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Temperature Effect on Decay of Ions and Radicals in Supercooled Liquids as Studied by Pulse Radiolysis and γ-Radiolysis: 1-Propanol and Ethanol

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The decay-rate constants, k, of dipentyl disulfide anions or benzyl radicals in 1-propanol and ethanol were measured over a temperature range of 107—230 K by pulse- and γ-radiolysis method. The decay-rate constants were found to range over nine orders of magnitude. The decay kinetics is a composite first-order reaction. Since the decay rates of reaction intermediates observed are diffusion-controlled, the decay-rate constants represent directly the rates of molecular transport in the supercooled liquids. It was found that the temperature dependence of the decay-rate constants could be expressed by the following equation.

$$\log\frac{k}{T} = -\frac{A}{T-T_g} + B,$$

where T is the absolute temperature, A and B are constants. T_g is the glass transition temperature. The molecular diffusion of the ions or radicals in the supercooled liquids was completely suppressed at the glass transition temperature. The temperature dependence of the decay-rate constant was compared with that of the viscosity of the matrix. It was found that the temperature, at which the molecular diffusion is completely suppressed is much higher than the temperature at which the viscosity is infinite.

1-Propanol and ethanol form supercooled liquids at low temperature. Reaction intermediates, such as ions and free radicals, are produced in these alcohols by exposure to γ-rays or high-energy electrons. When the ions or radicals do not react with the solvent, they diffuse in the solvent to recombine with other reactive species. The diffusion of the reaction intermediates in the supercooled liquids is an important process in condensed-phase radiation chemistry.

The temperature dependence of the rate constants of reaction intermediates in condensed media has been studied by several workers: Leone and Hamill,[1] Fuller *et al.*,[2] Gilles and Boyd,[3] and Čerček[4] reported that the rate constants for reactions of ionic species produced by pulse radiolysis were correlated with the viscosity of the solvents. The decay of free radicals produced by γ-radiolysis of organic solutions has been investigated at low temperatures by Dainton *et al.*[5] and Willard *et al.*[6] Since the previous studies on the decay of reaction intermediates were undertaken only by the use of either pulsed-electron beams or γ-rays, the decay-rate constants were obtained over at most three orders of magnitude.

Recently we have reported the decay-rate constants of solute ions produced by both the pulse- and γ-radiolysis of 2-methyltetrahydrofuran(MTHF) and of a methylcyclohexane(MCH)-2-methylbutane(2MB) mixture over wide temperature (88—230 K) and viscosity ranges.[7] By use of both pulse- and γ-radiolysis the decay-rate constants of the reaction intermediates were obtained over the range of nine orders of magnitude, and then it was found that the temperature dependence of the decay-rate constants is closely related to the glass transition temperature, T_g, of the solvents. However, the relation between the decay-rate constants and the viscosity could not be discussed in the previous paper,[7] since the viscosity of MTHF or a MCH–2MB mixture was not known over a wide temperature range.

The viscosity of 1-propanol or ethanol was measured over a wide temperature range.[8,15] In order to compare the decay-rate constants of reaction intermediates with the viscosity, we have now studied the decay of ions and radicals produced in the temperature range 107—230 K. The decay-rate constants were also obtained over nine orders of magnitude. The decay-rate constant of reaction intermediates represents directly a microscopic molecular transport property, while the viscosity reflects a macroscopic transport phenomenon. Thus, it was found that the diffusible behavior obtained by the measurement of such rate constants provides us with direct information on microscopic molecular transport in the supercooled liquid, in contrast to the viscosity behavior as a macroscopic transport phenomenon in the supercooled liquid.

Experimental

Spectrograde ethanol, supplied by Nakarai Kagaku Co., and standard pure 1-propanol, supplied by Hayashi Junyaku Co., were used as received. Standard pure dipentyl disulfide (DPDS) was used after the distillation *in vacuo* and standard pure benzyl chloride was used without further purification. The sample was degassed on a vacuum line and sealed off.

Pulsed-electron beams were generated with a Febetron 707 accelerator operated at an electron energy of 2 MeV, and the duration time of a pulse was 20 ns. The radiation dose of one pulse is about 6×10^4 rad. The dose was controlled by inserting a brass mesh between the sample and the electron beam exit. The sample, sealed into a quartz cell, is fixed in a sample holder of a metal Dewar which was described in a previous paper.[9] The temperature of the sample can be controlled within an error limit of ±0.1 K. The temperature rise of the sample was less than 0.5 K immediately after the pulse irradiation. An apparatus for optical absorption measurements consists of a Xenon lamp, a monochromator, a photomultiplier, an oscilloscope, and a polaroid camera.[10] The signals obtained from pulse radiolysis were analyzed by use of a UP10E personal computer (Nippon Univac Co., Ltd.).

γ-Irradiation was made with ^{60}Co γ-rays at a dose rate of 5×10^5 rad/h. The dose given to the n-C_3H_7OH–DPDS system was 3.5×10^5 rad, while that of the n-C_3H_7OH-$C_6H_5CH_2Cl$ and the C_2H_5OH-$C_6H_5CH_2Cl$ system was 1.0×10^5 rad.

After γ-irradiation in liquid nitrogen at 77 K, the sample was stored in liquid methane (100—111 K) or a liquid isopentane-methane mixture (112—120 K). The temperature of the liquid methane or liquid isopentane-methane mixture was controlled by addition of liquid nitrogen. The temperature of the sample can be fixed within an error limit of ±0.5 K. All optical absorption measurements on γ-irradiated samples were carried out at 77 K.

Results

Figure 1 shows optical absorption spectra of the irradiated n-C_3H_7OH containing 1 mol% DPDS (Fig. 1-a) and 3 mol% $C_6H_5CH_2Cl$ (Fig. 1-b). The absorption observed in the γ-radiolysis, shown by a solid line, was obtained at 77 K. Absorption bands around 420 nm (Fig 1-a) and 318 nm (Fig. 1-b) are attributed to DPDS anions[11] and benzyl radicals,[12] respectively. The absorption observed in the pulse radiolysis at 140 K, denoted by circles, indicates clearly the formation of DPDS anions (Fig. 1-a) and benzyl radicals (Fig. 1-b). When the C_2H_5OH-$C_6H_5CH_2Cl$ (3 mol%) system was irradiated by γ-rays at 77 K or pulsed-electron beams in the temperature ranges of 125—200 K, the optical absorption spectrum of benzyl radicals was also observed.

The decay of DPDS anions or benzyl radicals in the present systems, represented by the optical density of their absorption maxima, were similar to those of pyrene anions observed in the MCH-2MB(3:1 in volume)-pyrene and the MTHF-pyrene systems.[7]

Discussion

Decay Kinetics of Dipentyl Disulfide Anions and Benzyl Radicals. When DPDS anions and benzyl radicals decay by a first-order reaction or a second-order reaction, the decay should be described by Eq. 1 for the first-order reaction or Eq. 2 for the second-order reaction.

$$\log(\mathrm{OD}/\mathrm{OD}_0) \propto -kt, \qquad (1)$$

$$(1/\mathrm{OD}) - (1/\mathrm{OD}_0) \propto kt, \qquad (2)$$

where OD_0 is the initial optical density of the absorption of the anions or radicals, and OD is the optical density at a time, t, after irradiation. Figure 2 shows $[(1/\mathrm{OD})-(1/\mathrm{OD}_0)]$ of DPDS anions against time in the radiolysis of n-C_3H_7OH-DPDS(1 mol%) at 140 K. The slope at a dose of 1.7×10^4 rad does not coincide with that at 6×10^4 rad, indicating that the slope depends upon the initial concentration of DPDS anions. Thus, the second-order reaction plays a minor rolé in the decay of DPDS anions. Figure 3 shows $\log(\mathrm{OD}/\mathrm{OD}_0)$ of DPDS anions against time in the radiolysis of n-C_3H_7OH-DPDS(1 mol%) at 140 K. The decay curves at different initial anion concentrations (resulting from different doses) roughly superimposed on each other, but show a curvature convex to the origin, rather than the straight line for a "pure" first-order decay. Thus, the DPDS anions in n-C_3H_7OH decay by a composite first-order kinetics which was proposed previously by Willard *et al.* for the decay of alkyl radicals in γ-irradiated alkyl iodides.[13] The decay of benzyl radicals in the radiolysis of n-C_3H_7OH-$C_6H_5CH_2Cl$(3 mol%) and C_2H_5OH-$C_6H_5CH_2Cl$(3 mol%) was also expressed by a composite first-order kinetics. As was reported in our previous paper,[7] the pyrene anions in MTHF and in a MCH-2MB mixture decay by a composite first-order kinetics. Thus, it can be said that the anions and radicals in the supercooled liquids, such as 1-propanol, ethanol, MTHF, and a MCH-2MB mixture, do not decay by a simple first-order process but a composite first-order process.

Since the shape of the composite first-order decay curve probably arises from various distances of intra-spur diffusion before reactions, the observed decay curve consists of a differential decay rate. For analytical convenience the apparent decay-rate constants, k_{75}, k_{50}, and k_{35} are defined here to be $(-\ln 0.75)/t_{75}$, $(-\ln 0.5)/t_{50}$, and $(-\ln 0.35)/t_{35}$, where t_m is the time required for the decay to m% of the initial amount of ions or radicals.

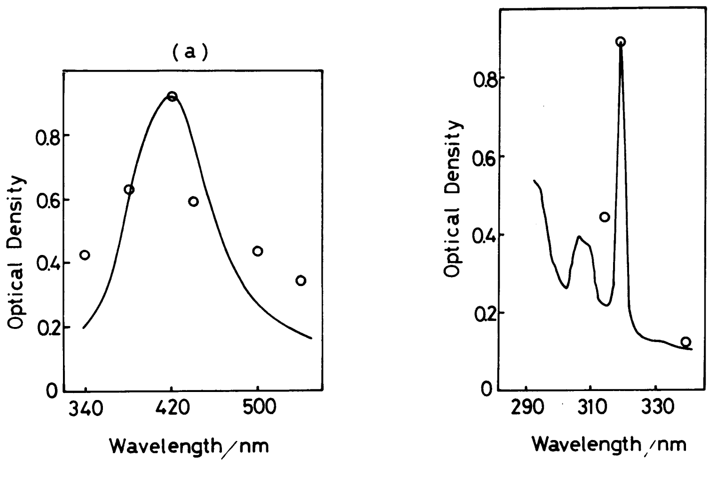

Fig. 1. a. Optical absorption spectrum of the l-propanol-dipentyl disulfide (1 mol%) system. ——: After γ-irradiation at 77 K; ○: After pulse irradiation at 140 K. b. Optical absorption spectrum of the l-propanol-benzyl chloride (3 mol%) system. ——: After γ-irradiation at 77 K; ○: After pulse irradiation at 140 K.

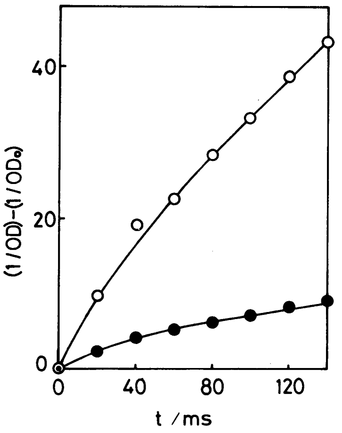

Fig. 2. The second-order kinetic plots of the decay of dipentyl disulfide anions in the pulse radiolysis of 1-propanol–dipentyl disulfide (1 mol%) at 140 K. ●: Irradiation dose; 6×10^4 rad, ○: Irradiation dose; 1.7×10^4 rad. OD and OD_0 are the optical density at time t and the initial optical density, respectively.

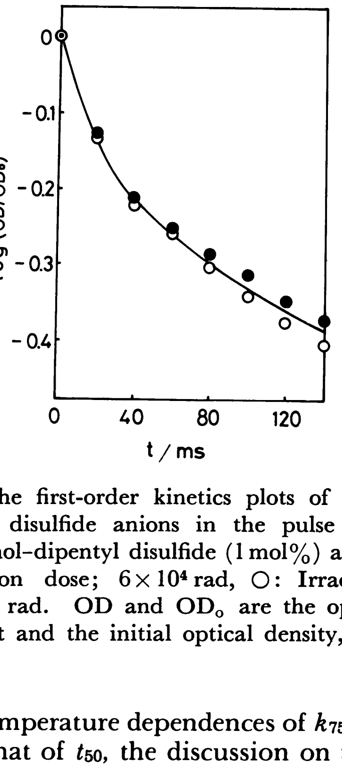

Fig. 3. The first-order kinetics plots of the decay of dipentyl disulfide anions in the pulse radiolysis of 1-propanol–dipentyl disulfide (1 mol%) at 140 K. ●: Irradiation dose; 6×10^4 rad, ○: Irradiation dose; 3.1×10^4 rad. OD and OD_0 are the optical density at time t and the initial optical density, respectively.

Since the temperature dependences of k_{75} and k_{35} coincide with that of t_{50}, the discussion on the decay-rate constant is limited here to k_{50}.

Decay of Dipentyl Disulfide Anions in Irradiated 1-Propanol. The formation of DPDS anions in the radiolysis of n-C_3H_7OH-DPDS(1 mol%) are described by the following reactions:

$$n\text{-}C_3H_7OH \rightsquigarrow n\text{-}C_3H_7OH^+ + e^-, \tag{3}$$

$$e^- + \text{DPDS} \longrightarrow \text{DPDS}^-. \tag{4}$$

They decay by the following neutralization reaction.

$$\text{DPDS}^- + M^+ \longrightarrow P, \tag{5}$$

where M^+ means the n-C_3H_7OH cation or DPDS cation formed by hole capture, and P denotes some products. Since the DPDS anions decay by a composite first-order reaction, they decay by recombination with cationic species in a spur. That is, most of DPDS anions decay by recombination with M^+ in close proximity.

An apparent activation energy, E, for the decay of DPDS anions is evaluated by $E=R\times d(\ln k)/d(1/T)$, where R is the gas constant. k is the apparent decay-rate constant for DPDS anions, defined by $(\ln 2)/t_{1/2}$ (*cf.* previous section). Then E=17, 29, and 71 kJ mol^{-1} are obtained for the temperature ranges of 170—155 K, 155—135 K, and 125—111 K, respectively. This implies that the Arrhenius-type activation energy is inappropriate to be defined under our experimental conditions. Since recombination of the anions in reaction (5) needs no activation energy, the apparent activation energy for the decay of DPDS anions arises from the diffusion controlled processes before recombination. The apparent activation energy (71 kJ mol^{-1}) for the decay of DPDS anions at 125—111 K may correspond to the barrier height for the molecular diffusion of DPDS anions at low temperature rather than for the tunneling neutralization. The tunneling neutralization may play a minor role in the decay of DPDS anions.

The temperature effect on the decay of reaction intermediates in the radiolysis will be discussed in terms of the relation between the decay-rate constant and the viscosity. When the rate constant for a bimolecular diffusion-controlled process expressed by Eq. 6 is connected with the diffusion coefficient expressed by the Stokes-Einstein relation (Eq. 7), Eq. 8 can be obtained.

$$k = 4\pi r_{ab}D_{ab}, \tag{6}$$

$$D = k_BT/6\pi r\eta, \tag{7}$$

$$k/T \propto \eta^{-1}, \tag{8}$$

where r_{ab} is the separation distance between two molecular species in collision, and $D_{ab}=D_a+D_b$ is the relative diffusion coefficient of the two species (a, b), and k_B is the Boltzmann's constant, r is the radius of a molecular species as a moving sphere, and η is the viscosity of solvent. The viscosity is related to the solvent-solvent molecular interaction, whereas the diffusion processes of reaction intermediates are related to the solute-solvent interaction. Equation 9 applies to the latter case.

$$k/T \propto \eta^{-n}, \tag{9}$$

where n is equal to or less than unity.[2)]

Since the decay of pyrene anions in the irradiated MTHF or a MCH-2MB mixture can be expressed by the Doolittle-type equation[7,14)] which has often been used for relaxation phenomena in supercooled liquids, we will examine whether the temperature effect on the decay-rate constant for DPDS anions can also be expressed by this type of equation (Eq. 10).

$$\log\frac{k}{T} = -\frac{A}{T-T_d^{\circ}} + B, \tag{10}$$

where A and B are constants. T_d° is the temperature at which the molecular transport of reaction intermediates is completely suppressed. T_d°, A, and B were

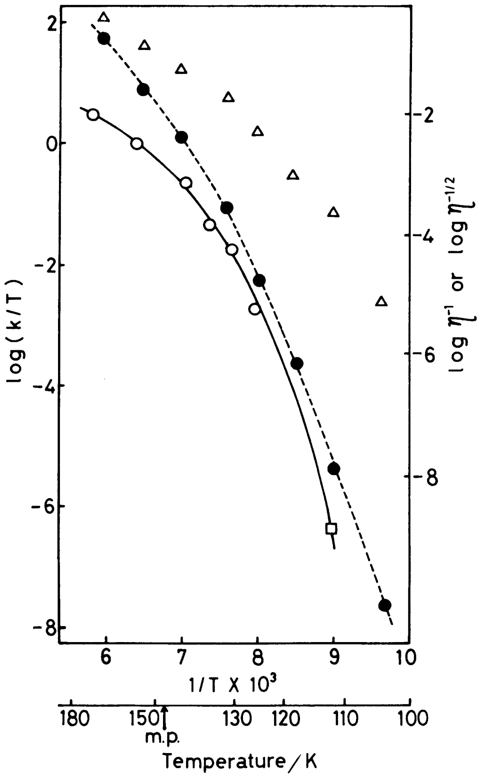

Fig. 4. Temperature dependence of the decay-rate constant of dipentyl disulfide anions in the irradiated 1-propanol-dipentyl disulfide (1 mol%). ○: Pulse radiolysis, □: γ-radiolysis, ——: Eq. 11 in text, ●: $\log \eta^{-1}$, ----: Eq. 12 in text, △: $\log \eta^{-1/2}$. The viscosity, η (in poise), of 1-propanol was quoted from Ref. 8.

determined so that they could best reproduce the experimental decay-rate constants.

Equation 11 is obtained for the decay of DPDS anions in n-C_3H_7OH which is illustrated by a solid line in Fig. 4.

$$\log \frac{k}{T} = -\frac{157.6}{T-94} + 2.577, \tag{11}$$

where k is in units of s^{-1}. The error limit of T_d^0 is ±2 K. The curve drawn by using Eq. 11 fits well the experimental (k/T) (*cf.* Fig. 4). The reported viscosity[8)] of n-C_3H_7OH is also shown in the figure. It is well-known that the viscosity can be expressed by the Doolittle-type equation,[14)] in which T_d^0 in Eq. 10 is replaced by T_v^0, a characteristic temperature in viscosity. The reported viscosity,[8)] η (in poise), of n-C_3H_7OH can be expressed by the following equation as a function of temperature.

$$\log \eta^{-1} = -\frac{409.3}{T-75} + 3.501 \tag{12}$$

Figure 4 shows that the temperature dependence of $\log (k/T)$ is different from those of $\log \eta^{-1/2}$ and $\log \eta^{-1}$.

Decay of Benzyl Radicals in Irradiated 1-Propanol and Ethanol. When n-C_3H_7OH containing 3 mol% $C_6H_5CH_2Cl$ or C_2H_5OH containing 3 mol% $C_6H_5CH_2Cl$ is irradiated by pulsed-electron beams or γ-rays, benzyl

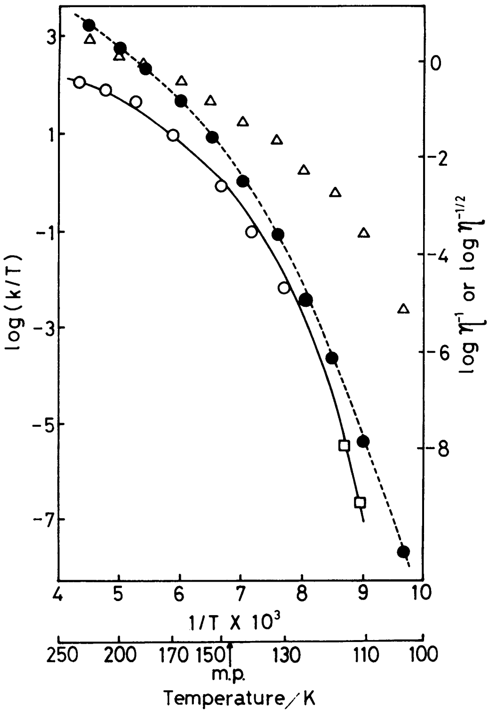

Fig. 5. Temperature dependence of the decay-rate constant of benzyl radicals in the irradiated 1-propanol-benzyl chloride (3 mol%). ○: Pulse radiolysis, □: γ-radiolysis, ——: Eq. 14 in text, ●: $\log \eta^{-1}$, ----: Eq.12 in text, △: $\log \eta^{-1/2}$. The viscosity, η (in poise), of 1-propanol was quoted from Ref. 8.

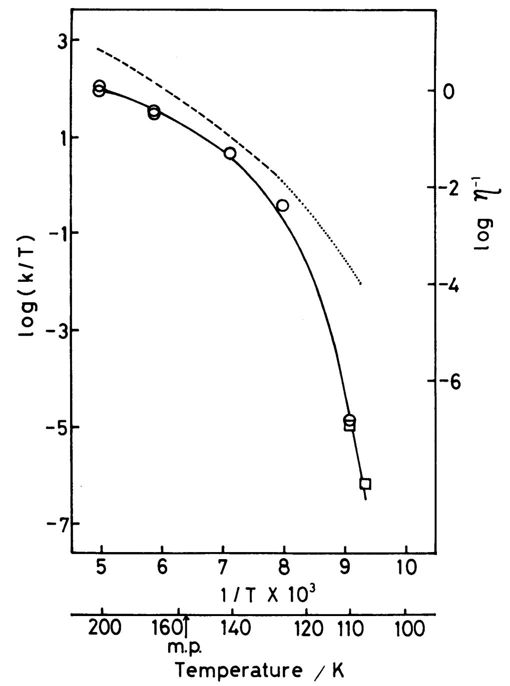

Fig. 6. Temperature dependence of the decay-rate constant of benzyl radicals in the irradiated ethanol-benzyl chloride (3 mol%). ○: Pulse radiolysis, □: γ-radiolysis, ——: Eq.15 in text, ----: $\log \eta^{-1}$, ······: $\log \eta^{-1}$ extrapolated by Eq. 16, see text. The viscosity, η (in poise), of ethanol was quoted from Ref. 15.

radicals are produced by the dissociative electron attachment.

Since the benzyl radicals decay by a composite first-order reaction, they may decay by the following geminate recombination with the Cl^- ion rather than random recombination with other radicals.

$$C_6H_5CH_2 + Cl^- \longrightarrow C_6H_5CH_2Cl^- \tag{13}$$

Willard *et al.* reported previously that the C_2H_5 radicals produced from dissociative electron capture by ethyl iodide at 77 K decay by geminate recombination of the $(C_2H_5+I^-)$ pair.[13] $C_6H_5CH_2Cl^-$ produced by reaction (13) decays by the recombination with n-$C_3H_7OH^+$ or $C_2H_5OH^+$. Another possibility that the benzyl radicals react with a small amount of impurities, such as oxygen, in the alcohol cannot be ruled out in this system. Since the reaction of a benzyl radical with 1-propanol or ethanol is endothermic, the benzyl radical cannot react with the solvent at such low temperatures as those in the present experiments.

Though ethanol is liquid at 170 K, the viscosity (0.62 poise) at this temperature is much higher than that (0.01 poise) at room temperature.[15] Thus, the random diffusion of benzyl radicals may be suppressed at 170 K, resulting in geminate recombination.

Figure 5 shows the apparent decay-rate constants ($\log(k/T)$) for benzyl radicals in the n-C_3H_7OH-$C_6H_5CH_2Cl$ (3 mol%) system. The experimental (k/T) can be well expressed by the following equation, as shown by a solid line.

$$\log\frac{k}{T} = -\frac{202.6}{T-92} + 3.500, \tag{14}$$

where k is in units of s^{-1}. It is noted that the value of T_d° (92 K) in Eq. 14 is approximately the same as that in Eq. 11 (T_d°=94 K) within an error limit.

Figure 6 shows the apparent decay-rate constants of benzyl radicals in the C_2H_5OH-$C_6H_5CH_2Cl$ (3 mol%) system. It is noted that the decay-rate constant at 110 K obtained by pulse radiolysis almost agrees with that by the γ-radiolysis. Equation 15 is obtained for the decay of benzyl radicals in the C_2H_5OH-$C_6H_5CH_2Cl$ system

$$\log\frac{k}{T} = -\frac{115.9}{T-95} + 3.144, \tag{15}$$

where k is expressed in units of s^{-1}. It was reported that the viscosity, η (in poise), of C_2H_5OH at the temperature T K can be expressed by Eq. 16 in the temperature range of 124—273 K.[15]

$$\log\eta^{-1} = -\frac{343.8}{T-59.7} + 3.325 \tag{16}$$

The temperature dependence of the viscosity is shown by a dashed line in Fig. 6. The viscosity values extrapolated below 124 K by using Eq. 16 are also shown by a dotted line. The temperature dependence of $\log(k/T)$ for the decay of benzyl radicals is different from that of $\log\eta^{-1}$ for C_2H_5OH.

Molecular Transport of Reaction Intermediates and Viscosity in Supercooled Liquids. The decay of reaction intermediates represents directly their molecular transport properties. It should be emphasized that the decay-rate constants in the supercooled liquids can be expressed by Eq. 10 over the wide temperature range in which the decay-rate constants change by nine orders of magnitude. Table 1 shows T_d° obtained from Eq. 10 together with the reported glass transition temperatures, T_g, of the supercooled liquids. It is interesting to note that T_d° corresponds well to T_g, though the reported values of T_g slightly differ to each other due to the different methods of measurement. Thus, Eq. 10 can be rewritten as follows:

TABLE 1. CHARACTERISTIC TEMPERATURE, T_d°, T_g, AND T_v° IN SUPERCOOLED LIQUIDS

Solvent	Diffusible intermediate	T_d°/K[a]	T_g/K	T_v°/K[b]
n-C_3H_7OH	Dipentyl	94	86—100[c], 93—100[d]	75
	Disulfide anion		94[e], 98[f]	
	Benzyl radical	92		
C_2H_5OH	Benzyl radical	95	90—96[c], 92—96[g]	60
			93—97[h], 93[e], 95[i], 96[f]	
MCH-2MB	Pyrene anion	80[j]	81[k]	63
MTHF	Pyrene anion	88[j]	88[l]	—

a) T_d° is the temperature at which the molecular diffusion of reaction intermediates is completely suppressed (*cf.* Eq. 10 in text). The error limit of T_d° is ±2 K. b) The viscosity can generally be expressed by the Doolittle-type equation of $\log\eta^{-1} = C/(T-T_\mathrm{v}^\circ)+D$ where C and D are constants. T_v° is the temperature at which the viscosity is infinite. c) W. Kauzmann, *Chem. Rev.*, **43**, 219 (1948). d) The value was obtained from specific heat measurements (G. S. Parks and H. M. Huffmann, *J. Phys. Chem.*, **31**, 1842 (1927)). e) The value was taken as the temperature at which the viscosity is ≈10^{13} poise, based on data in Ref. 9. f) The value quoted from Ref. 17. g) The value was obtained from specific heat measurements (G. S. Parks, *J. Am. Chem. Soc.*, **47**, 338 (1925)). h) The value was obtained from specific heat measurements (K. K. Kelley, *J. Am. Chem. Soc.*, **51**, 779 (1929)). i) The value was determined from the differential thermal analysis method (O. Haida, H. Suga, and S. Seki, *Proc. Japan Acad.*, **48**, 683 (1972)). j) The value was obtained from Ref. 7. k) The glass transition temperature of the mixture was estimated by interpolation from the T_g values of neat MCH and 2MB (*cf.* C. A. Angell, J. M. Sare, and E. J. Sara, *J. Phys. Chem.*, **82**, 2622 (1978)). l) The value was taken as the temperature at which the viscosity is ≈10^{13} poise, based on data from A. C. Ling and J. E. Willard (*J. Phys. Chem.*, **72**, 3349 (1968)).

$$\log\frac{k}{T} = -\frac{A}{T-T_{\mathrm{g}}} + B. \tag{17}$$

Therefore, it is concluded that the decay-rate constant for reaction intermediates in the supercooled liquids can be expressed by Eq. 17 and that the molecular diffusion is completely suppressed at the glass transition temperature.

The viscosity can be expressed by the Doolittle-type equation, and the temperature, T_{v}°, at which the viscosity is infinite, is also shown in Table 1. It is interesting to note that T_{d}° (or T_{g}) does not agree with T_{v}°. It should be pointed out that the viscosity represents a macroscopic transport property of the solvent, while the decay rate of reaction intermediates represents the microscopic molecular transport of solutes in the solvent.

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