

# Translational diffusion of transient radicals created by the photoinduced hydrogen abstraction reaction in solution: Anomalous size dependence in the radical diffusion

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Diffusion coefficients ( $D$ ) of various radicals created by the photoinduced hydrogen abstraction reactions from alcohols (ethanol and 2-propanol) are investigated by using the transient grating (TG) method. In all the reaction systems,  $D$ 's of the transient radicals, as well as those of the parent molecules, can be measured simultaneously. The results clearly show slower diffusive motions of the radicals, at least of the  $\pi$  radicals in the hydrogen abstraction reaction systems, compared with those of the parent molecules.  $D$ 's of the parent molecules usually agree well with the calculated values based on the Spornol and Wirtz modification of the Stokes–Einstein (SE) relation. Although the measured  $D$ 's of the radicals are closer to the values predicted by the simple SE equation, the agreements and the ratio of  $D$  between the radicals and its parent molecules depend on the molecular size. The ratio becomes closer to unity as the molecular size becomes large. Possible origins of this dependence are discussed. © 1995 American Institute of Physics.

## I. INTRODUCTION

Diffusion of radicals in solution often plays a key role in many chemical reactions. Not only does it determine reactivity or reaction mechanism,<sup>1</sup> but it also influences various physical phenomena such as chemically induced dynamic electron (nuclear) polarization (CIDEP, CIDNP) and magnetic field effects on the reactions.<sup>2</sup> For example, mutual diffusion of radicals in a radical pair governs the electron spin dynamics through the electron–electron interaction and, then, the spin dynamics controls the recombination probability of the radicals as well as the magnitude of the electron or nuclear spin polarization.<sup>2</sup> Therefore, the translational diffusion coefficients ( $D$ ) of radicals are always critical information for the analysis of the phenomena related to the chemical reactions.

It is rather surprising, however, how rare the data on  $D$  of such intermediate radicals are, in spite of many methods of measuring  $D$  of stable molecules developed so far.<sup>3</sup> Although some magnetic resonance methods have been applied to measure  $D$ 's of stable radicals,<sup>4</sup> what we are interested in is  $D$ 's of the transient radicals which participate in chemical reactions. It is also desirable to know  $D$ 's of their parent molecules at the same time to understand the radical diffusion in detail. There are several reasons for this scarcity; first, most of these methods require relatively long times for measurements. Naturally such methods cannot be applied to transient radicals that appear during chemical reactions for just short periods. Second, usually concentrations of the radicals are not very high unless very strong light intensity is used to produce the radicals. Further, even if such a high radical concentration can be established, it will induce undesirable side reactions and will not be suitable for the study on the diffusion.

In spite of these difficulties, there have been several re-

ports on the diffusion of transient species. Noyes has developed the photochemical space intermittency (PSI) method.<sup>5</sup> Burkhart *et al.* have measured  $D$ 's of some alkyl radicals using this method.<sup>6</sup> However, probably because of the difficulties in the procedure and relatively large uncertainties,<sup>7</sup> the application of this method has been limited. Nickel and co-workers have developed a method for measuring  $D$ 's of transient species by modifying the PSI method with an interference pattern between two laser beams.<sup>8</sup> They have detected delayed fluorescence and succeeded in determining  $D$ 's of several aromatic molecules in the triplet states with high accuracy. Although, potentially, this method could be applied to photochemical reaction systems, the sample is limited to a molecule that shows luminescence. More recently, Levin *et al.* suggested slow diffusion of a diphenylhydroxymethyl radical [benzophenone ketyl radical (BPK)] created by the photoinduced hydrogen abstraction reaction in glycerin on the basis of the magnetic field effect on the disappearing rate of the radical.<sup>9</sup> However, this method is not a direct detection of the diffusive motion in solution.

Recently we have demonstrated that the TG method has a capability of measuring  $D$  of transient radicals accurately.<sup>10,11</sup> The success of the measurement is based on the high sensitivity and much less time-consuming procedure. The short time measurement is a result of a short diffusion distance ( $\sim\mu\text{m}$  order) we need for the measurement. The high sensitivity comes from the background free detection in this method. By taking these advantages, the TG method has been demonstrated to be a convenient and useful method for measuring  $D$ 's of photochromic dyes,<sup>12</sup> species in the excited states,<sup>13</sup> and so on. We have applied this method to photochemical reaction systems.

The results of the TG measurements on the pyrazinyl radical<sup>10</sup> and BPK,<sup>11</sup> which are, respectively, created by the hydrogen abstraction reactions of pyrazine and benzophenone, show much slower (two to four times) diffusion of the radicals compared with their parent molecules (pyrazine and

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BP), although the molecular volumes are almost the same between the radicals and their parent molecules. However, the mechanism which controls the diffusive motions of radicals is still unclear because of the scarce data on  $D$ 's of radicals.

In this work, we investigate diffusion processes of a variety of radicals. The radicals are created by the photoinduced hydrogen abstraction reactions of various solutes from alcohols (ethanol and 2-propanol). For the reactants, we choose carbonyls (benzaldehyde, acetophenone, xanthone), quinones (benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, 1,4-chrysenquinone), and  $N$ -hetero aromatic molecules (phenazine, quinoline, quinoxaline, acridine, octahydrophenazine, 2,2-biquinoline). The photoinduced hydrogen abstraction reaction is one of typical photochemical reactions and have been studied frequently by many means. In many cases, the reaction mechanisms and the intermediate radicals are well understood.

There are three aims in this study. First, measurements of various radical systems will give us a clue to answer the questions: whether or not the slower radical diffusion is a general phenomenon and if there is a characteristic behavior depending on the type of molecules (such as ketones, quinones, and  $N$ -hetero aromatic molecules). Second, the measured  $D$ 's of the radicals will provide valuable data for the analysis of many works on photochemical reactions. Third, the molecular size effect on  $D$ 's may give us an insight for understanding the movement of the radicals in solution. We can measure  $D$ 's of various radicals as well as their parent molecules at the same time. Here it is found that  $D$ 's of all the radicals studied are generally smaller than those of the parent molecules, and they show anomalous molecular size dependence. Possible origins of the slow radical diffusion are discussed.

## II. EXPERIMENT

The experimental method has been published elsewhere.<sup>10,11</sup> We briefly describe the essential step for the measurement. An excimer laser (Lumonics Hyper 400) ( $\lambda = 308$  nm) was used for the photoexcitation of the solutes in alcoholic solvents (ethanol and 2-propanol). Typically, the excitation laser power for the TG measurement was  $<0.1$  mJ/pulse. After crossing two beams from the excimer laser in a sample solution, the time dependence of the grating probed by a He-Ne laser was monitored with a photomultiplier (Hamamatsu R928). The repetition rate of the excitation pulse was typically  $\sim 3$  Hz to prevent accumulation of photochemical products in the irradiation region. The irradiated volume is so small (typically  $\sim 4 \times 10^{-3}$  cm<sup>3</sup>) compared with the entire volume of the sample solution ( $\sim 4$  cm<sup>3</sup>) that the interference due to the reaction product in the signal is not serious during one measurement. The sample solution was replaced by a fresh one after every  $\sim 1000$  shots of the excitation laser pulse. However, there were some solutions which show relatively large effects of the reaction products. Whenever the effect of the product was noticeable, the solution was slowly stirred by a micromagnetic stirrer to dissipate the product away from the excitation region. The effect of the product on the signal and the effect of the stirring will be

described in a later section. The fringe spacing ( $\Lambda$ ) was calculated from the decay of the thermal grating signal with the thermal diffusion constant of benzene as described in Ref. 11.

An EPR signal was detected by a JEOL-FE3X ESR spectrometer with a 100 kHz field modulation under the laser light irradiation (repetition rate = 20 Hz). For the decay measurement, the signal from the spectrometer was averaged by the digital oscilloscope with a slower repetition rate (3 Hz). The response time of the spectrometer is several milliseconds.

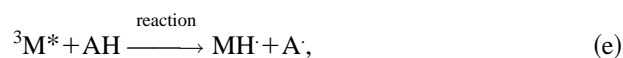
For a transient absorption measurement, the sample solution was irradiated by the excimer laser ( $\sim 10$  mJ/pulse) and probed by a 900 W Xe lamp. The probe light was monochromated with a Spex model 1704 and detected by the photomultiplier.

Spectrograde solvents (2-propanol and ethanol) were used as received. Sample solutions were deoxygenated by the nitrogen bubbling method just before the measurements. A typical concentration of the solutions was 0.01 M.

## III. RESULTS

### A. Mechanism of photochemical reaction

A sinusoidal pattern of the excitation light is produced in the sample solution by two coherent beams. At the bright region of the grating, reactants ( $M$ ) are excited to the excited singlet states. As the intersystem crossing (ISC) from the lowest excited singlet ( $S_1$ ) state to the lowest excited triplet ( $T_1$ ) state takes place efficiently for all the samples we used, they abstract hydrogen atoms from the alcoholic solvents in the  $T_1$  states. The reaction scheme of the solute  $M$  is described as follows:



where AH, MH, and  $\text{A} \cdot$  are, respectively, an alcoholic solvent and created radicals of the solute and the solvent. The inhomogeneous distributions of heat from processes (a)–(d) and of chemical species from (e) make a transient grating in the solution and it diffracts the probe beam. Since nonradiative transitions always participate in the deactivation processes, the thermal grating signal should be always anticipated in the TG signal. The signal due to the mass diffusion appears only when the modulation of the optical properties is induced by the presence of the species.

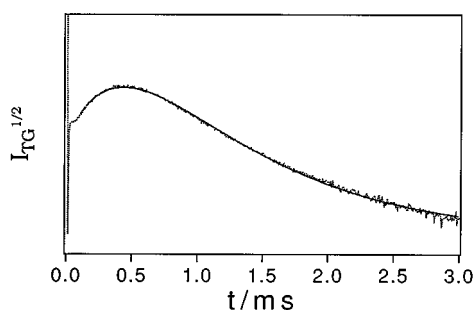


FIG. 1. Time profile of the TG signal after the photoexcitation of benzoquinone in 2-propanol (dotted line) and the best fitted curve with Eq. (2) (solid line).

## B. Diffusion of benzoquinone and benzosemiquinone radical

In this section, taking the benzoquinone (BQ) case as an example, we show how to determine  $D$ 's of the radicals created by the reaction scheme given in the previous section and their parent molecules. Typical time dependence of the TG signal after the photoexcitation of BQ in 2-propanol is depicted in Fig. 1. The initial strong spike-like signal is due to the contribution of the thermal grating. The decay of the signal is determined by the thermal diffusion and the fringe distance ( $\Lambda$ ). After it decays to the base line once, another slowly developing signal appears. Since this signal develops almost two to three orders of magnitude slower than that of the thermal grating, the time profile must reflect the molecular diffusion in the solution. This assignment is very plausible because optical properties of the aromatic molecules and the hydrogen attached radicals are totally different and, thus, the spatial inhomogeneity due to the created radicals and the consumption of the reactants will diffract the probe beam.

When the radical decays are determined by the first-order processes, the time dependence of the diffracted signal  $I_{\text{TG}}(t)$  induced by fringes with wave vector  $q$  can be calculated from the diffusion equation with the decay of the radicals and is given by<sup>10</sup>

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

where  $\alpha$  and  $\beta$  are constants which depend on the laser intensities of the probe and excitation beams as well as the experimental configuration.  $\delta n_{i(j)}^0$  is the refractive index change due to the creation of the species  $i=A\cdot$  and  $MH\cdot$  ( $j=AH$  and  $M$ ),  $\delta k_{i(j)}^0$  is the extinction coefficient change

due to the creation of the  $i(j)$  species,  $D_{\text{th}}$  is the thermal diffusion coefficient in the solution,  $D_{i(j)}$  is the mass diffusion coefficient of the  $i(j)$  species,  $k_i$  is the first-order disappearance rate constant of the intermediate radical  $i$  by a subsequent reaction and  $q=2\pi/\Lambda$ , which is calculated from the measured  $\Lambda$ . Of course, intermediate radicals frequently disappear by the self-termination reactions and the rate should be described by the second-order kinetics. In such circumstances, the time development of the TG signal cannot be expressed by a simple equation such as Eq. (1). Meyer and Nickel have used an approximate solution of the diffusion equation including the second-order kinetics to analyze their data.<sup>8</sup> However, we fortunately do not need to use such an approximate solution because the intermediate radicals we examined in this work live long enough compared with the observation time. Then it is appropriate to use Eq. (1) with  $k_i \sim 0$  for analyzing the time profile of the TG signal. The slow disappearing condition can be examined by the analysis of the time profile and/or by the measurement of the decay rate constant as a function of  $q^2$ . If the self-termination reaction significantly affects the time profile of the TG signal, the time profile should seriously deviate from what is predicted by Eq. (1) and it cannot be simply analyzed by an exponential function. Furthermore the decay rate constant of the TG signal should not show a linear dependence against  $q^2$ . Other assumptions made for deriving Eq. (1) are discussed in more detail in Refs. 10 and 11.

After the thermal grating is completely vanished, the square root of the TG signal ( $I_{\text{TG}}^{1/2}$ ) is expressed well by a sum of two exponential functions with different signs of the preexponential factors:

$$I_{\text{TG}}^{1/2} = a_s \exp(-k_s t) + a_f \exp(-k_f t), \quad (2)$$

where the subscripts  $s$  and  $f$  stand for the slow and fast components, respectively. The dip between the thermal grating and the population grating implies that the  $\delta k$  term in Eq. (1) is negligible, which is confirmed from the transient absorption measurement. The absolute signs of the preexponential factors in Eq. (2) can be determined as  $a_s > 0 > a_f$  and  $|a_s| > |a_f|$  from the facts that the signal once reaches the base line and  $\delta n_{\text{th}}^0$  in Eq. (1) should be negative.

The next task we have to consider is the assignment of the chemical species contributing to the TG signals. According to the photochemical investigations of BQ,<sup>14</sup> the triplet state BQ is deactivated to the ground state or abstracts hydrogen from alcohol to form transient radicals of the benzosemiquinone radical (BQH $\cdot$ ) and  $A\cdot$ , where  $A\cdot$  is the 2-hydroxypropyl radical (HPr $\cdot$ ) (Scheme 1). Therefore, the diffusion of BQ,  $A$ , BQH $\cdot$ ,  $A\cdot$  and reaction products from BQH $\cdot$  and  $A\cdot$  could be involved in the TG signal. According to the absorption studies, all of these species have their absorption bands at shorter wavelengths than the light of the He-Ne laser.<sup>14</sup> A theoretical consideration on the refractive index associated with the absorption band states that the refractive index change due to these species should be positive ( $\delta n_{i(j)} > 0$ ). Because of the depletion of the parent molecules (BQ and AH), these reactants create a negative phase grating [the minus sign of  $\delta n_j$  in Eq. (1)] and the formation of the radicals or the stable products create a positive phase grating

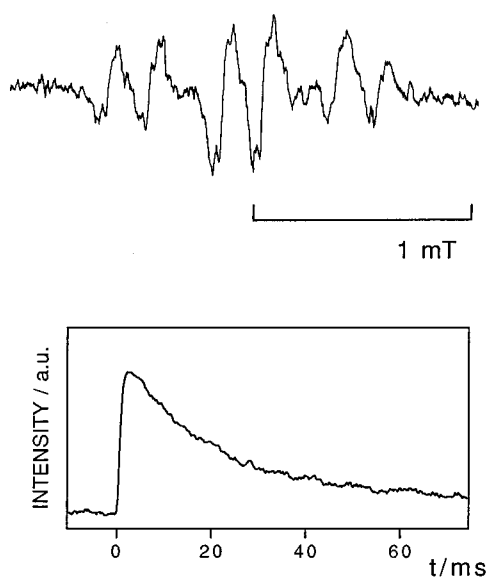


FIG. 2. A cw EPR spectrum measured during the pulsed laser photoexcitation of BQ/2-propanol with 20 Hz (upper) and a decay curve of the EPR signal (lower).

[plus sign of  $\delta n_i$  in Eq. (1)]. Therefore, the slow and fast components originate from the radical species (or the reaction products) and the parent molecules, respectively.

In the following, we identify the diffusing species based on several considerations.

(a) The slow component decays faster under the air saturation condition. Since it is unlikely that the dissolved nitrogen or oxygen change the diffusion process in the solution, the shorter decay must be due to the quenching of the diffusing species by oxygen. Therefore, the species of the slow component should be an unstable species, i.e., a transient radical.

(b) Figure 2 shows the cw EPR spectrum measured under the irradiation by laser pulse with 20 Hz repetition rate. The spectrum is unambiguously assigned to BQH $\cdot$ . There is no other detectable EPR signal. This fact gives conclusive evidence that the transient radical seen in the TG signal is BQH $\cdot$ . Furthermore, the fact that the signal can be detected under the cw operation of EPR with the pulse excitation indicates that the lifetime of BQH $\cdot$  is sufficiently long in the millisecond time range. Indeed, the signal decays nearly exponentially with a lifetime 32 ms under the excitation laser power  $\sim 2$  mJ/cm $^2$ .

(c) We have tried to detect a transient absorption signal. However, the signal was too weak to be detected with the same excitation laser power as in the TG experiment. The transient absorption signal can be detected with a stronger laser power ( $\sim 20$  mJ/cm $^2$ ) in the 410–360 nm range and the spectrum is reasonably consistent with that of BQH $\cdot$  reported previously.<sup>14</sup> The decay (Fig. 3) is expressed by the second-order decay and the half-lifetime ( $t_{1/2}$ ) is  $\sim 12$  ms under our experimental conditions.

(d) Another clue for the assignment of the chemical species contributing to the TG signal comes from the extinction

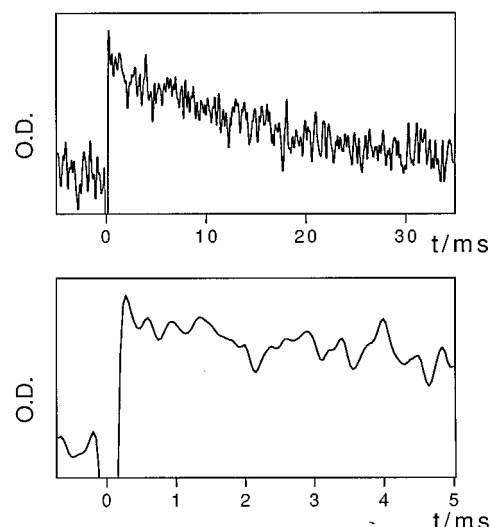


FIG. 3. Time profile of the transient absorption signal after the photoexcitation of a BQ/2-propanol detected at 400 nm (upper). The negative spike around  $t \sim 0$  is due to the scattering light of the excitation. Lower; the above profile is expanded in time to clearly show that the decay of the radical in the TG measurement is negligible.

coefficient of the species. Because of the small extinction coefficients of 2-propanol and HPr,<sup>11</sup> the TG signals due to these species are predicted to be weak compared with those of BQ and/or BQH $\cdot$ . Indeed, in the previous work, the observed TG signal after the photoexcitation of benzophenone in alcohols could be well explained in terms of the contributions of the benzophenone and benzophenone ketyl radical. The TG signals of 2-propanol and HPr were not detected. Based on these considerations, we believe that it is reasonable to attribute the slow and fast components to BQH $\cdot$  and BQ, respectively. The TG signal of 2-propanol and HPr should be hidden under the relatively strong signal due to BQH $\cdot$  as described in the previous paper.<sup>11</sup>

(e) A further support comes from the determined  $D$  values.  $D$ 's of the slow and fast components are totally different from those of 2-propanol and HPr. If these components are mixed in the TG signal, the time profile should deviate from the biexponential behavior of Eq. (2). The fact that the signal can be well analyzed by Eq. (2) strongly indicates that these chemical species do not contribute to the TG signal.

On the basis of the above argument, the rise time constant  $k_f$  is assigned to  $D_{BQ}q^2$  ( $D_{BQ}$  is  $D$  of BQ) and the decay rate constant  $k_s$  to  $D_{BQH}q^2 + k$  ( $D_{BQH}$  is  $D$  of BQH $\cdot$ ) Actually, all of the rate constants depend on the fringe spacing  $\Lambda$ . Figure 4 shows the  $q^2$  dependence of  $k_s$  and  $k_f$ . Each slope of the plot gives  $D$  of each chemical species. Although the intercepts, which give the intrinsic lifetimes of the species, should have nonzero values for the transient radicals, all plots indicate very small intercepts. Since the values are so small that we fix the intercept to be zero for determining the slope by the least-squares method. We estimate that the error introduced by this assumption is typically within 5%. The errors due to other sources were discussed previously and estimated to be about 10%.<sup>11</sup> The small intercept of the  $k_s$  vs

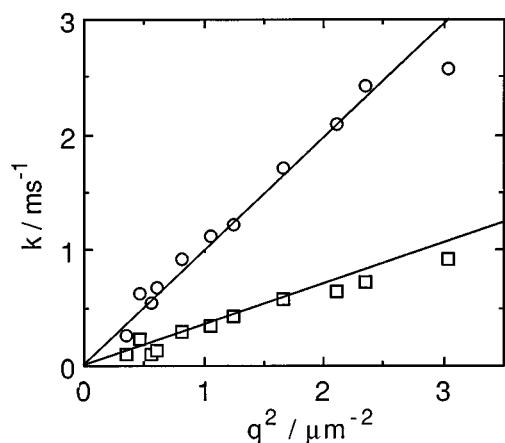


FIG. 4. Plots of the rate constants of  $k_s$  (squares) and  $k_f$  (circles) vs  $q^2$ .

$q^2$  plot indicates that the disappearing rate of the radical is slow compared with the smearing out time of the optical fringes by the diffusion process. The slow disappearing rate of BQH $\cdot$  is consistent with the measured decays of the EPR signal (Fig. 2) and the transient absorption (Fig. 3) as shown above. The slow decay may be a result from the low concentration of the radical ( $10^{-5}$ – $10^{-6}$  M).<sup>11</sup>

If the second-order decay due to the self-termination reaction is involved in the dynamics of the radicals, the slow decay curve of the TG signal should deviate from the single exponential function and the apparent decay rate constant obtained by fitting with a single exponential function should be larger than that without the reaction. Then it will lead to a seemingly faster diffusion of the radical. Therefore, if a minor chemical reaction of BQH $\cdot$  is involved, the true  $D$  of BQH $\cdot$  should be slightly smaller than that obtained here. In other words,  $D$ 's in this study could be upper limits.

The determined  $D$ 's are listed in Table I. The fact that  $D$  of HPr is totally different from  $D$ 's provides additional evidence for our assignment, that the slow decay of the signal is not due to HPr. It is worthy to compare the obtained  $D$  with that measured by an independent method for a further support. Although there has been no report on  $D$  of BQ in 2-propanol,  $D$  of toluene, which has a similar molecular volume to BQ, in 2-propanol has been reported ( $D \sim 1.60 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ).<sup>15</sup> This  $D$  is close enough to the value of BQ ( $1.93 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) in Table I. All of these discussions support that the analysis of the observed TG signal based on Eq. (1) is adequate.

Similar arguments also hold for the ethanol solvent case. A very similar temporal profile of the TG signal is observed. The assignment of the chemical species responsible for the signal can be made by a similar procedure except that the hydroxyethyl radical (HEt $\cdot$ ) is involved instead of HPr in the 2-propanol case.  $D$  of HEt $\cdot$  has been measured previously.<sup>11</sup>

### C. Other chemical systems

For most of the solutes we used, similar temporal profiles are observed as in the case of BQ. However, several

TABLE I. Diffusion coefficients of the transient radicals ( $D_{MH}$ ) and their parent molecules ( $D_M$ ) measured by the transient grating method in (A) 2-propanol and (B) ethanol solvents. Calculated values by the SE equation ( $D_{SE}$ ) and by the SW equation ( $D_{SW}$ ) are also listed.

Solute	$D_{MH}$	$D_M$	$D_{SE}$	$D_{SW}$
A. 2-Propanol				
Benzaldehyde	0.37	0.99	0.29	0.57
Acetophenone	0.34	0.93	0.28	0.61
Benzoquinone	0.36	0.98	0.29	0.79
$\alpha$ -Naphthoquinone	0.25	0.80	0.26	0.70
$\beta$ -Naphthoquinone	0.33	0.68	0.27	0.84
Xanthone	0.30	0.68	0.23	0.82
1,4-Chrysenoquinone	0.17	0.53	0.45	0.53
Pyrazine	0.35	1.4	0.31	1.00
Quinoline	0.31	0.77	0.28	0.53
Quinoxaline	0.26	0.73	0.27	0.60
Acridine	0.32	0.51	0.23	0.55
Phenazine	0.37	0.64	0.23	0.63
Octahydrophenazine	0.30	0.51	0.23	0.57
2,2-Biquinoline	0.34	0.45	0.17	0.50
B. Ethanol				
Benzaldehyde	0.66	1.5	0.57	1.09
Acetophenone	0.58	1.3	0.56	1.16
Benzoquinone	0.57	1.6	0.57	1.51
$\alpha$ -Naphthoquinone	0.43	1.2	0.53	1.34
$\beta$ -Naphthoquinone	0.57	0.84	0.45	1.09
Xanthone	0.47	1.1	0.46	1.59
1,4-Chrysenoquinone	0.73	0.88	0.35	1.03
Pyrazine	0.66	2.0	0.61	2.00
Quinoline	0.54	1.1	0.56	1.00
Quinoxaline	0.43	1.1	0.53	1.34
Acridine	0.52	0.90	0.46	1.04
Phenazine	0.66	1.1	0.45	1.16
Octahydrophenazine	0.57	0.84	0.45	1.09
2,2-Biquinoline	0.58	0.84	0.35	0.96

samples show a noticeable effect of the prolonged irradiation by the excitation laser. We take the phenazine system as an example.

Phenazine is also considered to abstract hydrogen from a hydrogen donor molecule in the  $T_1$  state.<sup>16</sup> After just one or two shots irradiation of the excitation beam to phenazine in the alcohol, the TG signal shows a rising component followed by a decaying one after the contribution of the thermal grating is diminished, which is very similar to the BQ case [Fig. 5(a)]. However, we notice that the temporal profile gradually varies with successive irradiation of the excitation beam. The intensity of the rising component becomes weak and another decaying component which appears with an increased number of irradiation shots [Fig. 5(b)]. We think that the new decaying component originates from a photochemical species created by the photoexcitation of an intermediate or a final product in the photochemical reaction of phenazine. The identification of the species cannot be made at present. To avoid the contribution of the secondary product to the TG signal, we stir the solution slowly to remove the secondary product from the irradiation region. By this stirring, we can average the TG signal for several shots of the excitation laser pulses to obtain a better S/N ratio. The effect of the stirring on the decay rate of the TG signal is checked by comparing the obtained time profile with that recorded

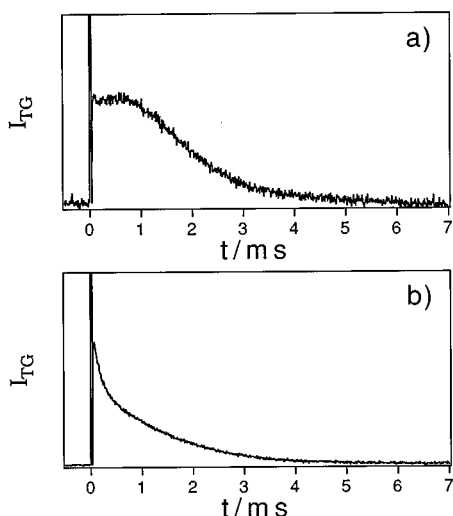


FIG. 5. Time profile of the TG signal after the photoexcitation of phenazine in 2-propanol with two laser shots for excitation (a) and with the prolonged excitation (b).

with two shots excitation, and found to be negligible in our observation time range.

The time profiles of the other reaction systems are also analyzed in a similar manner. In Fig. 6, some of the time profiles are shown as examples. Although the reaction mechanisms of all of them have not been elucidated, we can reasonably assume that their intermediate radicals are the hydrogen abstracted ones because of their similar functional groups (C=O or aromatic N) and from the analogs of the photochemical reactions of other similar compounds.<sup>17</sup> Similar temporal profiles obtained for all the samples suggest that the chemical species involved in the signal are the parent

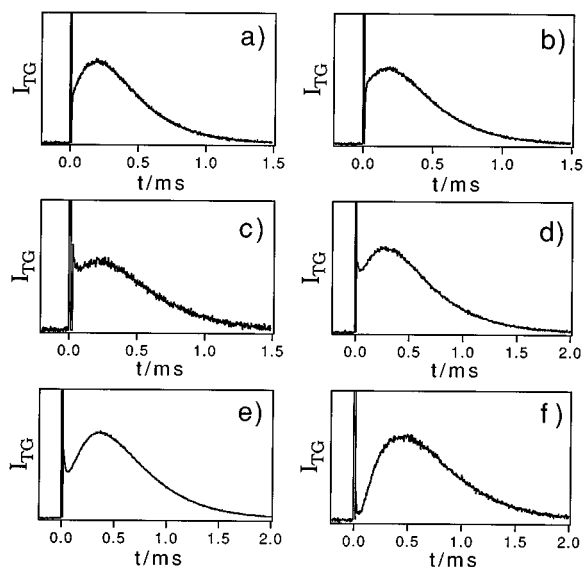


FIG. 6. Time profile of the TG signal after the photoexcitation of various solutes in 2-propanol (a) benzaldehyde; (b) acetophenone; (c) quinoline; (d) quinoxaline; (e) xanthone; (f) 2,2-biquinoline.

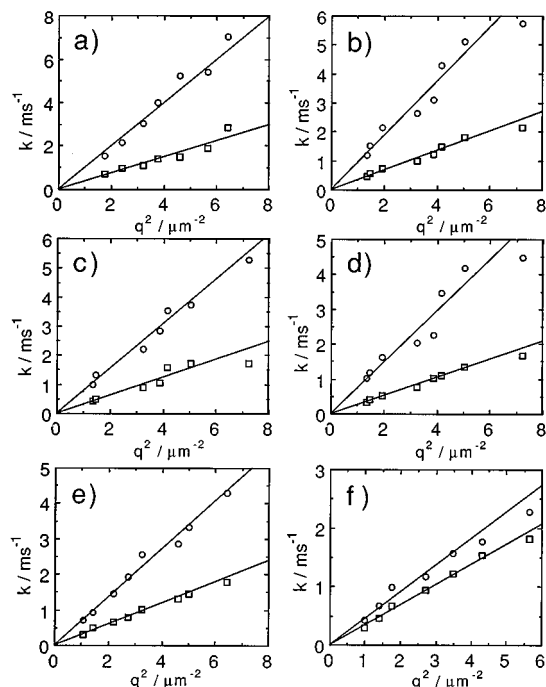


FIG. 7. Plots of the rate constants of  $k_s$  (squares) and  $k_f$  (circles) vs  $q^2$  for the same samples shown in Fig. 4.

aromatic compounds and their radicals. Indeed this is confirmed by several facts similar to the BQ case. For example, the quenching of the slow components by oxygen is observed for all the samples and this fact indicates that the slow diffusing species are the transient radicals. Sufficiently long lifetimes of these radicals are checked by the transient absorption method for several prototype radicals (such as quinoxaliny and acetophenone kethyl radicals). Even though we have to use the stronger laser power for the absorption measurements as stated previously, the decay curves can be expressed by the second-order kinetics with  $t_{1/2} \sim$  several milliseconds. Considering the low laser power for the TG measurements, the radical concentration is considered to be constant within the period for the TG measurement as shown in the BQ case. It should be noted that, again, the linear relationship of the  $k$  vs  $q^2$  plots (described below) ensures that the  $D$  measured by this method is actually the diffusion coefficients which are not affected by the disappearance reaction rate of the radicals. Furthermore, the fact that all of the time profiles can be analyzed by Eq. (2) supports the long lifetimes of the radicals and, at the same time, it suggests that the alcoholic species (2-propanol and HPr) do not contribute to the TG signal. This conclusion is reasonable because the observed signals are relatively strong compared to that of HPr and the determined  $D$ 's are different from that of HPr and 2-propanol.

The  $k$  vs  $q^2$  plots of all the solutes we have examined in both alcohols give straight lines with small intercepts (Fig. 7). It is noteworthy that species responsible for positive  $\delta n_i$ , which are assigned to the radicals, always give smaller slopes. The small intercepts imply chemical stabilities of all

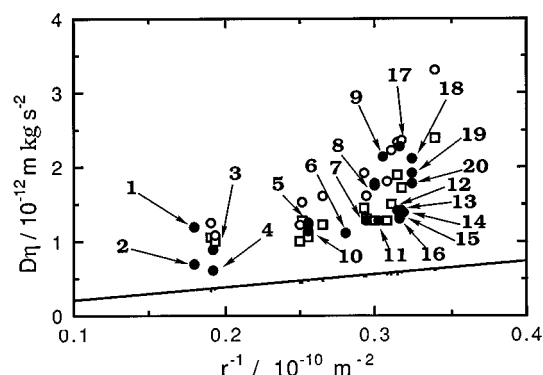


FIG. 8. Comparison of  $D_M$  measured in this work (in 2-propanol; open circles and in ethanol; open squares) and  $D_s$  of neutral stable molecules measured by other methods (closed circles). The samples are (1) coronene/Ac (Ref. 23), (2) coronene/CHX (Ref. 23), (3) perylene/Ac, (Ref. 23), (4) perylene/CHX (Ref. 23), (5) anthracene/AcN (Ref. 24), (6) trinitrobenzene/AcN (Ref. 25), (7) nitroanilen/AcN (Ref. 25), (8) benzoic acid/EtOH (Ref. 26), (9) toluene/EtOH, (Ref. 27), (10) anthracene/EtOH (Ref. 28), (11) biphenyl/EtOH (Ref. 28), (12) naphthalene/EtOH (Ref. 28), (13) propylbenzene/EtOH (Ref. 28), (14) 1,2,4-trichlorobenzene/EtOH (Ref. 28), (15) cyclohexane/1-butanol (Ref. 29), (16) cyclohexane/EtOH (Ref. 29), (17) cyclohexane/1-propanol (Ref. 29), (18) benzene/1-butanol (Ref. 30), (19) benzene/1-propanol (Ref. 30), and (20) benzene/EtOH (Ref. 30) (EtOH:ethanol, Ac; acetone, AcN, acetonitrile, CHX; cyclohexane). The straight line represents the calculated  $D\eta$  from the Stokes–Einstein relation.

the intermediate radicals. The obtained  $D$ 's of the radicals ( $D_{MH}$ ) and their parent molecules ( $D_M$ ) are summarized in Table I.

Because we are going to discuss the radical diffusion based on the above assignment, it is worthwhile to give a further support of the above assignment. For this purpose, we try to compare the  $D$ 's of neutral stable molecules measured by other traditional methods with those of the parent molecules measured in this work. Since the experimental conditions (such as temperature, solvents, solutes) are different in various reports, it is necessary to correct them. We correct the effect of solution viscosities by taking the product of  $D$  and the viscosity ( $\eta$ ) and plot  $D\eta$  against  $r^{-1}$  ( $r$  is the radius of the solutes) (Fig. 8). The idea behind these comparisons is based on the Stokes–Einstein (SE) relation [Eq. (3) in Sec. IV], which predicts  $D\eta$  to be inversely proportional to  $r$ . As will be discussed in Sec. IV, even though the SE relation does not predict quantitatively correct  $D$ 's of neutral molecules, this plot will be sufficient for examining the qualitative agreements between the  $D_M$  of our measurements and the literature values of  $D$ . We believe that the reasonable agreement seen in Fig. 8 confirms our assignment.

## IV. DISCUSSION

### A. Comparison of $D_{MH}$ with the calculated $D$

It should be noted that  $D_{MH}$  are generally smaller than  $D_M$ . This is not an apparent result because the difference in the molecular volume between the parents and their radicals is just one hydrogen atom, which is negligible compared to the whole molecular volume. The relation  $D_{MH} < D_M$  holds in all the radicals regardless of the nature of the solute (ketones, quinones,  $N$  hetero aromatic molecules).

During the course of our previous works on the pyrazine and benzophenone reaction systems, we have found that  $D$ 's of the radicals and their parent molecules agree reasonably well with the calculated  $D$ 's by the SE equation [Eq. (3)] and by a semiempirically modified SE equation [Eq. (4)], respectively.<sup>11</sup> In this section, we first examine if the same rule holds for other systems.

The SE equation, which describes  $D$  of a diffusing molecule in a homogeneous nonviscous solution with viscosity  $\eta$ , is given by<sup>3</sup>

$$D_{SE} = kT / \alpha \pi \eta r, \quad (3)$$

where  $r$  denotes the radius of a spherical molecule and  $\alpha$  is a factor for correction of the deviation from the spherical shape and of the boundary condition.

A semiempirical modification of Eq. (3) proposed by Spernol and Wirtz is given by<sup>18,19</sup>

$$D_{SW} = kT / 6 \pi \eta r f_{SW}, \quad (4)$$

$$f_{SW} = (0.16 + 0.4 r_M / r_A) (0.9 + 0.4 T_M^r - 0.25 T_A^r),$$

where  $r_M$  and  $r_A$ , respectively, represent the radii of the solute (M) and the solvent (A). The reduced temperatures  $T_M^r$  and  $T_A^r$ , which are parameters of the intermolecular interactions, are calculated by

$$T_X^r = (T - T_X^f) / (T_X^b - T_X^f)$$

using the freezing ( $T_X^f$ ) and boiling ( $T_X^b$ ) points of the solute ( $X=M$ ) or the solvent ( $X=A$ ). Sometimes  $f_{SW}$  is called a microscopic friction. The radii of the solutes (and radicals) are calculated from the molecular geometries and the van der Waals radii. The radii of the solvents are determined based on the same method used by Spernol and Wirtz from the density, molecular weight, and free volume (74%). The data of viscosities of the solvents are taken from Ref. 20.

The calculated values of  $D_{SW}$  listed in Table I agree well with the observed  $D$ 's for the parent molecules. Similar to the results of our previous report, this situation is totally different for the radicals; i.e.,  $D$ 's of the transient radicals are overestimated by  $D_{SW}$  but are in good agreement with  $D_{SE}$  ( $\alpha=6$ ), which does not take into account any specific interaction between the solute and solvent except the hydrodynamical force. However, with a closer examination of the observed and calculated  $D$ 's of the radicals, we notice that the difference between  $D_{MH}$  and  $D_{SE}$  depends on the radical. This point will be discussed in Sec. IV C.

### B. Radical diffusion in solution

As mentioned in the Introduction, Levin *et al.* have suggested the slow diffusion of  $BPK\cdot$  from the results of the magnetic field effect.<sup>9</sup> They have attributed the slowness to the “trapped” nature of the radicals in the “cage” of the radical pair.<sup>9</sup> The slow movement of the various radicals found in this work, however, cannot be due to such a cage effect because, in our observing time scale (tens  $\mu$ s–ms), the radicals created as a radical pair just after the excitation should escape from the cage and should be surrounded by the solvent molecules. Moreover, by taking advantage of the high sensitivity of the TG method, the radical concentration

can be kept low enough so that any free radical–free radical interaction can be neglected. This negligible radical–radical interaction is confirmed by measuring  $D$  of the radical at various light intensities and various concentrations of quinine in ethanol. The obtained  $D$  is insensitive to the changes in the light intensity and the concentration in our observation time scale.<sup>21</sup>

Burkhart *et al.* have measured  $D$ 's of several alkyl radicals and the benzyl radical by the PSI method and found that  $D$ 's of the alkyl radicals is smaller than those of the parent molecules, while that of the benzyl radical is in good agreement with the calculated value by the SE equation.<sup>6</sup> They suggested that the slow diffusion, which might be due to the radical–solvent interaction, could be less effective when the unpaired electron is delocalized in the  $\pi$  orbital. Our observation here is not consistent with their interpretation. Although all the radicals in this investigation are  $\pi$  radicals and the unpaired  $\pi$  electron should be delocalized in the entire molecular frame, they diffuse slower than their parent molecules.

In our previous work,  $D$ 's of HPr and HET have been measured by using acetone/2-propanol and acetaldehyde/ethanol reaction systems, respectively.<sup>11</sup> In contrast to the general slow diffusion of the  $\pi$  radicals, we found that  $D$ 's of HPr and HET are larger or comparable to those of 2-propanol and ethanol. Therefore, we cannot simply generalize the radical diffusion in solution to be slow. Nevertheless, we may conclude that the radicals with aromatic moiety diffuse slower and the radicals without it diffuse faster or comparable to those of their parent molecules.

It is interesting to note that  $D$  of the pyrazinyl radical is comparable to that of octahydrophenazine, whose molecular volume is about 2.5 times larger than that of the pyrazinyl radical. Octahydrophenazine is considered to be an alkyl substituted pyrazine and the unpaired electron should be localized in the pyrazine moiety. These considerations lead to a suggestion that only the unpaired  $\pi$  electron moiety makes the diffusion slow and that increasing the molecular volume by substitution does not simply decrease the diffusion, which is totally unexpected from the traditional theories on diffusion in solution. In Sec. IV C we consider the possible origins of the slow diffusion and the anomalous molecular size effect on  $D$ .

### C. Molecular size effect

There are several possibilities for explaining the anomalous slow diffusion of radicals. First, the slow diffusion could be interpreted in terms of a specific radical–solvent (or –other solute) interaction. In the presence of such an interaction, the radicals may be accompanied by several solvent (or solute) molecules during the movement. The increase of the apparent size of the radical should slow down the diffusion. One plausible candidate for the origin of the attractive interaction is the hydrogen bonding interaction created by the formation of –OH or –NH groups in the radicals. In our previous work, however, we found that the radical diffuses slower than the parent molecule even in nonpolar solvents which hardly involve hydrogen bonding with the radicals.<sup>10</sup> Therefore, the participation of hydrogen bonding is ex-

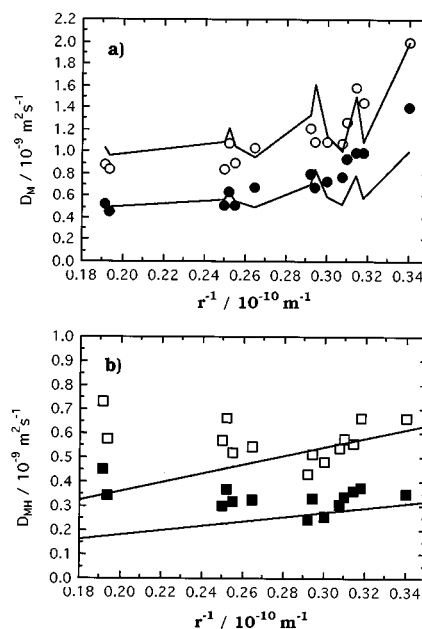


FIG. 9. Molecular size dependence of  $D_s$  of the parent molecules (a) and those of the transient radicals (b) in 2-propanol (closed circles) and in ethanol (open circles). The solid lines represent  $D_{SW}$  in (a) and  $D_{SE}$  in (b).

cluded. The attractive interaction, if it exists, should be due to the unpaired electron–solvent (solute) interaction.

So far, the molecular size effect has been examined for stable spherical molecules by Evans *et al.*<sup>22</sup> When the size of the solute is large compared with that of the solvent,  $D$  is proportional to  $1/r$  as predicted by the SE equation. With decreasing solute size, the  $1/r$  dependence of  $D$  deviates from the linear relation and increases exponentially. This is explained in terms of the breakdown of the important assumptions on which Eq. (3) is derived, namely the solute particle should be large enough for the solvent to be treated as a continuum. For the purpose of comparison with these previous works,  $D_{MH}$  and  $D_M$  vs  $1/r$  plots are shown in Fig. 9.  $D_M$  almost constantly decreases with increasing molecular size although there are several noticeable bumps. The  $1/r$  dependence of  $D_M$  can be reproduced by the SW equation even including these bumps. On the other hand, the  $D_{MH}$  plot first decreases with decreasing  $1/r$  until  $1/r \sim 0.3 \times 10^{-10} \text{ m}^{-1}$ , and then it increases gradually. In this “inverted” region, the radicals diffuse faster with increasing size.

From the above observation, we can generally summarize the diffusion of  $D_{MH}$  and  $D_M$  as follows: the larger the molecular size, the smaller the ratio of  $D_{MH}$  to  $D_M$ . In terms of the friction, this tendency can be treated as follows. The friction coefficient of a species  $i$  ( $i=M$  or  $MH$ ),  $f_i$ , is defined by

$$f_i = kT/D_i. \quad (5)$$

For the case that the SE equation holds, the Stokes friction coefficient is given by  $f_{SE} = 6\pi\eta r$  with the stick boundary condition. An excess friction,  $\Delta f$ , of the radical gained by the conversion from the parent molecule to the corresponding radical is given by

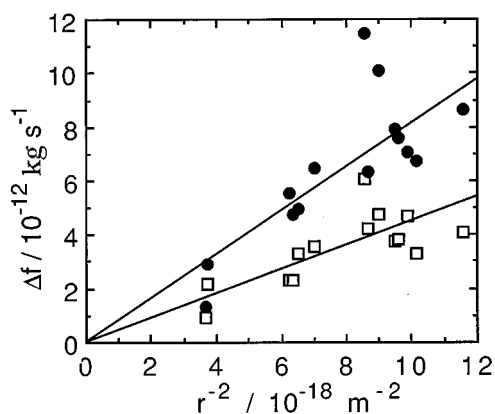


FIG. 10. Plots of the excess friction ( $\Delta f$ ) vs  $r^{-2}$ . The definition of  $\Delta f$  is given in the text [Eq. (6)]. Solid lines are a guide for the eyes.

$$\Delta f = f_{MH} - f_M. \quad (6)$$

This quantity is calculated for each solvent and plotted against  $1/r^2$  (for the sake of later discussion) in Fig. 10. It apparently shows a decreasing trend with increasing  $r$ .

The trend in the excess friction of the solutes studied herein may be accounted for in the following way. First we consider that the radical is diffusing accompanied by several solvents (or other solute) molecules and the effective molecular volume of the radical is defined by including the attached solvent molecules around the radical. Next we assume that one  $\pi$  unpaired electron has the capability of increasing the effective molecular volume only by a certain amount  $V_0$ , because the  $\pi$  unpaired electron–solvent interaction may be considered to be constant even with increasing the molecular volume.

Then the additional increase of the radius from the initial value  $r$ , by providing the unpaired electron, is given by

$$\Delta r \approx V_0 / 4\pi r^2. \quad (7)$$

Next, it may be reasonable to assume the relation  $\Delta f \propto \Delta r$  (remember that the SE equation implies  $f_{SE} \propto r$ ). Then we obtain a simple relation between  $\Delta f$  and  $r$  as

$$\Delta f \propto 1/r^2. \quad (8)$$

This relation can reasonably explain the observed  $1/r^2$  dependence of  $\Delta f$  qualitatively. The nearly zero intercept at  $r^{-2} = 0$  is reasonable because the effect of an unpaired electron is expected to be negligible for a very large molecule.

We must admit that the above model is oversimplified. The radicals cannot be tightly bounded with solvent (or solute) molecules. Realistically, a description that the radicals feel a larger friction from the surrounding molecules during the movement by the intermolecular interaction may be more adequate. In this paper, the excess friction is treated as an apparent excess volume of the radical. Furthermore, in the above treatment, we assumed that  $V_0$  is much smaller than the volume of the parent molecules. This is not a good assumption for the small radicals. Discussions without this as-

sumption and quantitative measurement of  $V_0$  will be published together with results of measurements at various temperatures in the near future.

To clarify the factors which control the radical diffusion in solution, it is also important to investigate the diffusion processes of other types of radicals such as  $\sigma$  radicals. We are currently investigating these radical diffusions.

## V. CONCLUSIONS

Translational diffusion coefficients ( $D$ 's) of the transient radicals created by the photoinduced hydrogen abstraction reaction of various solutes (quinones, ketones, and  $N$ -heteroaromatic molecules) from ethanol and 2-propanol are measured by using the transient grating method. Comparing the results with  $D$ 's of their parent molecules, we can conclude that most of the radicals we investigated here diffuse two to four times slower than their parent molecules even though their molecular volume should be very similar. The slow diffusion cannot be due to a specific radical–radical interaction or hydrogen bonding effect between the solutes and the solvents. The observed  $D$  values of the parent molecules agree well with the one calculated from the SW equation, while  $D$ 's of the radicals are more or less reproduced by the SE equation. The ratio of  $D$  between the radical and their parent molecules sensitively depends on the molecular size.

## ACKNOWLEDGMENT

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