slowly at 77 K. In 3MHx–(224TMP–22DMB)systems the decay rate of e_t^- increases with decreasing 3MHx concentration. Taking the decay into consideration, the optical density of e_t^- immediately after the 10 min γ-irradiation, normalized to the 1 mm optical path length, is shown in Fig. 2 as a function of e.f. of 3MHx. It can be seen from Fig. 2 that the optical densities of e_t^- in 3MHx–(224TMP–22DMB) systems are lower than those expected from a linear relationship (dashed line) between OD of e_t^- and e.f. of 3MHx, especially at lower concentrations, and that e_t^- is not observable for $\lesssim$0.2 e.f. 3MHx. The V_0 value for 0.2 e.f. 3MHx–(224TMP–22DMB) system in which no e_t^- is observable is calculated to be 0.67 eV. Then, we are tempted to say that electrons cannot be trapped in the glassy hydrocarbon matrices whose V_0 is lower than $\approx$0.67 eV.

The viscosity of 3MHx–(224TMP–22DMB) systems probably decreases with decreasing 3MHx concentration, which reflects on the decay rate of e_t^-. Thus, we cannot exclude the possibility that e_t^- has decayed out completely for low 3MHx concentrations before the optical measurements are made. Taking the case of 0.5 e.f. 3MHx–(224TMP–22DMB) system as an example, only 14% correction for the e_t^- decay is required for the observed OD at the shortest time to obtain OD at time zero**, whereas the observed e_t^- yield is about a half of that expected from a simple mixture law. Further, we note that the decay of e_t^- does not occur over an hour in 0.2 e.f. 1-propanol–(224TMP–

** Since the correction for e_t^- decay was made by extrapolation of data points from steady-state experiments, the resulting initial OD or e_t^- yield should not be taken as identical to that obtained by pulse radiolysis measurements.

22DMB) system.[7] These observations indicate that the matrix viscosity alone is insufficient for the interpretation of decrease in the e_t^- yield. The decrease in the e_t^- yield at lower 3MHx concentrations mentioned above may probably be explained in terms of lower V_0 and viscosity of (224TMP–22DMB). It should be pointed out that both lower values of V_0 and viscosity arise from a larger free volume in the medium.[8]

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References

1) A. Hummel and W. F. Schmidt, *Radiat. Res. Rev.*, **5**, 199 (1974).
2) a) R. A. Holroyd and R. L. Russell, *J. Phys. Chem.*, **78**, 2128 (1974); b) R. A. Holroyd, *J. Chem. Phys.*, **57**, 3007 (1972).
3) W. Tauchert, H. Jungblut, and W. F. Schmidt, *Can. J. Chem.*, **55**, 1860 (1977).
4) D. Grand and A. Bernas, *J. Phys. Chem.*, **81**, 1209 (1977).
5) H. Hase, T. Higashimura, and M. Ogasawara, *Chem. Phys. Lett.*, **16**, 214 (1972).
6) T. Kimura, K. Fueki, P. A. Narayana, and L. Kevan, *Can. J. Chem.*, **55**, 1940 (1977).
7) T. Kimura, S. Fukuda, and K. Fueki, unpublished results.
8) R. A. Holroyd, S. Tames, and A. Kennedy, *J. Phys. Chem.*, **79**, 2857 (1975).