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Scavengeable Electron Yield in the Radiolysis of Liquid and Solid Hydrocarbons

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Yields of scavenged electrons have been measured in MCH, 3MP, cumene and *tert*-butylbenzene at 20°C and −196°C. It has been found that the yield of scavenged electrons is considerably lower at −196°C in the glassy state than at 20°C in the liquid state. The temperature effect on electron scavenging indicates that the difference in the yields of scavenged electrons between the liquid and glassy states is attributed to the variation not of temperature but of the physical conditions of the matrix. We have also investigated the effect of composition in MCH-MTHF mixtures and that of the viscosity of the matrix upon the yield of scavenged electrons at −196°C, which has led us to the assumption that the extent of interactions between thermalized electrons and the matrix would affect the yield of scavenged electrons at −196°C. Since such interactions may be related to the mean free path of electrons, we have calculated the contribution of the electron jump distance to the electron scavenging efficiency. The calculated results appear to explain qualitatively the experimental results.

Recent development in the techniques for measurement of reaction intermediates, such as ESR or optical absorption, has brought about very useful information in the field of radiation chemistry. These measurements have usually been made for reaction intermediates in rigid matrices. In order to utilize such information to understand primary processes in radiation chemistry or to correlate it with reaction mechanisms, the application of product analysis to rigid systems is highly desirable.

Our previous studies on the radiolysis of glassy hydrocarbons at −196°C unexpectedly revealed that the scavenged electron yield is much lower than that expected from the liquid phase experiments.[1,2] Shirom and Willard[3] and Shida and Imamura[4] have also reported low scavengeable electron yields in hydrocarbon glasses at −196°C.

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[1] T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, This Bulletin, **41**, 2861 (1968).

[2] T. Kimura, K. Fueki and Z. Kuri, *ibid.*, **42**, 3088 (1969).

[3] M. Shirom and J. E. Willard, *J. Chem. Phys.*, **47**, 206 (1967).

[4] T. Shida and M. Imamura, presented at 23rd Annual Meeting of the Chemical Society of Japan, April, 1970, Tokyo.

However, we could little observe effect of irradiation temperature on hydrogen formation for a number of hydrocarbons.[5] These apparently conflicting observations should be clarified to get a complete understanding of radiolysis mechanisms in condensed phases. The question why the yield of scavenged electrons is much lower at $-196°C$ is an important one. In this paper we present factors responsible for the lower yield of scavenged electrons in hydrocarbon glasses at $-196°C$.

We use bromobenzene or *o*-bromotoluene as an electron scavenger to obtain the yield of scavenged electrons. These substances scavenge an electron to form a phenyl radical, which immediately abstracts an H atom from a solvent molecule to form benzene and a solvent radical:

$$RH \rightsquigarrow RH^+ + e^- \quad (1)$$

$$C_6H_5Br + e^- \longrightarrow C_6H_5\cdot + Br^- \quad (2)$$

$$C_6H_5\cdot + RH \longrightarrow C_6H_6 + R\cdot \quad (3)$$

Benzene formation *via* Br atom abstraction by an H atom can be excluded.[6]

$$H + C_6H_5Br \not\longrightarrow C_6H_5\cdot + HBr \quad (4)$$

Thus we can determine the scavenged electron yield from the yield of benzene. To measure the yield of scavenged electrons, N_2O is widely used in the liquid phase, and biphenyl in the glassy state. However, there is ambiguity in the ratio of the nitrogen yield to the scavenged electron yield at $-196°C$,[1] and biphenyl cannot be used for conventional kinetic studies of liquid phase radiolysis. The merit of the use of halogen substituted benzene (or toluene) are (i) the yield of benzene is equal to the yield of electrons scavenged, and (ii) the method can be applied to both liquid and glassy states.

Experimental

Materials. Methylcyclohexane (MCH) was a product of Tokyo Kagaku Seiki (99.9%) and used without any treatment. Cumene and *t*-butylbenzene were Nakarai guaranteed reagents and fractionally distilled before use. Aldrich 3-methylpentane (3MP) was shaken with concentrated sulfuric acid in a separating flask, and washed with distilled water. After drying over sodium sulfate, 3MP was passed through a silica gel column and then fractionally distilled. Nakarai guaranteed reagent isopentane was used after the same purification as for 3MP. Bromobenzene and *o*-bromotoluene were Nakarai guaranteed reagents, and were fractionally distilled after passing through an activated alumina column. K & K 2-methyltetrahydrofuran (MTHF) was refluxed over potassium hydroxide, fractionally distilled, and passed through an activated alumina column. The middle fraction was used immediately after purification. Tokyo Kasei extra pure reagent biphenyl was used after being recrystallized three times.

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

Irradiation. A 3000 Ci ^{60}Co source was used for γ irradiation. Irradiation doses were 2.14×10^{20} eV/g at 20°C, 1.69×10^{20} eV/g at $-72°C$, 5.05×10^{19} eV/g at $-120°C$, and 1.71×10^{20} eV/g at $-196°C$.

Analysis. Yields of benzene and toluene produced were determined by a Hitachi K 53 gas chromatograph with FID. The columns used were *n*-hexatriacontane and TCP. Optical absorption measurements were carried out as follows. Samples were degassed in a glass tube and transferred to a rectangular quartz cell (10 mm × 5 mm). After irradiation in the dark at $-196°$, absorption measurements were carried out with a Hitachi EPU-2 spectrophotometer. The dose was 9.85×10^{17} eV/g in the experiments.

Results and Discussion

Figure 1 shows benzene yields from bromobenzene-MCH systems γ-irradiated at 20°C and $-196°C$. Since the ionization potential of MCH is higher than that of bromobenzene, charge transfer from the MCH positive ion to bromobenzene may occur and contribute to benzene formation to some extent. For the sake of confirmations, we added cumene as a positive ion scavenger to the bromobenzene-MCH systems. The results obtained are shown in Fig. 1. The concentration of cumene (21.5 mol%) is high enough to scavenge MCH positive ions adequately.[2] Direct benzene formation from cumene was negligible as will be described later. In the liquid state at 20°C the benzene yield was not affected by the presence of cumene, but at $-196°C$ it was lowered slightly at higher bromobenzene concentrations (above ~1 mol%). The reason for this may be that charge

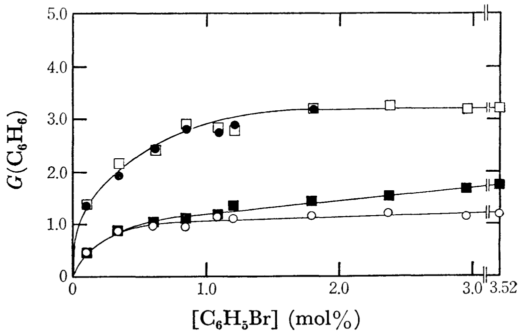

Fig. 1. Yields of benzene from γ-irradiated bromobenzene-MCH systems.

□ at 20°C in the absence of cumene, ■ at $-196°C$ in the absence of cumene, ● at 20°C in the presence of 21.5 mol% of cumene, ○ at $-196°C$ in the presence of 21.5 mol% of cumene

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[5] T. Kimura, K. Fueki and Z. Kuri, This Bulletin, **43**, 1657 (1970).

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

transfer from MCH positive ions to bromobenzene molecules occurs both at 20°C and -196°C:[*1]

$$\mathrm{MCH^+ + C_6H_5Br \longrightarrow MCH + C_6H_5Br^+} \tag{5}$$

Bromobenzene positive ions seem to react with bromide ions at 20°C, but with electrons at -196°C, since more than half of the electrons are scavenged to form bromide ions at 20°C but only a small fraction at -196°C. The reaction of bromobenzene positive ions with electrons might lead to benzene formation, although that with bromide ions does not seem to yield benzene:

$$\mathrm{C_6H_5Br^+ + Br^- \longrightarrow no\ C_6H_6 \quad at\ 20^\circ C} \tag{6}$$

$$\mathrm{C_6H_5Br^+ + e^- \longrightarrow C_6H_6 \quad at\ -196^\circ C} \tag{7}$$

It is expected that cumene supresses reaction (5). Thus, in the presence of cumene the yield of benzene will decrease *via* suppression of reaction (7) at -196°C if reaction (7) occurs at all, but not at 20°C (reaction (6)). It has been found, however, that in the bromobenzene concentration range below 1 mol%, benzene yields from cumene-free systems coincide with those from cumene-added systems at both 20°C and -196°C. Therefore we can say that charge transfer from the MCH positive ion to bromobenzene contributes little to benzene formation in this bromobenzene concentration range and that the positive charge scavenger does not affect the efficiency of electron scavenging. The benzene yields in the presence of cumene shown in Fig. 1 are in agreement with previous results.[1)]

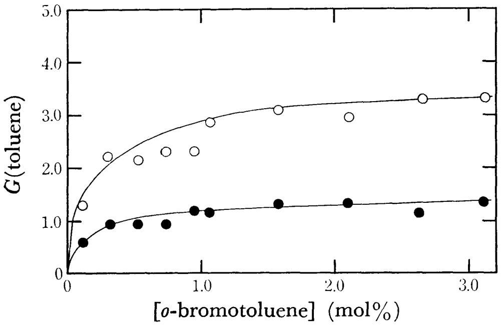

Fig. 2. Yields of toluene from γ-irradiated *o*-bromotoluene-3MP systems.
○ at 20°C, ● at -196°C

Figure 2 shows toluene yields from *o*-bromotoluene-3MP systems γ-irradiated at 20°C and -196°C. Since the limiting value of toluene yield at 20°C is 3.3 G and that at -196°C is 1.3 G, the contribution of positive charge transfer to toluene formation is negligible. The limiting toluene yield in 3MP at -196°C, namely, the scavengeable electron yield agrees well with that by Shirom and Willard.[3)]

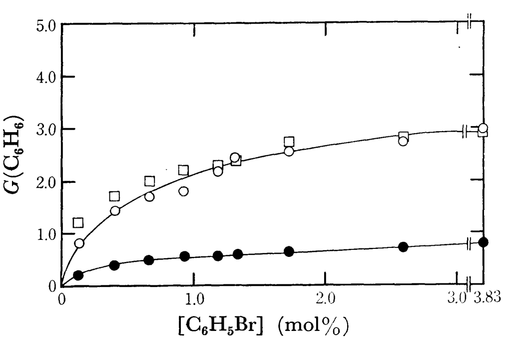

Fig. 3. Yields of benzene from γ-irradiated bromobenzene-cumene systems.
○ at 20°C, □ at -72°C, ● at -196°C.

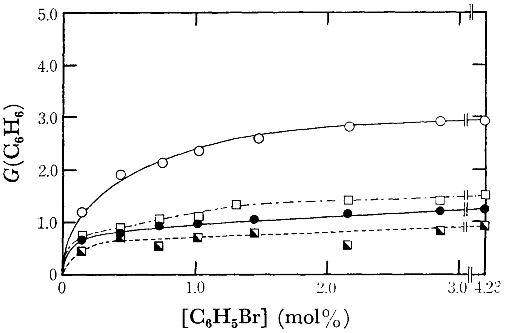

Fig. 4. Yields of benzene from γ-irradiated bromobenzene-*t*-butylbenzene systems: ○ at 20°C, □ at -72°C, ◪ at 120—°C, ● at -196°C.

In both cases of MCH and 3MP, the scavenged electron yields at -196°C are considerably lower than those at 20°C. Such a difference in the yield may be caused by the variation of temperature or the change in physical properties of the system (including phase change). To ascertain this, we investigated the temperature-dependence of electron scavenging. For this purpose we used cumene and *t*-butylbenzene because they form glass at -196°C, and their melting points lie in an experimentally feasible temperature region. Figures 3 and 4 show benzene yields from bromobenzene-cumene and bromobenzene-*t*-butylbenzene systems γ-irradiated at various temperatures. The benzene yield from pure cumene is 0.027 G at 20°C and 0.018 G at -196°C, and that from *t*-butylbenzene is 0.089 G at 20°C and is undetectably low -196°C. Since the ionization potentials of cumene and *t*-butylbenzene are lower than that of bromobenzene, positive charge transfer from solvent positive ions to solute molecules will not be possible. The limiting values of the yield of scavenged electrons in cumene and *t*-butylbenzene at 20°C are slightly lower than those in MCH and 3MP. Only the limiting value in cumene is somewhat lower at -196°C. In both cases of cumene and *t*-butylbenzene, the limiting values of scavenged electrons

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[*1] We previously suggested that positive charge transfer is hardly affected by temperature.[2)]

at 20°C are considerably different from those at -196°C, as in the cases of MCH and 3MP. The experimental points for the yields of benzene produced from bromobenzene-cumene systems at -72°C and 20°C fit a single curve, though they deviate slightly at lower bromobenzene concentrations. The slight difference might be due to the change in density of cumene. On the other hand, in the case of *t*-butylbenzene, the experimental curve for benzene yield at -72°C is very similar to that at -196°C. Thus it can be concluded that the difference in scavenged electron yield between liquids and solids is not caused by the difference in temperature, but can be ascribed to the change in physical properties of solvents. We calculated the maximum scavengeable electron yield for a better understanding of the above situation. For this purpose the empirical equation proposed by Warman *et al.*[6] was used:

$$G(\mathrm{e}^-) = G_{\mathrm{fi}} + G_{\mathrm{gi}}(\alpha_s[\mathrm{S}])^{1/2}/\{1+(\alpha_s[\mathrm{S}])^{1/2}\} \qquad (8)$$

where G_{fi} is the yield of free electrons, G_{gi} is that of electrons which undergo geminate recombination, [S] is molarity of scavenger and α_s is an empirical parameter. The data were taken from experiments on *t*-butylbenzene systems at 20°C and -196°C (Fig. 4). The results calculated from the equation are plotted in Fig. 5. In the calculation, we assumed that the free electron yield, G_{fi}, is zero at 20°C and -196°C and that the density of *t*-butylbenzene at -196°C is 1.0. Since we have taken $G_{\mathrm{fi}}=0$, the value extrapolated to $[\mathrm{S}]\to\infty$ means the maximum scavengable electron yield. The maximum scavengable electron yields thus obtained are 4.0 G at 20°C and 1.8 G at -196°C.

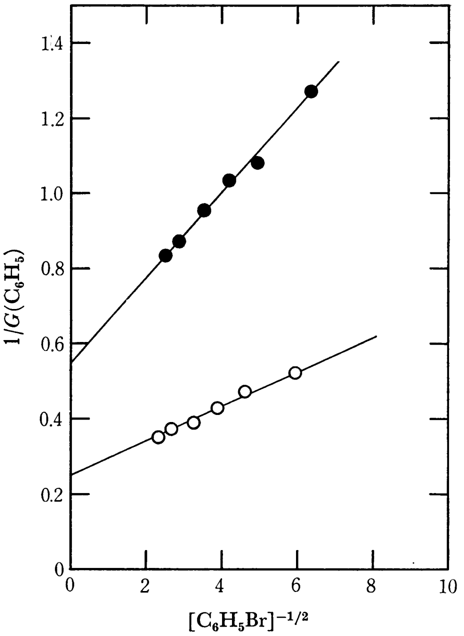

Fig. 5. Plot of $1/G(C_6H_6)$ as a function of $[C_6H_5Br]^{-1/2}$ in bromobenzene-*t*-butylbenzene systems irradiated at 20°C (○), at -196°C (●).

We can cite some possible reasons why the scavengable electron yield is much lower at -196°C: (i) decrease in the reactivity of solutes to electrons, (ii) decrease in the yield of initially ejected electrons, and (iii) recombination of a significant fraction of electrons with positive ions even in the presence of solutes in high concentrations. In order to test whether (i) is acceptable or not, we determined the values of α_s, which corresponds to the reactivity of the solutes to electrons, from the slopes of straight lines in Fig. 5. The values obtained are $\alpha_s=27.1$ at 20°C and $\alpha_s=22.5$ at -196°C. As these values indicate, the reactivity of bromobenzene to electrons at -196°C is not so different from that at 20°C, and so (i) cannot be a dominant factor. It is difficult to determine which is more probable, (ii) or (iii). Though the scavengeable electron yield in hydrocarbons at -196°C is lower, a major fraction of electrons can be scavenged in MTHF at -196°C[7,8]; the yield of biphenyl anion from γ-irradiated MTHF glass containing biphenyl as a solute reaches 2.8—3.0 G. Using the data by Kato *et al.*[8] and assuming $G_{\mathrm{fi}}=0.15$, we obtain $G_{\mathrm{gi}}=3.9$ in the same manner as that described above. Since the free ion yield in diethylether is 0.19 and that in *n*-butylether is 0.11,[9] the value assumed above for MTHF seems reasonable. Thus, we obtain a value of 4.05 as the total electron yield from γ-irradiated MTHF at -196°C. This indicates that there is no difference in the maximum scavengable electron yield between a liquid at 20°C and glass at -196°C. This contradictory result between MTHF and hydrocarbon glass seemed to suggest a clue to the problem. Thus we determined scavengable electron yields from mixtures of MTHF and a hydrocarbon at -196°C by measuring the yield of biphenyl anion from γ-irradiated MCH-MTHF glass at -196°C. The results are shown in Fig. 6. The absorption spectrum of biphenyl anion has $\lambda_{\max}$ at 409 mμ, and $\varepsilon_{409\mathrm{m}\mu}$ 3.7×10^4 *l*/mol·cm.[7] Samples were prepared so as to contain 0.026 mol/*l* of biphenyl at room temperature. It is difficult to measure biphenyl anion in γ-irradiated pure MCH because of the cracking in MCH glass. In order to keep the system in transparent stable glass, 20 vol% of 3MP was added to MCH.

Since the scavenged electron yield in MCH is 1.55 G and that in MTHF is 2.75 G (Fig. 6), and if we assume that reason (ii) is right and that the yield of electrons initially ejected from MCH at

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[7] J. P. Guarino, M. R. Ronayne and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).

[8] N. Kato, K. Fueki and Z. Kuri, unpublished results.

[9] G. R. Freeman and J. M. Fayadh, *J. Chem. Phys.*, **43**, 86 (1965).

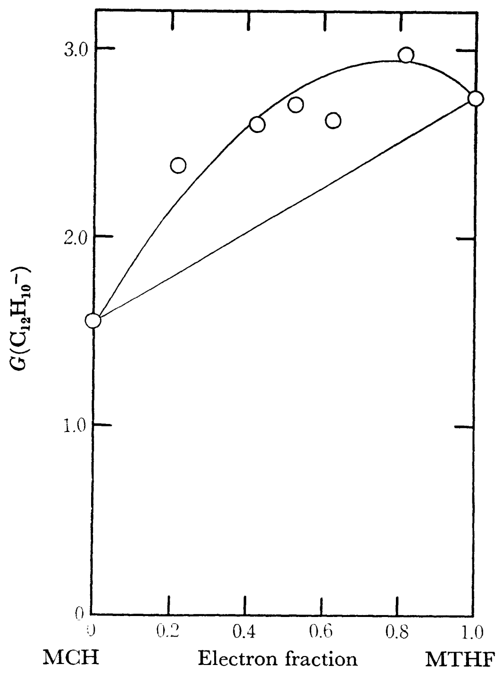

Fig. 6. Yields of biphenyl anion from γ-irradiated MCH-MTHF mixtures at −196°C, which contain 0.026 mol/l of biphenyl.

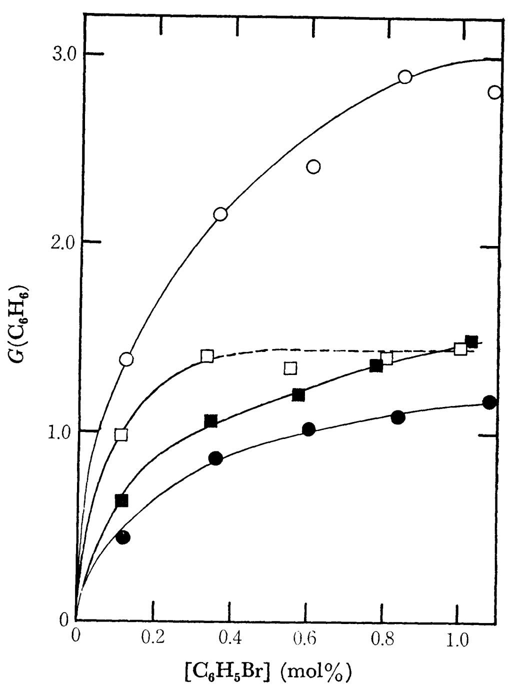

Fig. 7. Yields of benzene from γ-irradiated bromobenzene-hydrocarbon systems with various viscosities.

○ in liquid MCH at 20°C, □ in isopentane-MCH (10 : 1 Vol. ratio) mixed glass at −196 °C, ■ in isopentane-MCH (6 : 5 Vol. ratio) mixed glass at −196°C, ● in MCH glass at −196°C.

−196°C is 2.1 G,4) about 70% of electrons are scavenged in both matrices. Accordingly, the yield of scavenged electrons from MCH-MTHF mixtures is expected to be proportional to the electron fraction; the experimental points are expected to be on the straight line in Fig. 6. However, all the experimental points for MCH-MTHF mixtures lie well above the straight line. For example, the scavenged electron yield, expected at an electron fraction of MTHF of 0.21, is $1.55(1-0.21)+2.75\times0.21$ G= 1.8G, but the observed yield is 2.38G. Since the yield of electrons initially ejected is $4.05\times0.21+2.1(1-0.21)$ G=2.5G in this case on the basis of the above assumption, it may be said that the efficiency of electron scavenging increases from 70% in MCH to 95% in this mixture. This would be explicable if a positive ion scavenger acts to increase the efficiency of electron scavenging in the region of electron scavenger concentrations studied, but the experimental results of Fig. 1 do not support this explanation. Thus, reason (ii) is not sufficient for the interpretation of our problem.

Finally, let us consider reason (iii). Why a significant fraction of electrons are recombined with positive ions without being scavenged by solutes at higher concentrations at −196°C remains to be answered. The maximum scavengeable electron yield is low in solid hydrocarbons, while it is about 4 in liquid hydrocarbons, and in liquid and solid MTHF. This suggests that interactions between thermalized electrons and solvent molecules affect the yield of scavengeable electrons. In cases of polar solvent, solvated or trapped electrons are observed, indicating strong interactions between electrons and solvents. In the case of liquid hydrocarbons, such interaction must exist to some extent because the motion of themalized electrons is diffusion-controlled. We consider that the electron-solvent interaction would be weaker in the case of solid hydrocarbons.

To develop such a consideration further, we measured the yield of scavenged electrons in hydrocarbon glass with various viscosities, which were prepared by adding isopentane to MCH. The results are shown in Fig. 7, together with the results on liquid and glassy MCH. As the solubility of bromobenzene in isopentane is low, the experimental curve reaches a plateau at lower bromobenzene concentrations in glass with higher concentrations of isopentane (the broken line in Fig.7). We can see that the yield of scavenged electrons depends upon the viscosity of the matrix. This seems to indicate that the electron-solvent interaction depends upon the viscosity of the solvent in hydrocarbon glass.

The interaction may be reflected by the distance of electron jump; the weaker the interaction, the longer the electron jump distance, λ. Thus, we have calculated the effect of λ on the probability of electron scavenging at −196°C. The procedure of calculation is the same as that reported previously.[1] The probability of electron scavenging, Φ_-, is expressed as

$$\Phi_- = \phi_{\mathrm{fi}} + \phi_-(1-\phi_{\mathrm{fi}}) \tag{9}$$

$$\phi_{\mathrm{fi}} = \exp(-r_c/y) \tag{10}$$

$$\log(1-\phi_-) = \frac{6\varepsilon(y^3-\lambda^3)}{4.32}(b_-/\lambda^2)(kT/e) \times \log(1-f_- N_s) \tag{11}$$

where $r_c = e^2/\varepsilon kT$, e is the charge on an electron, ε is the static dielectric constant, k is Boltzmann's constant, T is the absolute temperature, y is an initially separated distance between positive ion and a thermalized electron, b_- is the number of new neighbors that an electron encounters per diffusive jump, f_- is the encounter efficiency, and N_s is the mole fraction of the scavenger. The probability of electron scavenging at an average positive ion-electron distance at −196°C was calculated as a function of λ, using the values $b_- = 6$ and $f_- = 1$. The average positive ion-electron distance in liquid cyclohexane is reported to be 50—60 Å[10] and 65.8 Å.[11]

Since the distance between a positive ion and an electron appears to be inversely proportional to the density of the medium,[11] we used the value, $r_{\mathrm{av}} = 50$ Å, considering the change in density at −196°C. The calculated results at several solute concentrations are shown in Fig. 8. It can be seen that the probability of electron scavenging decreases rapidly with the increase of λ. We cannot obtain the theoretical absolute yield of scavenged electron from the results because we have not calculated the yield integrated over the electron distribution, but we can see how the electron-solvent interaction could contribute to the scavenged electron yield. It is likely that the extent of this interaction plays an important part in ionic processes, especially in the radiolysis of hydrocarbon glass.

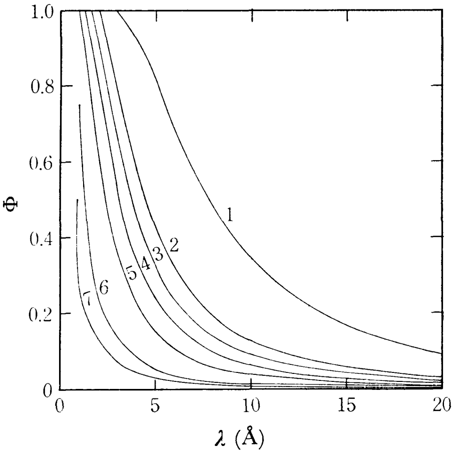

Fig. 8. Probability of electron scavenging as a function of jump distance of electron for $r = 50$ Å at −196°C. Mole fraction of electron scavenger: 1) 0.03, 2) 0.01, 3) 0.007, 4) 0.005, 5) 0.003, 6) 0.001, 7) 0.0005

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10) S. Sato, This Bulletin, **41**, 304 (1968).

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