A Further Study of the Scavengeable Electron Yield in the Radiolysis of Hydrocarbon Glasses at −196°C

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The yield of scavengeable electrons produced by γ-irradiation in mixtures of cyclopentane and methylcyclohexane at −196°C has been determined by electron-scavenging experiments with bromobenzene. It has been found that the maximum yield of scavengeable electrons in these mixture glasses increases with an increase in the cyclopentane concentration and that it reaches the total ionization yield in a liquid hydrocarbon. The implication of these results for the yield of radiation-induced ionization in condensed systems is discussed.

In order to determine the yield of electrons produced by ionizing radiations in nonpolar condensed systems, we must reply upon electron-scavenging experiments with some electron scavenger, because in such systems any direct method of observing solvent-trapped electrons, such as ESR and optical absorption, can only provide information about a small fraction of the electrons produced.

In a previous study[1] we have shown that bromobenzene can be used as an electron scavenger in hydrocarbons and have measured the yield of scavengeable electrons in methylcyclohexane(MCH), 3-methylpentane, cumene, and *t*-butylbenzene in the liquid state at 20°C and in the glassy state at −196°C. In that study it was found that the yield of scavengeable electrons in glassy hydrocarbons is much lower than that in liquid hydrocarbons. The possible causes for this difference in the electron yield were discussed in some detail. In the experiments with mixtures of isopentane and MCH at −196°C, we have shown that the yield of scavengeable electrons depends on the viscosity of the system, and suggested that the electron-solvent interaction would affect the yield of scavengeable electrons. However, because of the limitation of the solubility of bromobenzene in these mixtures, we could not determine the maximum yield of scavengeable electrons in isopentane-MCH glasses.

In this work we will extend such a study to mixtures of cyclopentane and MCH, where bromobenzene dissolves to a higher concentration, and will determine from the Schuler plot the maximum yield of scavengeable electrons in these mixture glasses.

Experimental

Materials. The methylcyclohexane was a product of Tokyo Kagaku Seiki (99.9%) and was used as received. The cyclopentane (a Nakarai Kagaku guaranteed reagent) was shaken with concentrated sulfuric acid in a separating flask, washed with distilled water, and then dried with sodium sulfate. After passage through a silica gel column, the cyclopentane was fractionally distilled before use. The bromobenzene (a Nakarai Kagaku guaranteed reagent) was passed through an activated alumina column and then fractionally distilled.

Sample Preparation. Each sample was degassed in a 10-mm glass tube by the freeze-pump-thaw technique and then sealed off.

Irradiation. Irradiation was performed with γ-rays from a ^{60}Co source. The dose delivered to the sample was 3.6×10^{19} eV/g.

Analysis. The yield of benzene produced was determined by means of a Hitachi K53 gas chromatograph with a flame ionization detector. The column used was *n*-hexatriacontane (4 mm × 4 m).

Results and Discussion

A fraction of the electrons produced by γ-irradiation in liquid or glassy hydrocarbons containing bromobenzene are captured by bromobenzene to yield bromide anions and phenyl radicals. The phenyl radical thus produced immediately abstracts a hydrogen atom from a solvent molecule, even at −196°C, to form a benzene molecule and a solvent radical.[2]

$$\mathrm{RH} \rightsquigarrow \mathrm{RH}^+ + e^- \qquad (1)$$

$$e^- + C_6H_5Br \rightarrow C_6H_5 + Br^- \qquad (2)$$

$$C_6H_5 + RH \rightarrow C_6H_6 + R \qquad (3)$$

It can be seen from Eqs. (2) and (3) that the yield of benzene produced corresponds to that of the electrons scavenged. It has been shown that the abstraction of a bromine atom by the hydrogen atom from bromobenzene does not occur to any appreciable extent.[3] The contribution to benzene formation of the neutralization reaction of the bromobenzene cation with a negative species can also be excluded at bromobenzene concentrations below about 0.1 M.[1]

In the present study we have measured the yield of benzene produced from bromobenzene in mixtures of cyclopentane (CP) and MCH γ-irradiated at −196°C as a function of the bromobenzene concentration. The compositions of these mixtures were varied over a wide range from pure MCH to a volume ratio of CP to MCH=7/4. Such a variation in the composition results in a substantial change in the viscosity of the system, although the viscosity is not known quantitatively. We have also measured the yield of benzene from bromobenzene in MCH at 20°C for comparison with the results obtained at −196°C.

These results are presented in Figs. 1 and 2 in a converted form to be described below. It can be seen from Fig. 1 that the yield of benzene at −196°C increase with an increase in the CP concentration at a

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[1] T. Kimura, K. Fueki, and Z. Kuri, This Bulletin, **43**, 3090 (1970).

[2] S. Noda, K. Fueki, and Z. Kuri, *ibid.*, **41**, 2882 (1968).

[3] J. M. Warman, K. -D. Asmus, and R. H. Schuler, *J. Phys. Chem.*, **73**, 931 (1969).

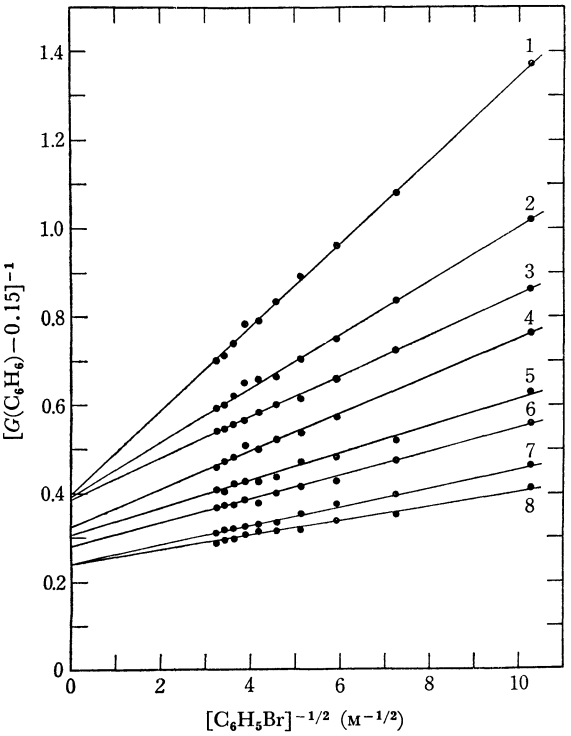

Fig. 1. Plot of $[G(C_6H_6)-0.15]^{-1}$ as a function of $[C_6H_5Br]^{-1/2}$ in CP-MCH mixtures containing bromobenzene at −196°C.
1: pure MCH, 2: CP/MCH=1/10, 3: CP/MCH=2/9, 4: CP/MCH=3/8, 5:CP/MCH=4/7, 6: CP/MCH=5/6, 7: CP/MCH=6/5, 8: CP/MCH=7/4.

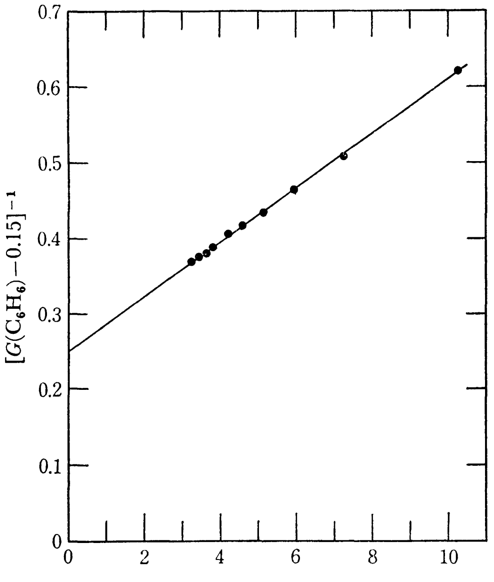

Fig. 2. Plot of $[G(C_6H_6)-0.15]^{-1}$ as a function of $[C_6H_5Br]^{-1/2}$ in MCH containing bromobenzene at 20°C.

specified concentration of bromobenzene. Here we have applied the semiempirical equation developed by Schuler and his coworkers[3] to our data on electron scavenging. The maximum yield of scavengeable electrons can be determined by using the following equation:

$$\frac{1}{G(C_6H_6)-G_{fi}}=\frac{1}{G_{gi}}+\frac{1}{G_{gi}\alpha_s^{1/2}}\frac{1}{[S]^{1/2}} \tag{4}$$

where G_{fi} and G_{gi} are the yield of free electrons and that of electrons which undergo geminate recombination respectively, where α_s is an empirical parameter, and where [S] is the molarity of the scavenger. Taking $G_{fi}=0.15$,[4] the values of $[G(C_6H_6)-0.15]^{-1}$ are plotted against $[C_6H_5Br]^{-1/2}$ in Figs. 1 and 2. The experimental data at both −196°C and 20°C fit straight lines well, as was to be expected from Eq. (4). From the intercepts of the straight lines, the maximum yields (G_m) of scavengeable electrons are determined as $G_m=G_{fi}+G_{gi}$. The values of α_s are obtained from the slopes of the straight lines. These values are listed in Table 1. The value of G_m in the CP-MCH mixtures at −196°C increases with an increase in the CP concentration or with a decrease in the matrix viscosity, reaching 4.28 for the mixtures with volume ratios of CP to MCH>1. This limiting value of G_m at −196°C is in agreement with the value of G_m in MCH at 20°C (4.15 G) within the limits of experimental error. The principal source of error in G_m at −196°C is perhaps in the dosimetry at this temperature.

TABLE 1. SCAVENGEABLE ELECTRON YIELDS IN CP-MCH MIXTURES AT −196°C AND MCH AT 20°C

Irradiation temperature	Volume ratio of CP : MCH	G_m	α_s (M^{-1})
−196°C	pure MCH	2.65	18
−196°C	1 : 10	2.69	42
−196°C	2 : 9	2.73	69
−196°C	3 : 8	3.23	59[a]
−196°C	4 : 7	3.41	98
−196°C	5 : 6	3.72	110
−196°C	6 : 5	4.28	140
−196°C	7 : 4	4.28	190
20°C	pure MCH	4.15	48

a) This value is probably underestimated.

Recently, Shida[6] has reported the yields of radiation-induced ionization in a variety of organic systems at −196°C. He measured by optical absorption spectroscopy the disulfide anion produced on scavenging electrons in mixture glasses containing disulfide, obtaining $G=2.10$ for the yield of scavengeable electrons in aliphatic hydrocarbons. This value of 2.10 is compared with our value of 2.65 for MCH at −196°C. It is possible that this discrepancy arises partly from the different methods of extrapolating the experimental data adopted by the two studies. Nevertheless, both of these results indicate that the yield of scavengeable electrons produced in hard hydrocarbon glasses at −196°C is significantly lower than that in liquid hydrocarbons.

As may be seen in Table 1, the value of α_s at −196°C

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[4] The yield of free electrons was determined by the clearing-field method to be 0.155 for CP and 0.148 for cyclohexane at 23°C.[5]

[5] W. F. Schmidt and A. O. Allen, *J. Phys. Chem.*, **72**, 3730 (1968).

[6] T. Shida, *ibid.*, **74**, 3055 (1970).

increases with an increase in the CP concentration or a decrease in the matrix viscosity. The parameter, α_s, is given by the ratio of the second-order rate constant, k_s, for the electron scavenging process to the parameter, λ:[7]

$$\alpha_s = \frac{k_s}{\lambda} \tag{5}$$

λ is proportional to $D=D_+ + D_-$, where D_+ and D_- are the diffusion coefficients of the positive ion and the electron respectively. Since D_- is generally much greater than D_+, λ is approximately proportional to the diffusion coefficient of the electron, which is itself related to the electron mobility by the relation:

$$D_- = \frac{\boldsymbol{k}T}{\boldsymbol{e}}u_- \tag{6}$$

where u_- is the mobility of the electron; $\boldsymbol{e}$, the electronic charge; $\boldsymbol{k}$, the Boltzmann constant; and T, the absolute temperature. Thus, if k_s is nearly constant in these systems, the variation in values of α_s at −196°C may be ascribed to the change in the electron mobility; *i. e.*, the harder the matrix, the greater the mobility of the electron. We are tempted to state that, in the harder hydrocarbon glasses, the electrons behave more like "quasi-free" electrons, while in the softer glasses the electrons behave more like "solvated" electrons. This might be further related to the rate of molecular relaxation in the matrix, but our present knowledge on this problem is too little to provide any satisfactory explanation for this.

It may also be seen in Table 1 that the α_s for the softer glasses at −196°C is much greater than that for liquid MCH at 20°C. It should be noted, however, that the temperature can affect the diffusion coefficient, given by Eq. (6), if the mobility is kept constant, and can then affect α_s through Eq. (5). Thus, the value of α_s at −196°C is reduced by a factor of 4 for a constant mobility when the temperature is raised to 20°C. For example, a value of $\alpha_s=190$ for the softest glass at −196°C is reduced to 47 at 20°C, which is very close to the α_s for MCH at 20°C. This may indicate that the mobility of the electron in the softest glass studied almost reaches that in liquid MCH.

Such a consideration of α_s may be relevant to the interpretation of the yield of scavengeable electrons. The smaller value of α_s at a specified temperature implies a faster geminate recombination between positive ions and electrons at that temperature. Thus, it is likely that, in hard hydrocarbon glasses at −196°C, a substantial fraction of the electrons recombine with the geminate positive ions too fast to be captured by any electron scavengers, and that the Schuler plot is not necessarily applicable over a wide range of solute concentrations and that its simple extrapolation does not provide the total ionization yield in these systems. It should be noted, however, that the present results do not exclude the possibility that the initial ionization yield is substantially lower in hard hydrocarbon glasses at −196°C than in liquid hydrocarbons.

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7) S. J. Rzad, P. P. Infelta, J. M. Warman, and R. H. Schuler, *J. Chem. Phys.*, **52**, 3971 (1970).