

# Temperature dependence of diffusion of radical intermediates probed by the transient grating method

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Diffusion processes of intermediate radicals created by the photoinduced hydrogen abstraction reactions of ketones, quinones, and *N*-hetero aromatic molecules in ethanol and 2-propanol are studied at various temperatures by using the transient grating (TG) method. The temperature dependences of the translational diffusion coefficients ( $D$ 's) of both the radicals and the parent molecules can be expressed by the Arrhenius relationship. The activation energies ( $E_D$ ) for diffusion of the radicals are larger than those of the parent molecules and the difference in  $E_D$  depends on the molecular size. The different  $E_D$  is explained in terms of the molecular volume dependence of  $E_D$ ; that is, larger molecular volumes of the radicals could be the cause of the larger  $E_D$ . The larger apparent molecular volumes of the radicals are consistent with a model of microscopic aggregation of the surrounding molecules around the radical. © 1995 American Institute of Physics.

## I. INTRODUCTION

The translational diffusion process of a reaction intermediate radical in a fluid is an important process for understanding mechanisms<sup>1</sup> and dynamics<sup>2</sup> of chemical reactions. However, only a few attempts have so far been made to elucidate the diffusion mechanism of transient radicals mainly because of the experimental difficulties.<sup>3,4</sup>

Recently, we have demonstrated that the laser induced transient grating (TG) method is a very useful and convenient technique to measure the diffusion coefficients ( $D$ ) of short-lived radicals accurately.<sup>5-8</sup> We have found that the intermediate radicals created by photoinduced hydrogen abstraction reactions diffuse much more slowly than the stable parent molecules in organic solvents though the radical and the parent molecule possess nearly the same size and the same shape. This fact is very important because it points out that  $D$  of a transient radical should not be simply substituted by that of a stable molecule with a similar molecular volume in an analysis of chemical reaction dynamics. However, we are still seeking the exact origin of the slow diffusion of the radicals.

To understand diffusion in solutions, it is useful to investigate factors which control the diffusion process. For example, according to the Stokes–Einstein (SE) relation,  $D$  is governed by three parameters, the radius of the solute molecule  $r_A$ , the viscosity of the solvent  $\eta$ , and the temperature  $T$ .<sup>9,10</sup> Therefore, for elucidating the diffusion mechanism of the radicals, the first step is to investigate the influence of these factors.

In previous work, the viscosity dependence of  $D$  has been studied for benzophenone ketyl radical (BPK) and benzophenone (BP) in various solvents.<sup>7</sup> The results showed that  $D$ 's of BPK as well as BP are inversely proportional to the viscosity of the solvent. The  $D$  of BPK was found to be smaller than that of BP in a variety of solvents regardless of the solvent properties, such as the polarity, the dipole mo-

ment, and the protic (or aprotic) character of the solvent. From these observations, we have concluded that the hydrogen bonding between the radical and the solvent cannot be the essential origin of the slow diffusion. Also, we have investigated the solute size dependence of  $D$  using various solutes, such as ketones, quinones, and *N*-hetero aromatic molecules.<sup>8</sup> The result suggested that the slow diffusion of radicals is not related to their detailed molecular structure. Instead, we found that the ratios of  $D$ 's of the radicals to those of the parent molecules depend on the molecular size, and anomalous dependence of  $D$  on the molecular size was observed.  $D$ 's of the radicals first decrease with decreasing of  $1/r_A$  until a certain point, and then increase gradually, though  $D$ 's of the parent molecules constantly decrease with decreasing of  $1/r_A$ . In the inverted region, the radicals diffuse faster with increasing the size. These observations have been interpreted in terms of a larger friction of the radicals due to an attractive intermolecular interaction.

In this paper, we focus our attention on the temperature dependence of  $D$  to obtain a further insight into the diffusion processes of the transient radicals in solution. The temperature dependences of  $D$  of stable molecules have been studied extensively in liquids and solids so far.<sup>9,10</sup> Almost all the results revealed that the logarithm of  $D$  is proportional to the reciprocal of  $T$ . This Arrhenius-type expression of  $D$  is described as follows with a diffusion activation energy  $E_D$  and a pre-exponential factor  $D_0$ .

$$D = D_0 \exp\left(-\frac{E_D}{k_B T}\right). \quad (1)$$

If radical diffusion is governed solely by the molecular dynamics of the solvent, we expect that the temperature dependence of  $D$  should be expressed by this Arrhenius type expression and  $E_D$  should be close to that of the viscosity ( $E_\eta$ ). However, when the solute interacts with the solvent rather strongly by a specific interaction such as hydrogen bonding and the interaction influences the diffusion process seriously,  $E_D$  should deviate from  $E_\eta$ . For example,  $E_D$  for hydrogen

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bonded molecules was found to be larger than  $E_\eta$  by about 2–4 kcal/mol because of the activation energy of the hydrogen bonding.<sup>11</sup> Or if the fraction of the hydrogen-bonded structure depends on the temperature, the Arrhenius plot of  $D$  would not be represented well by a single activation energy.<sup>12</sup> In other words, the specific intermolecular interaction between solutes and solvents like a hydrogen bonding can be manifested itself by a larger  $E_D$  than  $E_\eta$  and/or a deviation from a linear relation in the Arrhenius plot.

We expected that the existence of the specific solute–solvent interaction could be clarified from the results. However, we found that  $D$ 's of the radicals as well as the parent molecules are expressed by the Arrhenius relation with a single activation energy and the values of  $E_D$  are close to the activation energies of the viscosities. This resemblance indicates that the diffusional dynamics of the radicals are governed by the hydrodynamic force of the solvents. Noticeable differences in  $E_D$  depending on the solutes and that between the radicals and the parent molecules are consistently explained in terms of the molecular size dependence of  $E_D$ , which has been reported previously.<sup>8</sup>

## II. EXPERIMENT

The details of the experimental setup for the TG measurements have been described elsewhere.<sup>13</sup> Briefly, a laser beam from an excimer laser (Lumonics Hyper EX-400) with a 10 ns pulse width and 308 nm wavelength was used for excitation. The transient grating was generated by crossing two laser beams split from the excitation pulse. The repetition rate of the excitation pulse was 1–3 Hz. A probe beam from a He–Ne laser was partly diffracted by the grating when the phase matching condition was satisfied. The diffracted beam (TG signal) isolated from the excitation beam with a glass filter (Toshiba R-62) and a pinhole ( $\phi \sim 2$  mm) was detected by a photomultiplier tube (Hamamatsu R-928) and recorded with a digital oscilloscope (Tektronix 2430A). The signal was averaged about 320 times by a microcomputer to improve the signal to noise ratio. The fringe spacing  $\Lambda$  was roughly estimated from the crossing angle  $\theta$  and then calibrated from the decay of the thermal grating signal by using the thermal diffusion constant of benzene ( $10.1 \times 10^{-8}$  m<sup>2</sup>/s).<sup>14</sup> The temperature of the sample solution was controlled by flowing temperature-regulated methanol around a cell holder with a temperature control system (Lauda RS D6D).

Spectroscopic grade solvents, ethanol and 2-propanol (purchased from Wako Chemical Co.), and solutes were used without further purification. Typical concentrations of the solutes were  $\sim 10^{-2}$  M. Sample solutions were deoxygenated by the nitrogen bubbling method and flowed by a peristaltic pump (Atto SJ-1211) to avoid the effect of reaction products in the signal.

The van der Waals volumes  $V_w$  of the molecules were obtained from the atomic increments method given by Edward.<sup>15,16</sup> The radii of the molecules  $r_A$  were calculated from  $V_w$  using the relation;  $r_A = (3V_w/4\pi)^{1/3}$ .

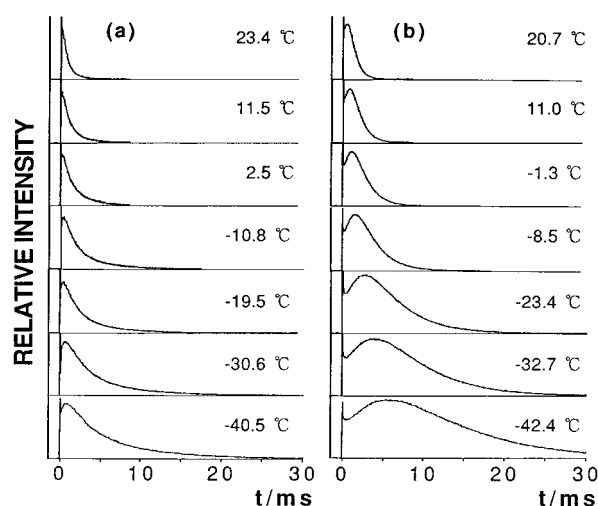


FIG. 1. Temporal profiles of the TG signals after the photoexcitation of (a) acetone/2-propanol (2-PrOH), (b) benzophenone/2-PrOH at various temperatures.

## III. RESULTS

Figure 1 shows that the time dependence of the TG signals after the photo excitation of acetone in 2-propanol and benzophenone in 2-propanol at various temperatures. All signals consist of a strong signal which decays in a few microseconds and a subsequent slowly developing one. The spike-like signal in Fig. 1 originates from the thermal grating created by the nonradiative transitions of the photoexcited molecules. The decay of the thermal grating signal is determined by the heat conduction process. After the thermal grating signal decays to the baseline completely, another signal appears and then decays again with a lifetime of millisecond order. The time development of this component reflects the spatial movement of several chemical species and, from this profile,  $D$  of each species can be measured.

The method of calculating  $D$  for various species from the time dependence of the TG signals has already been reported in previous papers.<sup>5–8,14</sup> Therefore, we briefly summarize the method below. A sinusoidal bright–dark pattern in the sample solution is created by crossing two coherent beams (optical grating). After the photoexcitation by the optical grating, intermediate radicals are created by the photo-induced hydrogen abstraction reaction and the parent molecules are depleted in the bright region. Then, since the spatially periodic concentration distributions of the created radicals and reactants are induced in the solution, the optical properties (refractive index and/or absorption coefficient) of the sample solution are spatially modulated.<sup>17</sup> The diffracted probe light intensity (the TG signal) is related to the magnitude of these modulations. Since the diffusion process between the fringes smears out the modulation, the temporal profile of the signal should be a function of  $D$ .

Analytically, the intensity of the TG signals can be described by a sum of the square of the refractive index change  $\delta n$  and the absorption coefficient change  $\delta k$ , both of which are induced by the optical grating.<sup>18</sup> Since all the chemical species used in this work and involved in the reactions do not

absorb at the probe beam wavelength,<sup>19–22</sup> the TG signals obtained under this condition should consist of only the refractive index change, and the time dependence of the TG signal intensity  $I_{\text{TG}}(t)$  is given by<sup>5,6</sup>

$$I_{\text{TG}}(t)^{1/2} = A \left\{ \delta n_{\text{th}}^0 \exp(-D_{\text{th}} q^2 t) + \sum_j \delta n_j^0 \exp((-D_j q^2 + k_j) t) - \sum_i \delta n_i^0 \exp(-D_i q^2 t) \right\}, \quad (2)$$

where  $A$  is a constant and  $q$  is the magnitude of the wave vector of the grating ( $q = 2\pi/\Lambda$ ). The first term of Eq. (2) represents the decay of the TG signal by the heat conduction process and  $D_{\text{th}}$  is the thermal diffusion coefficient. The value of  $D_{\text{th}}$  calculated from the decay rate constants of the initial part of TG signals is in excellent agreement with the literature value.<sup>9,23</sup> The second term of Eq. (2) describes the mass diffusion process of the radical  $j$  and the parent molecule  $i$ , and  $D_j$  and  $D_i$  denote diffusion coefficients of these species.  $k_j$  is the first-order disappearance rate constant of the intermediate radical  $j$  by subsequent reactions, and  $\delta n_j^0$  and  $\delta n_i^0$  describe the refractive index changes just after the excitation by the presence of the radical  $j$  and the parent molecule  $i$ , respectively. Both values ( $\delta n_j^0$  and  $\delta n_i^0$ ) are positive because all the chemical species participated in the photoinduced hydrogen abstraction reaction possess absorption bands in the wavelength region shorter than 633 nm.<sup>19–22</sup>

The TG signal in the acetone/2-propanol system [Fig. 1(a)] decays with a single-exponential function, and previously we have assigned the chemical species which gives this signal to 2-propanolyl radical (HPr·). The decay rate of the signal is determined only by the smearing out time of the grating by the translational diffusion of this radical ( $D_j q^2 \gg k_j$ ).<sup>7</sup> The slow component of the TG signal of benzophenone/2-propanol [Fig. 1(b)] is composed of the growth and slow decay. The square root of the signal was described well by the sum of two exponential functions with different signs for the pre-exponential factors. We have attributed the fast negative component to the concentration grating signal of BP and the slow positive component to the signal due to the transient radical BPK.<sup>7</sup> The two different rate constants indicate the different diffusion coefficients of BP and BPK.

The time profiles of the TG signals in Fig. 1 show that the decays of the TG signals of all the species become slower with decreasing temperature.  $D$  at each temperature is obtained from the  $q^2$  dependence of the rate constant. For example, the plot of the decay rate constant for HPr· in 2-PrOH at a low temperature ( $-46^\circ\text{C}$ ) is shown in Fig. 2. This plot shows a good linear relation between  $k$  and  $q^2$  and the slope gives  $D$  of HPr·. The small intercept with the ordinate of the plot indicates that the intrinsic lifetime of HPr· is negligible in the observation time scale, which is consistent with the results at room temperature reported previously.<sup>5–8</sup> The determined  $D$ 's are plotted against the temperature in Fig. 3

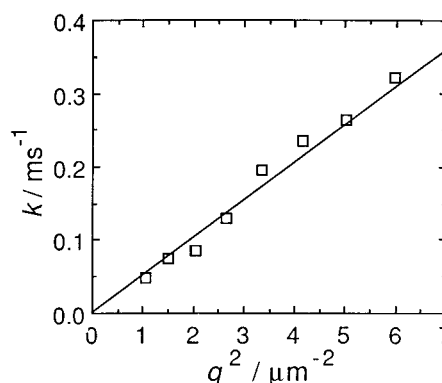


FIG. 2. Plot of the decay rate constants of TG signals due to the mass diffusion process of 2-propanolyl radical in 2-PrOH ( $k$ ) against the square of the grating vector ( $q^2$ ).

and the Arrhenius-type plots are shown in Fig. 4. All of the  $\log D$  vs  $1/T$  plots show a linear relationship. The activation energies of BP ( $E_{\text{parent}}$ ) and BPK ( $E_{\text{radical}}$ ) obtained from the slopes are listed in Table I. An important point to be noticed from Table I is the resemblance of  $E_D$  of the radicals and the parent molecules with the activation energy of the viscosity ( $E_\eta$ ). Furthermore, although  $E_D$  of BPK and BP are similar, the small difference is beyond our experimental uncertainty.  $E_D$  of BPK is slightly smaller than that of BP. We will come back to this point in a later section.

Sometimes the time profile of the TG signal is determined by a successive reaction from the intermediate as well

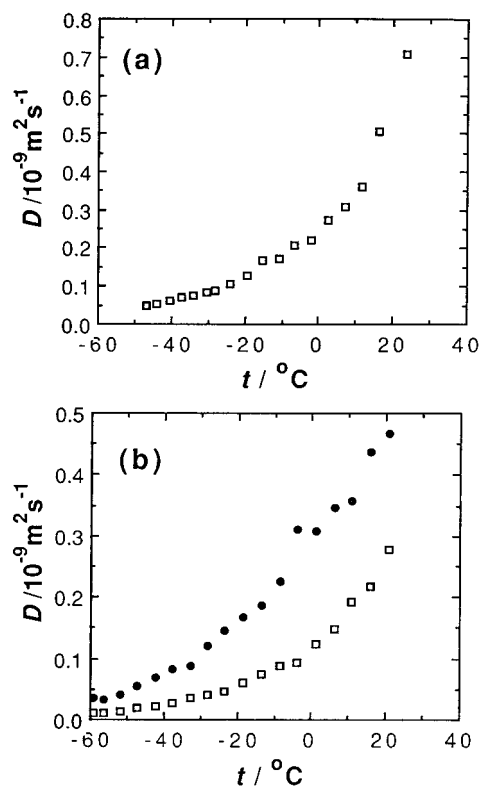


FIG. 3. Temperature dependence of  $D$  obtained from the TG signals of (a) acetone in 2-PrOH, ( $\square$ ; HPr·) and of (b) BP in 2-PrOH ( $\square$ ; BPK,  $\bullet$ ; BP).

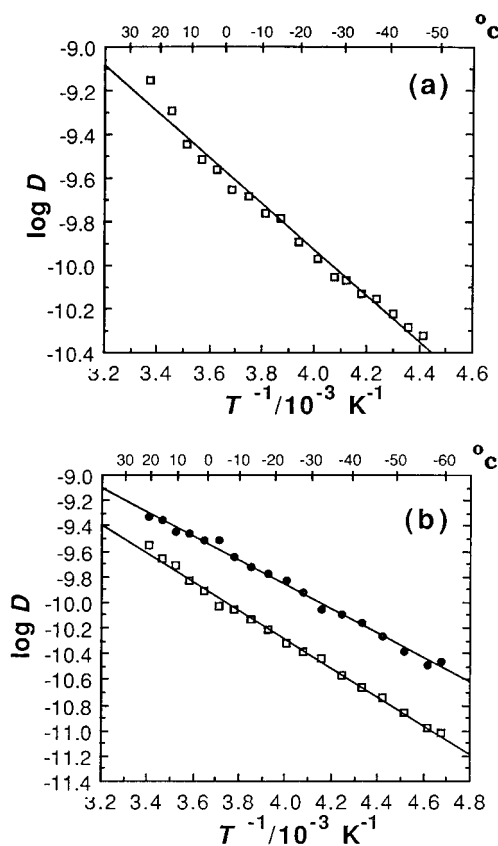


FIG. 4. (a) Plot of  $\log D$  vs  $1/T$  (Arrhenius plot) of HPr in 2-PrOH ( $\square$ ) and (b) those of BPK ( $\square$ ) and BP ( $\bullet$ ) in 2-PrOH.

as the diffusion process. In the previous papers, we excluded the participation of the chemical reaction from the  $k$  vs  $q^2$  plot which shows a linear relationship.<sup>5-8,14</sup> The linear relation of the  $\log D$  vs  $1/T$  plot and the resemblance of  $E_\eta$  are further support for the suggestion that the time profiles of the TG signals are determined by the diffusion process of both species, and not by a successive chemical reaction because of the following reason. If some chemical reactions of the radicals, such as the extinction by the secondary reaction, are involved in the dynamics of the TG signal, the Arrhenius plot

TABLE I. The activation energies for diffusion of the transient radicals created by a photoinduced hydrogen abstraction reaction ( $E_{\text{radical}}$ ) and their parent molecules ( $E_{\text{parent}}$ ) in 2-propanol and ethanol. For comparison, the activation energy of solvent viscosity are  $E_\eta = 5.854$  kcal/mol in 2-PrOH,  $E_\eta = 3.957$  kcal/mol in EtOH.

Solute	$E_{\text{radical}}$ (/kcal mol <sup>-1</sup> in 2-PrOH)	$E_{\text{parent}}$	$E_{\text{radical}}$ (/kcal mol <sup>-1</sup> in EtOH)	$E_{\text{parent}}$
Acetone	4.85±0.20			
Acetaldehyde			3.23±0.31	
Benzophenone	5.12±0.10	4.34±0.12	3.53±0.20	3.16±0.13
Benzaldehyde	5.21±0.06	4.08±0.04	3.70±0.03	2.85±0.05
Acetophenone	5.19±0.05	4.45±0.12	3.43±0.06	3.15±0.12
Benzoquinone	5.06±0.31	4.36±0.29	3.52±0.07	2.62±0.09
Pyrazine	4.87±0.26	4.37±0.52	3.61±0.10	3.09±0.22
Phenazine	5.16±0.15	4.17±0.27	3.44±0.13	3.07±0.26
Xanthone	5.07±0.13	4.40±0.09	3.50±0.09	3.22±0.14
2,2-biquinoline	5.30±0.31	4.56±0.28	3.53±0.15	3.46±0.08

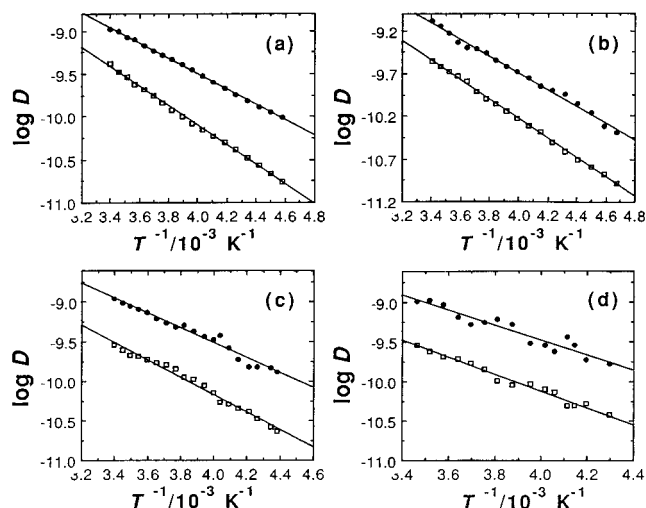


FIG. 5. Arrhenius plots for various solutes in 2-PrOH, (a) benzaldehyde, (b) acetophenone, (c) benzoquinone, (d) pyrazine,  $\square$  and  $\bullet$  represent the radicals and the parent molecules, respectively.

would not show a linear relation or  $E_D$  should be much larger than  $E_\eta$  because the activation energy for the chemical reaction would not be the same as that for diffusion. Based on similar reasoning, if diffusion is dominantly controlled by a specific interaction such as the hydrogen bonding, the Arrhenius plot is expected neither to be expressed with a single activation energy nor to be  $E_D \sim E_\eta$ . Therefore, the linear Arrhenius plot suggest that the diffusion process is dominantly controlled by the hydrodynamic force of the solvent.

The Arrhenius plots obtained in other reaction systems are shown in Fig. 5. The straight lines in these figures are the best fitted lines by the least square method. Table I summarizes  $E_D$  of the radicals and their parent molecules in 2-propanol and in ethanol. As shown before in the BP case,  $E_D$  of the radical are slightly smaller than those of the parent molecule in all the reaction systems. More importantly, although  $E_D$  in a solvent is close to that of  $E_\eta$ , there is a definitive variation depending on the solutes.

## IV. DISCUSSION

### A. Molecular size dependence of $E_D$

Figures 4 and 5 show that the difference in  $D$  of the radicals and the parent molecules decreases with increasing temperature, and the intercepts of the Arrhenius plots of the parent molecules and the radicals seem to have similar values. This suggests that the radicals are harder to move in those solvents than the parent molecules. This large value of  $E_D$  may cause the anomalously slow diffusion of radicals.

According to the SE theory,  $D$  depends on the radius of the solute molecule  $r_A$ , the viscosity of the solvent  $\eta$ , and the temperature  $T$ .  $\eta$  depends on temperature and is frequently given by<sup>24</sup>

$$\eta = \eta_0 T \exp\left(\frac{E_\eta}{k_B T}\right), \quad (3)$$

where  $E_\eta$  is the activation energy of viscosity  $\eta$ . The SE equation can be written with Eq. (3) as

$$D_{SE} = \frac{k_B}{6\pi r_A \eta_0} \exp\left(-\frac{E_\eta}{k_B T}\right). \quad (4)$$

When Eq. 4. is compared with Eq. 1, we obtain the following relationship

$$E_D = E_\eta.$$

The temperature dependences of the viscosities of 2-PrOH<sup>25</sup> and EtOH<sup>26</sup> have been already reported and from these values, we obtain  $E_\eta = 5.854$  kcal/mol for 2-PrOH and  $E_\eta = 3.957$  kcal/mol for EtOH. The results in Table 1 indeed show that the obtained  $E_D$  in 2-propanol and ethanol are close to these  $E_\eta$ . This resemblance would indicate that the diffusion process of the radical as well as the parent molecules are mainly controlled by the solvent dynamics as stated before. Moreover, if the specific interaction such as the hydrogen bonding between the radical and the solvents dominantly control the diffusion process, the activation energy would not be close to  $E_\eta$ .

As stated previously, there is a definite difference between  $E_D$  of the radicals and the parent molecules and the solute dependence of  $E_D$  is also noticeable. Before discussing the difference in  $E_D$  between the radicals and the parent molecules, we consider the dependence of  $E_D$  on the molecular size of the parent molecule. Figure 6 is the plot  $E_D$  against the reciprocal of the solute radii  $r_A$  in 2-propanol and ethanol. From Fig. 6,  $E_D$  seems to relate to  $1/r_A$ . For simplicity, we assume that  $E_D$  is linear in  $1/r_A$ ,

$$E_D = -\frac{\alpha}{r_A} + E_\eta, \quad (5)$$

where  $\alpha$  is a constant. The relation ensures that if  $r_A \sim \infty$ , then  $E_\eta = E_D$ . Therefore, the formula of the Arrhenius relationship of diffusion [Eq. (1)] must be rewritten as the following formula:

$$D = D_0 \exp\left(\frac{-(\alpha/r_A) + E_\eta}{k_B T}\right). \quad (6)$$

We believe that the various values of  $E_D$  in Table I is due to the effect of the molecular size.

The size dependence of  $E_D$  for stable molecules has been studied by Evans *et al.*<sup>27,28</sup> They empirically described  $D/10^{-9} \text{m}^2 \text{s}^{-1}$  ( $D_{EV}$ ) by

$$D_{EV} = \frac{AT}{\eta^p}, \quad (7a)$$

where  $A$  is a constant, which is equivalent to  $k_B/6\pi r_A$  in the SE equation. Evans *et al.* found that both  $A$  and  $p$  depend on the solute molecular size by measuring  $D$  of many solutes at variable temperatures. They proposed that  $A$  and  $p$  are given by<sup>28</sup>

$$A = \exp(a/r_A + b), \quad (7b)$$

$$p = c/r_A + d, \quad (7c)$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are constants, which are determined by Evans *et al.* as  $a = 5.9734 \text{ \AA}$ ,  $b = -7.3401$ ,  $c$

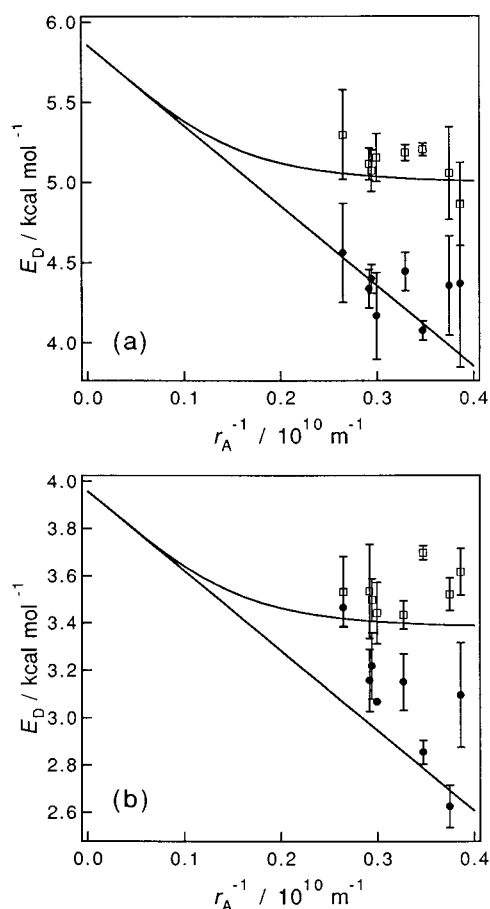


FIG. 6. Plot of the activation energies for diffusion of the radicals ( $\square$ ) and of the parent molecules ( $\bullet$ ) vs radii of the solutes in (a) 2-PrOH and (b) EtOH. Straight line is the calculated one for the parent molecules from  $D_{EV}$  [Eq. (8)]. Curved line is calculated one for the transient radicals from Eq. (11) with  $V_0 = 8 \times 10^2 \text{ \AA}^3$ .

$= -0.86365 \text{ \AA}$  and  $d = 1.0741$ . Equation (7b) indicates that  $D$  increases exponentially with the increase in  $1/r_A$ . Equation (7c) means that the effective viscosity of the solvent against the solute increases with increase of the solute molecular size. When  $r_A$  approaches infinity,  $\eta^p$  becomes  $\eta$ .

Our experimentally observed relation [Eq. (6)] is very close to the relation derived by Evans *et al.* Since the viscosity of the solvent is expressed by Eq. (3), the equation of Evans *et al.* can be described by the following:

$$D_{EV} = \frac{AT^{1-p}}{\eta_0^p} \exp\left[\frac{-E_\eta((c/r_A) + d)}{k_B T}\right]. \quad (8)$$

Therefore, when  $p$  is close to 1 the activation energy for diffusion is given by

$$E_D = E_\eta \left(\frac{c}{r_A} + d\right). \quad (9)$$

Comparing Eq. (5) and Eq. (9), we find that both equations become identical when  $\alpha = -E_\eta c$ ,  $d = 1$ . Indeed, the value of  $d$  obtained by Evans *et al.* was 1.0741, which is sufficiently close to unity. Therefore, the molecular size dependence of  $E_D$  proposed for the parent molecule [Eq. (5)] is almost equivalent to the previously proposed relation [Eq.

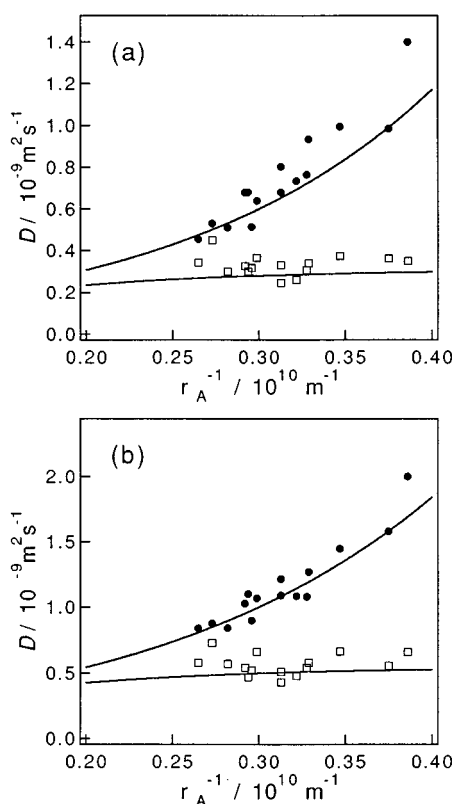


FIG. 7. The molecular size dependence of  $D$  of radical's ( $\square$ ) and of parent molecule's ( $\bullet$ ) in (a) 2-PrOH and (b) EtOH at room temperature (from Ref. 8). Curved line is calculated value of  $D$  by Eqs. (12), (13), with  $V_0 = 5 \times 10^2 \text{ \AA}^3$ .

7(a)]. Equation (6) is identical to Eq. (8) when  $AT^{1-p}/\eta_0^p = D_0$ . The values of  $E_D$  calculated from Eq. (9) with  $c = -0.85365$ ,  $d = 1$ , and  $E_\eta = 5.854 \text{ kcal/mol}$  in 2-PrOH,  $E_\eta = 3.957 \text{ kcal/mol}$  in EtOH are plotted in Fig. 6. Since this line agrees with experimental values fairly well, it is recognized that the temperature dependence of the stable (parent) molecules is described by Eq. (9).

The  $1/r_A$  dependence of  $E_D$  can be explained by the breakdown of the continuous fluid approximation of the solvent in the theory of the hydrodynamics. The viscosity of the solvent is the macroscopic parameter and the hydrodynamic theory treats the solvent as continuous fluid. When the solute size is as small as the solvent molecular size, the solvent can be no longer treated as continuous fluid and the microscopic viscosity (local viscosity around the solute molecules) of the solvent is apparently reduced. In such a solvent, the activation energy for diffusion is reduced. Contrarily, when the solute molecules become larger, the solvent molecules can be treated as continuous fluid to a good approximation. If the solute molecule has infinite size, the microscopic viscosity should coincide with the macroscopic viscosity  $\eta$ . Actually, Fig. 6 suggests that the values of  $E_D$  of the parent molecules are close to the value of  $E_\eta$  ( $E_\eta = 5.854 \text{ kcal/mol}$  in 2-PrOH,  $E_\eta = 3.957 \text{ kcal/mol}$  in EtOH) when  $1/r_A$  approaches zero; i.e.,  $r_A$  approaches infinity.

## B. $E_D$ of transient radicals

On the basis of the molecular size dependence of  $E_D$  described in the previous section, we will interpret the different  $E_D$  of radicals and parent molecules in terms of the previously proposed model of the radical diffusion.<sup>8</sup> In a series of our investigations on the radical diffusion, we considered that the transient radicals are surrounded by the solvent or solute molecules with an attractive intermolecular interaction, and the effect of the attractive interaction was treated as an increase of the effective molecular volume. Namely, we have treated the small  $D$  of the radicals in terms of the apparent molecular size expansion.

Let us think the apparent radius of the radical ( $r$ ) which is increased from the radius of the parent molecule ( $r_A$ ) by gathering additional molecules around the radical. Assuming that the additional volume by the interaction is  $V_0$ ,  $r$  is calculated from

$$r = (r_A^3 + (3V_0/4\pi))^{1/3}. \quad (10)$$

If we replace  $r_A$  in Eq. (6) by  $r$ ,  $E_D$  of the radical is described by

$$E_D = - \frac{\alpha}{(r_A^3 + (3V_0/4\pi))^{1/3}} + E_\eta. \quad (11)$$

This equation reduces to Eq. (5) when  $r_A^3 \gg 3V_0/4\pi$ . In other words,  $E_D$  of the radical becomes closer to that of the parent molecule with increasing the molecular volume. When  $r_A$  becomes smaller,  $E_D$  of the radicals approaches a constant value. The curved lines in Fig. 6 are fitted lines calculated from Eq. (11) with  $V_0 = 8 \times 10^2 \text{ \AA}^3$  in 2-propanol and ethanol. They reproduce the observed molecular size dependence of  $E_D$  fairly well.

It should be noted that Eq. (9) as well as Eq. (11) predict that  $E_D$  of the parent and the radical should approach  $E_\eta$  as the molecular size increases. For the parent molecule, this tendency is consistent with the continuous model of the medium in the hydrodynamic theory. For the radicals, when the molecular size becomes large, the character of the radical (probably the spin density) is diluted and the diffusion process becomes similar to that of the parent molecule. Then the activation energy should be again close to  $E_\eta$ .

Above results and the analyses are consistent with the radical diffusion model that the radical diffuses in solution with a larger effective volume than the actual molecular size because of the attractive intermolecular interaction. This attractive intermolecular interaction is recently supported by time resolved transient Raman spectroscopy.<sup>29</sup> The apparent volume expansion is considered to be the origin of the anomalously slow diffusion of the transient radicals. In the analyses in this section, we assume that the increase of the effective volume is a constant which is independent of the solute size and the temperature. If we assume that the volume expansion is the result of the aggregation of the solvent molecules around the radicals, the estimated volume  $V_0 = 8 \times 10^2 \text{ \AA}^3$  corresponds to about ten solvent molecules in 2-propanol or ethanol.

### C. Molecular size dependence of $D$

In our previous paper,  $D$ 's of the radicals are compared with those of the parent molecules as a function of the molecular size at room temperature.<sup>8</sup>  $D$ 's of the parent molecules increase with increasing  $1/r_A$  whereas  $D$ 's of the radicals are rather insensitive to the molecular size. This different behavior was discussed in term of an excess friction gained by forming the radicals. In this section, we try to explain the molecular size dependence of  $D$  at room temperature by a different way; namely, by using the model discussed in the previous section.

From Eqs. (1), (9), and (11), the diffusion coefficients of the parent molecule  $D_i$  and of the radical  $D_j$  are given by

$$D_i = D_{i0} \exp\left(\frac{-(\alpha/r_A) + E_\eta}{k_B T}\right), \quad (12a)$$

$$D_j = D_{j0} \exp\left[\frac{-\frac{\alpha}{(r_A^3 + 3V_0/4\pi)^{1/3}} + E_\eta}{k_B T}\right]. \quad (12b)$$

These two formulas satisfy the condition of  $D_i > D_j$  and  $D_i = D_j$  at  $r_A \sim \infty$ . The pre-exponential factors ( $D_{i0}$  and  $D_{j0}$ ) are described by the following formulas from Eq. (8) with  $T^{1-p} \sim 1$ :

$$D_{i0} = \frac{\exp(a/r_A + b)}{\eta_0^{(c/r_A + d)}}, \quad (13a)$$

$$D_{j0} = \frac{\exp(a/(r_A^3 + 3V_0/4\pi)^{1/3} + b)}{\eta_0^{(c/(r_A^3 + 3V_0/4\pi)^{1/3} + d)}}. \quad (13b)$$

We try to reproduce the molecular size dependence of  $D$ 's of both the radicals and parent molecules by using Eqs. (12) and (13). The plot of  $D$  vs  $r_A$  is reproduced in Fig. 7 from Ref. 8.<sup>16</sup> For calculating  $D$ 's, we fix the values  $a$ ,  $b$ ,  $c$ , and  $d$  ( $a = 5.9734 \text{ \AA}$ ,  $b = -7.3401$ ,  $c = -0.86365 \text{ \AA}$  determined by Evans *et al.*<sup>28</sup> and  $d = 1$ ) and use the increase of the molecular volume  $V_0$  as an adjustable parameter. The best fitted lines by Eqs. (12) and (13) are obtained using  $V_0 = 5 \times 10^2 \text{ \AA}^3$  as shown in Fig. 7. The calculated values of  $D$  are in excellent agreement with the experimental ones for both the radicals and parent molecules. The value  $V_0 = 5 \times 10^2 \text{ \AA}^3$  is close to  $V_0 = 8 \times 10^2 \text{ \AA}^3$  which obtained from the fitting of the size dependence of the activation energies in the previous section. This fact supports the reliability of our radical diffusion model.

### V. CONCLUSIONS

The temperature dependence of the diffusion process of the intermediate radicals created by the photoinduced hydrogen abstraction reactions of ketones, quinones, and  $N$ -hetero aromatic molecules in 2-propanol and ethanol is investigated by using the transient grating (TG) method. The translational diffusion coefficients ( $D$ 's) of the radicals as well as that of the parent molecules can be expressed by the Arrhenius-type expression with one activation energy. We find that the values of the diffusion activation energies ( $E_D$ ) of the radicals are larger than those of the parent molecules and also they

depend on the solute molecular size. When the solute molecular sizes become larger, the values of  $E_D$  become larger. The solute molecular size dependence of the parent molecule's  $E_D$  could be explained by the empirical formula obtained by Evans *et al.*

Different values in  $E_D$  between the transient radicals and their parent molecules are interpreted in terms of a diffusion model we proposed before; the radicals are surrounded by other molecules (solvent and/or parent molecules) in solution by an attractive interaction. The equation of  $E_D$  as a function of solute radii derived by assuming that the apparent volume increase of the radical is constant for all of the radicals can reproduce the molecular size dependence of  $E_D$  of the radicals. The results of this investigation will give us a clue to understand the anomalous slow diffusion process of transient radicals.

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