# Diffusion Process of the Benzyl Radical Created by Photodissociation Probed by the Transient Grating Method

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Translational diffusion processes of the benzyl radical (BR) created by the photodissociation from dibenzyl ketone (DBK) were studied by using the transient grating (TG) method in organic solvents (hexane, cyclohexane, ethanol, and 2-propanol). The values of the diffusion constants (*D*) of BR, DBK, and carbon monoxide (CO) and the rates for the self-termination reaction of BR in these solvents are accurately determined from the TG signals. The ratios of *D* of BR to that of DBK are independent of the solvent, and they are close to 1.25, which is expected from the ratio of the molecular volume of BR to that of DBK. This result is contrary to those of radicals created by the photoinduced hydrogen abstraction reaction, which show anomalously slow diffusions. A possible origin of this difference is discussed by comparison of the spin densities, dipole moments, and polarizabilities of BR and the radicals produced by hydrogen abstraction.

## 1. Introduction

Since the diffusion process of molecules in solution is one of the fundamental and important processes, diffusion constants (*D*) have been measured by various methods and theoretically treated in many ways.[1] Simply, according to the hydrodynamic theory, *D* is given by the Stokes−Einstein (SE) formula:[1]

$$D_{SE} = k_B T/6\pi r_A \eta \qquad (1)$$

where $r_A$, $\eta$, and $T$ are the radius of the solute, the viscosity of the solution, and the temperature, respectively. However, in many cases, the calculated *D* by the SE equation cannot reproduce the experimentally observed *D*. The discrepancy may come from several factors. For example, the SE equation is based on some assumptions such that the solvent is treated as a continuous fluid, the form of the solute molecule is spherical, and solute−solvent and/or solute−solute interactions are disregarded. Perrin proposed a method for correcting the deviation from the spherical shape.[2] Spernol and Wiltz modified the SE equation in terms of a molecular interaction semiempirically.[3] Many empirical equations have been proposed so far.[4−7] By using these modified equations, the calculated *D*, in many cases, can reproduce the experimental *D*.

An interesting case will arise when there is a strong intermolecular interaction among the molecules. In such a case, these calculated *D* no longer agrees with the experimental *D*. For example, ions[8] or ion radicals[9] have strong interactions with solvents by the Coulombic potentials and this electrostatic interaction influences the diffusion process. This effect should be taken into account in the diffusion theories. For example, Zwanzig,[10] Hubbord, and Onsager,[11] and Bagchi[12] have proposed dielectric friction models. As shown from these examples, it is apparent that *D* is very sensitive to the environment around the solute molecule. Therefore, we can study the intermolecular interaction and the microscopic structure of the environment through the measurement of *D*.

In this respect, it is very interesting to observe the diffusion process of the intermediate radicals for studying the radical−solvent and/or radical−solute interaction and the microscopic solvation structure of the radicals. Since radicals have unpaired electrons and the chemical reactivities of radicals are generally high, we expect that the molecular interaction of radicals is quite different from those of stable molecules and ionic species. Moreover, the diffusion processes of radicals are essential for understanding the reaction mechanisms[13] and the dynamical properties of radicals.[14] In spite of such importance, it is very difficult to detect the translational motion of the intermediate radicals by traditional methods.[15,16]

Recently, we have succeeded in measuring *D* of the short-lived radicals accurately by using the time-resolved transient grating (TG) method, which requires only a short time (micro- to millisecond) for the measurement of *D*.[17−23] We have found that *D* of the radicals created by photoinduced hydrogen abstraction reactions of ketones, quinones, and N-hetero aromatic molecules from alcoholic solvents are 2−3 times smaller than those of the parent molecules, even though the radicals and parent molecules possess nearly the same sizes and the same shapes.[17,18] Such an anomalously slow diffusion of the radicals suggests a strong intermolecular interaction between the radicals and the surrounding molecules. Extended researches have been reported, such as the solvent dependence,[19] the solute size dependence,[20] the temperature dependence,[21] the effect of a charge in a radical,[22] the effect of chemical stabilities of radicals,[23] and transient Raman studies for the intermolecular interaction.[24]

The origin of such a strong molecular interaction of the radicals is still unclear. However, the difference between the radicals and the parent molecules is only the unpaired electron. That electron should lead to the anomalously slow diffusion process of the radicals. We must examine the role of the unpaired electron in affecting the diffusion process in solution. So far we have mostly studied the diffusion of the radicals created by photoinduced hydrogen abstraction reactions.[17−21] In this study, we measure *D* of the benzyl radical (BR), which is created by the photodissociation reaction from dibenzyl ketone (DBK). We have two aims in this study. First, since BR frequently appears in chemical reactions as an intermediate radical, it would be interesting and important to know the diffusion constant of BR for the analysis of the chemical reaction. Second, *D* of BR is compared with those of other transient radicals created by the hydrogen abstraction reactions to see if there is a noticeable difference in *D*. If there is a

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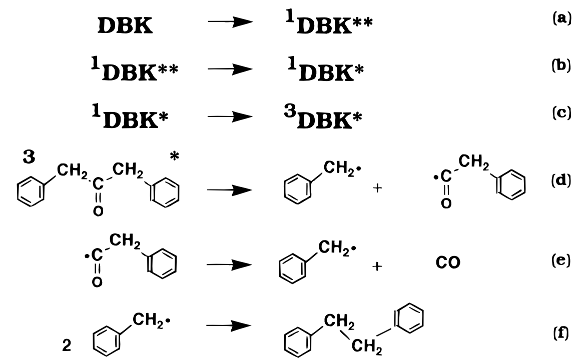
**SCHEME 1**



difference, a detailed comparison of the molecular character could provide an insight into the mechanism of the slow diffusion of many transient radicals.

The photodissociation process of DBK has been studied extensively in various solvents.[25-35] The reaction scheme is shown in Scheme 1. The lowest excited triplet ($T_1$) state of DBK is created by the intersystem crossing from the lowest excited singlet ($S_1$) state within a picosecond time scale after the UV irradiation (process a−c). The α cleavage of the C−CO bond (Norish type 1) occurs from the excited triplet state of DBK and brings BR and the phenylacetyl radical within a few nanoseconds (process d).[25] Successively, carbon monoxide (CO) is separated from the phenylacetyl radical in a few hundred nanoseconds at room temperature in the solution phase and another BR is produced (process e).[26] The quantum yield of the photodissociation of DBK has been reported to be ∼0.7.[27] BR is known as a relatively stable radical because the unpaired electron of BR is delocalized into the phenyl ring.[13] The recombination reaction of two BR to bibenzyl is a dominant subsequent reaction compared with a reaction between BR and the solvent molecules (process f). It has been reported that the reaction process of the self-termination of BR is a pseudo-diffusion-controlled reaction and the steric factor of this reaction is 0.8.[28] The rate constant ($2k_2$) of such a second ordered reaction has been measured in various solvents and it is reported to be $\sim 10^9$ M$^{-1}$ s$^{-1}$ as discussed in a later section.[29-35]

## 2. Experiment

Experimental details of the TG method have been published elsewhere.[15-23,36,37] We briefly summarize the method. A sinusoidal bright-dark pattern of light intensity was created in a sample cell by the interference of two coherent pump beams, which were produced from one laser beam from an excimer laser ($\lambda$ = 308 nm) (Lumonics Hyper EX-400). Solute molecules were excited by the light and photochemical reactions take place. Due to the spatially modulated light intensity and the subsequent chemical reaction, the optical properties (refractive index and/or absorbance) of the sample are spatially modulated (transient grating).[38] These gratings diffract a probe beam (He−Ne laser) when the phase matching condition was satisfied. This diffracted beam is the TG signal and the time dependence of this signal reflects the diffusion process of the chemical species in the solution. The repetition rate of the excitation pulse was 1−3 Hz. The excitation laser power at the crossing point measured by a pyroelectric joulemeter (Molectron J3-O9) was ∼0.3 mJ/cm². The TG signal was isolated from any scattered light with a glass filter (Toshiba R-62) and a pinhole ($\phi \sim 2$ mm), detected by a photomultiplier tube (Hamamatsu R-928), and recorded with a digital oscilloscope (Tektronix 2430A). The time profile of the signal was analyzed with a microcomputer. In many cases, signals after about 320 shots were averaged to improve the S/N ratio. The fringe spacing $\Lambda$ was roughly estimated from the crossing angle $\theta$ and then calibrated by the decay rate of the thermal grating signal from a benzene solution containing a light-absorbing solute and the reported thermal diffusion constant.[37]

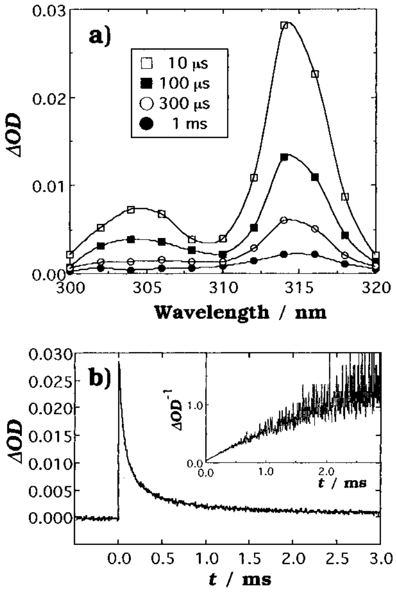


**Figure 1.** (a) Transient absorption spectrum after photoexcitation of DBK in 2-propanol during 10 $\mu$s to 1 ms. (b) Time profile of the TA signal at 314 nm.

For a transient absorption (TA) measurement, the sample was excited by the excimer laser light (1−5 mJ/cm²) and probed by light from a 100 W Xe lamp. The probe light was monochromated with a Spex Model 1704 and detected by a photomultiplier. The TG and TA measurements were carried out at room temperature (∼20 °C).

Pulsed field gradient spin-echo (PGSE) measurements [NMR spectrometer (JEOL JNM-EX270-W)] were made to independently measure the $D$ of stable molecules.[39] The PGSE measurements were carried out at 30 °C.

Spectroscopic grade solvents ($n$-hexane, cyclohexane, ethanol, and 2-propanol) and solute (DBK) were purchased from Nacalai tesque Co. DBK was purified by recrystallization from ethanol. The solvents were used without further purification. Typical concentrations of the solutes were 0.05 M for the TG measurement and 0.01 M for the TA measurement. The sample solutions were deoxygenated by the nitrogen bubbling method and fresh samples were used every ∼1000 shot irradiations to avoid the effect of reaction products to the signal.

## 3. Results

**3.1. Transient Absorption.** We first examine the chemical stability of BR during the observation time range of the TG signal by the TA method. Figure 1a shows the transient absorption spectrum monitored at 10 $\mu$s after the photo excitation of DBK in 2-propanol (0.01 M). This spectrum is in excellent agreement with the reported absorption spectrum of BR.[40] The time profile of the TA signal of BR is shown in Figure 1b. The decay profile can be expressed well by the second-order self-termination reaction with $\tau_{1/2} = 1/2k_2C(0) = 150$ $\mu$s ($C(0)$ is the initial concentration of BR) in 2-propanol at the excitation laser power ∼1.3 mJ/cm². The excitation laser power dependence of $2k_2C(0)$ is shown in Figure 2a. Figure 2b shows the $\Delta\mathrm{OD} = C(0)\cdot\epsilon_{\mathrm{Max}}$ at the peak of the extinction coefficient ($\epsilon_{\mathrm{Max}}$) of BR (314 nm) plotted against the excitation laser power. ΔOD is proportional to the laser power, which indicates that

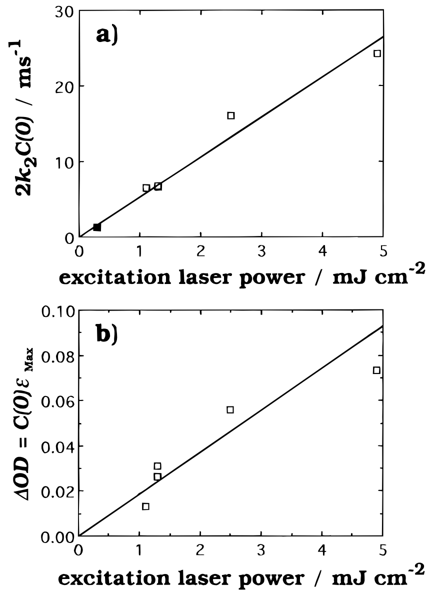


**Figure 2.** (a) Relationship between $2k_2C(0)$ and excitation laser power. $2k_2C(0)$ are obtained from the time profile of the TA signal (open squares) and from the intercept of $q^2$ plot of $k$ of the TG signal (Figure 4) (closed squares). (b) Relationship between $C(0)\cdot\epsilon_{\mathrm{Max}}$ and excitation laser power.

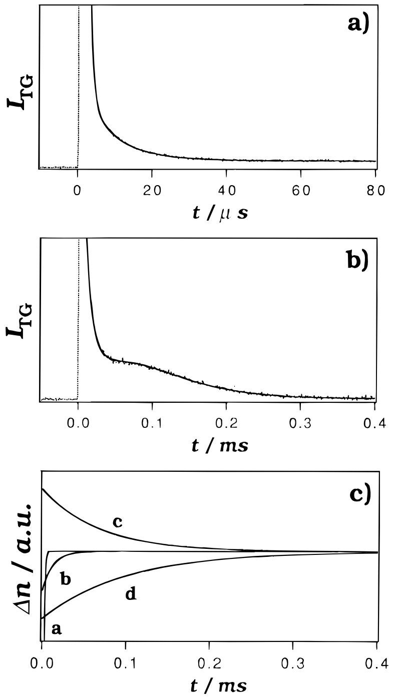


**Figure 3.** (a) Time profiles of the TG signal after the photoexcitation of DBK in 2-propanol at room temperature with $q^2 = 19\ \mu\mathrm{m}^{-2}$ (broken line) and the fitting line by eq 2 (full line) in the microsecond time scale and (b) in the millisecond time scale. (c) The assignments of these components are (a) heat conductivity, (b−d) translational diffusion process of CO, BR, and DBK, respectively.

the one photon excitation process is dominant within this range of the laser power.

**3.2. Time Dependence of the TG Signals.** Figure 3 shows that the time dependence of the TG signal after the photoexcitation of DBK in 2-propanol. Similar signals were obtained in other solvents (*n*-hexane, cyclohexane, and ethanol). In a rather fast time scale (Figure 3a), three components are observable in the TG signal. The fast component decays in a few microseconds and an intermediate component decays in a few tens of microseconds. Finally, there is a background signal which does not decay to the baseline completely in this time scale. In a wider time range and an enlarged vertical scale (Figure 3b), the slower component becomes apparent, and we found that the signal consists of a slow rise and a slow decay. The signal decays to the baseline completely in this time scale.

On the basis of a theoetical prediction as described later, we tried to reproduce the square root of the observed TG signal ($I_{\mathrm{TG}}(t)^{1/2}$) with a four-exponential function (eq 2).

$$I_{\mathrm{TG}}(t)^{1/2} = A_{\mathrm{a}} \exp(-k_{\mathrm{a}}t) + A_{\mathrm{b}} \exp(-k_{\mathrm{b}}t) - A_{\mathrm{c}} \exp(-k_{\mathrm{c}}t) + A_{\mathrm{d}} \exp(-k_{\mathrm{d}}t) \quad (2)$$

where $k_{\mathrm{a}} > k_{\mathrm{b}} > k_{\mathrm{c}} > k_{\mathrm{d}}$ and $A_{\mathrm{a}} - A_{\mathrm{d}} > 0$ are the preexponential factors. By using the nonlinear least-squares method, the TG signal can be fitted very well by eq 2 as shown in Figure 3c. Generally, a rather large ambiguity is expected for the curve fitting with four exponential functions. However, in this case, since the time constants of the three components are very different (e.g., $k_{\mathrm{a}} = 1.3\ \mu\mathrm{s}^{-1}$, $k_{\mathrm{b}} = 89\ \mathrm{ms}^{-1}$, and ($k_{\mathrm{c}} = 13\ \mathrm{ms}^{-1}$ and $k_{\mathrm{d}} = 11\ \mathrm{ms}^{-1}$) for the $q^2 = 19\ \mu\mathrm{m}^{-2}$ case) and the signs of $A_{\mathrm{c}}$ and $A_{\mathrm{d}}$ are opposite, they can be easily separated. Even though $k_{\mathrm{c}}$ and $k_{\mathrm{d}}$ are rather close, the determined values are stable for varying the initial values for the least-squares method. The errors of the time constants obtained by this fitting are less than 10%. The TG signals observed in other solvents can be fitted by the same manner.

**3.3. Origin of the TG Signals.** Any sinusoidally modulated refractive index or absorbance gives rise to the TG signal.[41] In this reaction system, no absorbance change was observed after the photoexcitation at the probe wavelength (633 nm) as reported previously[42,40] and as confirmed in the previous section. Hence, we consider only the refractive index change as the cause of the TG signal. Apparently, the fastest decaying component ($A_{\mathrm{a}}$) should be originated from the modulation of the temperature (thermal grating) caused by the nonradiative transitions of the photoexcited molecules (process a−c in Scheme 1). The decay of the thermal grating signal is determined by the heat conduction process. By solving the thermal diffusion equation with an appropriate initial condition, the time dependence of the temperature variation [$\Delta T(t,q)$] is expressed by[17]

$$\Delta T(t,q) = \Delta T(0,q) \exp(-D_{\mathrm{th}}q^2t) \quad (3)$$

where $\Delta T(0,q)$ is the initial temperature rise, $q$ is the magnitude of the wave vector of the grating ($q = 2\pi/\Lambda$, where $\Lambda$ is the fringe spacing), and $D_{\mathrm{th}}$ [$=\lambda_\omega/C_{\mathrm{p}}\ \rho$ ($\lambda_\omega$, thermal conductivity; $C_{\mathrm{p}}$, heat capacity; $\rho$, density)] is the thermal diffusion constant. Comparing eq 3 with eq 2, we obtain

$$k_{\mathrm{a}} = D_{\mathrm{th}}q^2 \quad (4)$$

$D_{\mathrm{th}}$ determined from the TG signals in these solvents are in excellent agreement with the literature values in ref 43. The other slower TG signal must represent the dynamics of chemical species.

As described in Introduction, the photochemical reaction of DBK has been extensively studied (Scheme 1). The photodissociation of DBK creates CO and BR. Therefore, three chemical species CO, BR, and DBK could contribute to the TG signal. On the basis of these considerations, the TG signal obtained from this reaction system should be described as

$$I_{\mathrm{TG}}(t)^{1/2} \propto \Delta n = \left(\frac{\mathrm{d}n}{\mathrm{d}T}\right)\Delta T(t) + \left(\frac{\mathrm{d}n}{\mathrm{d}C_{\mathrm{CO}}}\right)C_{\mathrm{CO}}(t) + \left(\frac{\mathrm{d}n}{\mathrm{d}C_{\mathrm{BR}}}\right)C_{\mathrm{BR}}(t) - \left(\frac{\mathrm{d}n}{\mathrm{d}C_{\mathrm{DBK}}}\right)C_{\mathrm{DBK}}(t) \quad (5)$$

where $\mathrm{d}n/\mathrm{d}C_{\mathrm{CO}}$, $\mathrm{d}n/\mathrm{d}C_{\mathrm{BR}}$, and $\mathrm{d}n/\mathrm{d}C_{\mathrm{DBK}}$ are the concentration dependences of the refractive index change by the presence of CO, BR, and DBK, respectively, and $C_{\mathrm{CO}}(t)$, $C_{\mathrm{BR}}(t)$, and $C_{\mathrm{DBK}}(t)$ are the time response functions of the peak-null difference of the concentrations of these species. Since DBK is depleted in the bright region of the interference pattern, the sign of the DBK term is minus. As the refractive index decreases with the increase of the temperature, the refractive index change of the thermal grating is negative ($\mathrm{d}n/\mathrm{d}T < 0$). Since all of the absorption bands of both BR and DBK are located in a wavelength region shorter than the probe wavelength, the presence of both BR and DBK creates a positive refractive index change at the probe wavelength ($\mathrm{d}n/\mathrm{d}C_{\mathrm{BR}}$, $\mathrm{d}n/\mathrm{d}C_{\mathrm{DBK}} > 0$). According to the Kramers−Kronig relation and the absorption bands of CO, the refractive index change by the presence of CO is expected to be positive, too. However, the creation of CO increases the volume of the system so that a part of the space which is filled by the solvent molecule is placed by CO. Since the polarizability of CO is smaller than that of the solvent, the refractive index change by the creation of CO becomes negative ($\mathrm{d}n/\mathrm{d}C_{\mathrm{CO}} < 0$) as previously shown by our group.[44] On the basis of these considerations, it is concluded that only the $\mathrm{d}n/\mathrm{d}C_{\mathrm{BR}}$ term in eq 5 gives a positive contribution, and the other contributions should be negative. Considering these signs in eq 5 and the decay rate constants of the TG signal which are determined mainly by the diffusion constants of the chemical species as discussed in a later section, the fitted components, $A_{\mathrm{a}}$, $A_{\mathrm{b}}$, $A_{\mathrm{c}}$ and $A_{\mathrm{d}}$ in eq 2 are attributed to $\mathrm{d}n/\mathrm{d}T$, $\mathrm{d}n/\mathrm{d}C_{\mathrm{CO}}$, $\mathrm{d}n/\mathrm{d}C_{\mathrm{BR}}$, and $\mathrm{d}n/\mathrm{d}C_{\mathrm{DBK}}$, respectively.

$C_{\mathrm{CO}}(t)$, $C_{\mathrm{BR}}(t)$, and $C_{\mathrm{DBK}}(t)$ are governed by the translational diffusion and subsequent chemical reactions of the transient species. The time dependence can be obtained from the following differential equations

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2} - f_i(x,t) \quad (6)$$

where $i$ represents the chemical species (CO, BR, or DBK). $C_i(x,t)$ and $f_i(x,t)$ are time- and space-dependent concentrations and reaction velocities of these species, respectively.

In the case of the stable molecules, DBK and CO, the time profiles of the concentration modulation are determined by only the diffusion process ($f_i(x,t) = 0$). The solution of this equation is given by

$$\hat{C}_i(q,t) = \hat{C}_i(q,0)\exp(-D_i q^2 t) \quad (7)$$

where $\hat{C}_i(q,t)$ is the $q$-component of the Fourier transform of $C_i(x,t)$. Therefore, by comparing eq 7 with eq 2, we obtain

$$k_{\mathrm{CO}} = D_{\mathrm{CO}} q^2$$

$$k_{\mathrm{DBK}} = D_{\mathrm{DBK}} q^2 \quad (8)$$

The $q^2$ dependences of $k_{\mathrm{CO}}$ and $k_{\mathrm{DBK}}$ are shown in Figure 4. The plots of CO and DBK show a good linear relationship with a negligibly small intercept with the ordinate axis, which agrees with the prediction of eq 8. $D_{\mathrm{CO}}$ and $D_{\mathrm{DBK}}$ in other solvents obtained from the slope of similar plots are listed in Table 1.

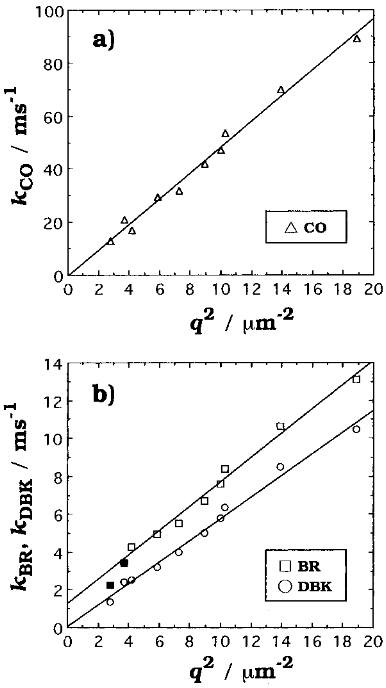


**Figure 4.** Plots of the decay rate constants ($k$) of (a) CO and (b) BR (squares), and DBK (circles) components of the TG signal against $q^2$.

**TABLE 1: Diffusion Constants ($D$) of CO, DBK, and BR and Rate Constants ($2k_2$) of the Self-Termination Reaction of BR Measured by the TG Method in Several Solutions at the Room Temperature**

| | $D/10^{-9}$ m$^2$ s$^{-1}$ | | | | $2k_2C(0)$/ ms$^{-1}$ |
|---|---|---|---|---|---|
| solvent | CO | DBK | BR | BR/DBK | |
| hexane | 8.8 ± 1.2 | 3.3 ± 0.3 | 4.1 ± 0.2 | 1.24 ± 0.17 | 6.7 ± 2.2 |
| cyclohexane | 5.5 ± 0.8 | 0.78 ± 0.1 | 0.95 ± 0.1 | 1.22 ± 0.15 | 2.5 ± 0.6 |
| ethanol | 5.7 ± 0.6 | 0.92 ± 0.08 | 1.1 ± 0.06 | 1.20 ± 0.08 | 1.9 ± 0.4 |
| 2-propanol | 4.9 ± 0.4 | 0.57 ± 0.04 | 0.64 ± 0.06 | 1.12 ± 0.09 | 1.3 ± 0.4 |

**3.4. Analysis of the TG Signals from BR.** The plot of $k_{\mathrm{BR}}$ vs $q^2$ also shows a linear relationship in a certain $q^2$ range, but it deviates from the liner relation in a small $q^2$ range. The nonlinear behavior suggests that the modulation of the BR component decays by not only the diffusion process but also subsequent chemical reactions. If this reaction proceeds with the first-order reaction [$f(t) = k_1 C(x,t)$], the solution of eq 6 is given by

$$\hat{C}_{\mathrm{BR}}(q,t) = \hat{C}_{\mathrm{BR}}(q,0)\exp[(-D_{\mathrm{BR}} q^2 t + k_1)t] \quad (9)$$

The decay rate constants ($k$) of the TG signal in eq 2 is given by

$$k_{\mathrm{BR}} = D_{\mathrm{BR}} q^2 + k_1 \quad (10)$$

Therefore, the intercept of the $k$ vs $q^2$ plot gives $k_1$ and the slope gives $D_{\mathrm{BR}}$. However, previous researches on the BR reaction indicate that the main reaction of BR is the self-termination reaction and we also confirm it as described in section 3.1. In this case, eq 6 should be described with $f(x,t) = 2k_2 C(x,t)^2$ and the differential equation can no longer be solved analytically, but numerical analysis is required. Here, we first consider an analytical treatment with a short-time approximation and then the result is compared with the numerical result.

If we ignore the diffusion process in eq 6, the time dependence of $C(t)$ is described as

$$C(t) = \frac{C(0)}{1 + 2k_2C(0)t} \tag{11}$$

During a short period after the excitation, in which a condition of

$$1 + 2k_2C(0)t \gg \frac{(2k_2C(0)t)^2}{2!} + \cdots + \frac{(2k_2C(0)t)^n}{n!} + \cdots \tag{12}$$

is satisfied, the second-order reaction can be approximated by the first-order reaction with a rate constant of $2k_2C(0)$. Under this approximation, the solution of eq 6 is given by

$$\hat{C}_{BR}(q,t) = \hat{C}_{BR}(q,0)\exp\{[-D_{BR}q^2t + 2k_2C(0)]t\} \tag{13}$$

and the decay rate constant ($k$) of the square root of the TG signals is given by

$$k_{BR} = D_{BR}q^2 + 2k_2C(0) \tag{14}$$

Therefore, as long as the short-time approximation is correct, the TG signal can be analyzed with an exponential function and the intercept and the slope of the $k$ vs $q^2$ plot give $2k_2C(0)$ and $D_{BR}$, respectively.

To obtain a reliable fitting by eq 13, we should make the fitting range for the least-squares method as wide as possible. Normally, the data up to a time when the square root of the TG signal intensity ($I_{TG}^{1/2}$) becomes 1/20 of the initial intensity of the species grating signal is used. For satisfying the short-time approximation during this fitting range, we should limit the TG measurement in a rather large $q^2$ range. Neglecting the subsequent reaction, the TG signal decays to the ~1/20 intensity at around

$$Dq^2t \sim 3 \tag{15}$$

by the diffusion process. Therefore, combining with eq 14, we can conclude that the TG signal measured in a range of

$$Dq^2/k_2C(0) > 4 \tag{16}$$

can be used for determining $D$ from the $k$ vs $q^2$ plot. In other words, the TG signal measured in this range can be analyzed as if the subsequent reaction is the first order decay with a rate constant of $2k_2C(0)$. We solve the second-order reaction-diffusion coupled equation (eq 6) with $f(x,t) = 2k_2C(x,t)^2$) numerically to examine this applicable range (eq 16). Figure 5 shows $C(q,t)/C(q,0)$ calculated numerically by eq 6 (solid lines) and calculated by eq 13 (dotted lines) for $Dq^2/k_2C(0) =$ 1, 2, 4, and 6. Evidently, from the figure, when eq 16 is satisfied, the time profile from eq 6 is sufficiently close to that from eq 13 within the experimental error of this work (±10%).

In this way, we judged that the first and second points of the plot (Figure 4) are out of the range of $q^2 > 4k_2C(0)/D_{BR}$. Therefore, we fit the other data by the least-squares method without these two points. The results of this fitting give $D_{BR} = 0.64$ m$^2$ s$^{-1}$, $2k_2C(0) = 1.31$ m s$^{-1}$ in 2-propanol. The values of $D_{BR}$ and $2k_2C(0)$ in various solvents determined by this method are listed in Table 1.

Next, the consistency of the results from the TG experiment and from the TA experiment is examined. The plot of $2k_2C(0)$ against the laser power from the transient absorption (Figure 2b) shows $2k_2C(0) = 1.6$ m s$^{-1}$ at 0.3 mJ/cm$^2$ (a typical laser power for the TG measurement). The reaction rate obtained from the plot of the decay rate vs $q^2$ (1.3 ms$^{-1}$) is close to $2k_2C(0)$ from the transient absorption measurement. Therefore, we believe that the above procedure for determining $D_{BR}$ from the $k$ vs $q^2$ plot is adequate.

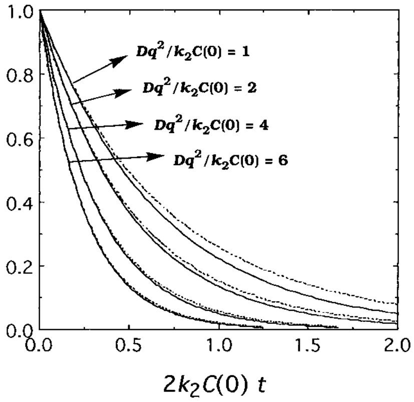


**Figure 5.** Comparison of the time profiles of the concentrations which decay by the second-order reaction−diffusion coupled equation calculated from eq 6 with $f(x,t) = 2k_2C(x,t)^2$ (solid lines) and from eq 13 (dotted lines) with $Dq^2/k_2C(0) = 1$, 2, 4, and 6.

**TABLE 2: Diffusion Constants (*D*) of the Radicals and Parent Molecules Measured by the TG Method at ~20 °C and *D* of the Parent Molecules Measured by the PGSE Method at ~30 °C**

| | | $D/10^{-9}$ m$^2$ s$^{-1}$ | | |
|---|---|---|---|---|
| | | TG | | PGSE |
| solute | solvent | radical | parent | parent |
| dibenzyl ketone | 2-propanol | 0.64[a] | 0.57[a] | 0.57 |
| | cyclohexane | 0.95[a] | 0.78[a] | 0.73 |
| pyrazine | 2-propanol | 0.38[b] | 1.2[b] | 1.5 |
| | ethanol | 0.74[c] | 1.6[c] | 1.6 |
| benzoquinone | 2-propanol | 0.36[c] | 0.98[c] | 1.1 |
| benzophenone | 2-propanol | 0.33[d] | 0.68[d] | 0.65 |

[a] This work. [b] References 17, 18 and 59. [c] References 20 and 59. [d] Reference 19.

We further confirm the adequacy of our TG analysis by independent measurement of $D_{DBK}$. Though $D$ of the transient species BR cannot be measured by other traditional methods, $D$ of the stable parent molecule DBK can be measured besides the TG method. We use the PGSE method for $D_{DBK}$. The values of $D_{DBK}$ determined by the PGSE method at 30 °C are shown in Table 2. This table also shows similar comparisons of $D$ of benzophenone, pyrazine, and benzoquinone which have been reported by the TG method previously. All of the $D$ obtained by the PGSE method are very close to the values determined by the TG method. $D_{CO}$ obtained by this work agrees with $D$ reported in ref 45 fairly well. This fact again supports the assignment of the signal.

At the laser power for the TG experiment (0.3 mJ/cm$^2$), $\Delta OD = C(0)\cdot\epsilon_{Max}$ is 0.006 and $k_2/\epsilon_{Max} = 1.19 \times 10^5$ M$^{-1}$ s$^{-1}$. This value is used to estimate the value of $k_2$ and $C(0)$ in a later section. The initial concentration of BR ($C(0)$) at the condition of the TG measurement (~0.3 mJ/cm$^2$) is estimated to be $5.0 \times 10^{-7}$ to $5.5 \times 10^{-6}$ M from the reported $\epsilon_{Max} = 1100-12\,000$ cm$^{-1}$ M$^{-1}$ as described in the next section. This value of $C(0)$ is consistent with the estimated value (~$10^{-6}$ M) from the excitation laser power (~0.3 mJ/cm$^2$), the extinction coefficient of DBK at 308 nm (~200 cm$^{-1}$ M$^{-1}$),[42] and the quantum yield of photodissociation of DBK (~0.7).[27]

## 4. Discussion

**4.1. Estimation of Rate Constant $2k_2$ of Self-Termination Reaction.** We plot the determined $k_2/\epsilon_{Max}$ in various solvents against the inverse of the viscosities ($1/\eta$) in Figure 6. The

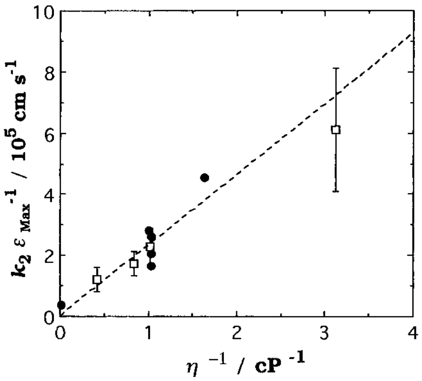


**Figure 6.** Plot of $k_2/\epsilon_{\mathrm{Max}}$ vs $1/\eta$. The dotted line is guide for eyes. Data from previous studies are shown by the closed circles and those determined from the TG method are shown by the open squares.

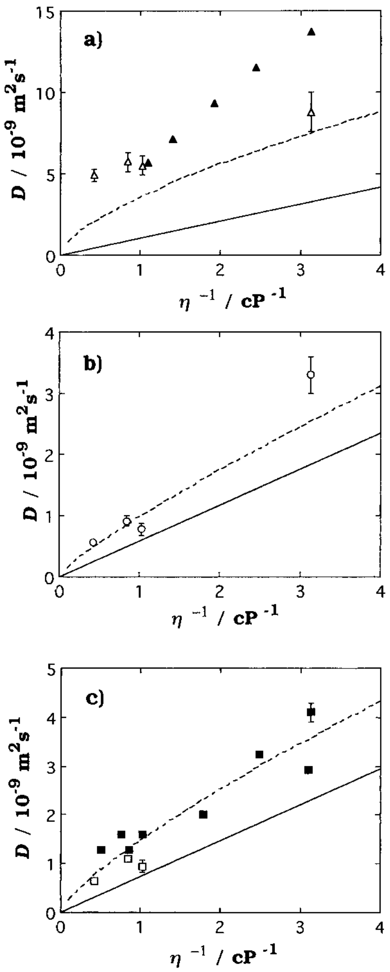


**Figure 7.** Viscosity dependence of diffusion constants of (a) CO, (b) DBK, and (c) BR from the TG measurement (this work) (open symbols) and from previous work (closed symbols). Solid line is calculated from the Stokes–Einstein equation (eq 1) and broken line is calculated from eq 17.

linear relationship between $k_2/\epsilon_{\mathrm{Max}}$ and $1/\eta$ supports the previously reported conclusion that the self-termination reaction of BR is the diffusion-controlled process. Next, we compare these $k_2/\epsilon_{\mathrm{Max}}$ from the TG measurement with those reported previously from the transient absorption measurements. The values of $k_2$ and $\epsilon_{\mathrm{Max}}$ have been reported by many groups: $\epsilon_{\mathrm{Max}} = 1100$ cm$^{-1}$ M$^{-1}$ and $k_2 = 1.8 \times 10^7$ M$^{-1}$ s$^{-1}$ by McClarthy and MacLachlan reported in a mixed solvent of ethanol and glycol,[29] $k_2 = 2.3 \times 10^9$ M$^{-1}$ s$^{-1}$ and $\epsilon_{\mathrm{Max}} = 12\,000$ cm$^{-1}$ M$^{-1}$ by Hagemann and Schwartz in cyclohexane,[30] $\epsilon_{\mathrm{Max}} = 1500$ cm$^{-1}$ M$^{-1}$, $k_2 = 6.8 \times 10^9$ M$^{-1}$ s$^{-1}$ by Meiggs et al. in methanol,[31] $\epsilon_{\mathrm{Max}} = 8800$ cm$^{-1}$ M$^{-1}$, $k_2 = 1.8 \times 10^9$ M$^{-1}$ s$^{-1}$,[32a] or $k_2 = 2.3 \times 10^9$ M$^{-1}$ s$^{-1}$ [32b] by Fischer and co-workers in cyclohexane, $\epsilon_{\mathrm{Max}} = 5500$ cm$^{-1}$ M$^{-1}$ and $k_2 = 1.55 \times 10^9$ M$^{-1}$ s$^{-1}$ in water by Christensen et al.,[33] $k_2 = 3.5 \times 10^9$ M$^{-1}$ s$^{-1}$ in benzene by Lauter and Dreeskamp,[34] and $k_2 = 4 \times 10^9$ M$^{-1}$ s$^{-1}$ by Burkhart.[35] As shown above, the reported $\epsilon_{\mathrm{Max}}$ and $k_2$ are so much scattered. Even if we plot these reported $k_2$ against $1/\eta$, we cannot see any correlation between $k_2$ and $1/\eta$. However, if we plot $k_2/\epsilon_{\mathrm{Max}}$ against $1/\eta$ (Figure 6), it is found that both quantities have a linear relationship (broken line in Figure 6). The probable cause of the scattered $k_2$ in the literature comes from the uncertainty of $\epsilon_{\mathrm{Max}}$ estimated by these groups. The $k_2/\epsilon_{\mathrm{Max}}$ values obtained in this work are plotted together in Figure 6. We find that our $k_2/\epsilon_{\mathrm{Max}}$ determined from the TG experiment are consistent with these literatural values.

**4.2. *D* of the Chemical Species.** In Figure 7, $D$ is plotted against $1/\eta$. $D$ of the each species (DBK, CO, and BR) decrease with decreasing $1/\eta$ regardless of the solvent properties (polarity, dipole moment, protic character etc.). The calculated $D$ from the SE equation ($D_{\mathrm{SE}}$) are shown in Figure 7 (full lines). It is known that $D_{\mathrm{SE}}$ underestimates $D$ in many cases and actually, the experimental values of $D$ in Figure 7a,c are larger than $D_{\mathrm{SE}}$. In a previous study,[21] we found that $D$ of stable molecules can be reproduced by an empirical equation derived by Evans et al. ($D_{\mathrm{EV}}$).[7]

$$D_{\mathrm{EV}} = \frac{T\exp(a/r_{\mathrm{A}} + b)}{\eta^{c/r_{\mathrm{A}}+d}} \tag{17}$$

where $a$, $b$, $c$, and $d$ are constants, which are determined by Evans et al. as $a = 5.9734$ Å, $b = -7.3401$, $c = -0.863\,65$ Å, and $d = 1.0741$. The broken lines in Figure 7 indicate the viscosity dependence of $D_{\mathrm{EV}}$. We found that $D_{\mathrm{EV}}$ is closer to $D$ for all species.

Previously, we have reported that the $D$ of various transient radicals created by the photoinduced hydrogen abstraction of ketones, quinones, and N-hetero aromatic molecules show anomalously slow diffusions.[17–21] $D$ of such radicals are close to $D_{\mathrm{SE}}$ rather than $D_{\mathrm{EV}}$.[19,20] However, Figure 7c shows that $D_{\mathrm{BR}}$ is larger than $D_{\mathrm{SE}}$ and close to $D_{\mathrm{EV}}$ similar to $D_{\mathrm{BR}}$ and $D_{\mathrm{DBK}}$. This fact suggests that the diffusion process of BR is analogous to those of stable molecules. Indeed, $D$ of BR are close to the literature values of $D$ of toluene (closed squares of Figure 7c),[45] which is a stable molecule with nearly the same size and shape as BR.

Furthermore, we compare $D_{\mathrm{DBK}}$ with $D_{\mathrm{BR}}$. According to the SE relationship, $D$ should be inversely proportional to the radii of the solute molecules. As the molecular volume of BR is close to half of that of DBK, the ratio $D_{\mathrm{BR}}/D_{\mathrm{DBK}}$ should be nearly equal to $2^{1/3} = 1.25$. Actually, these ratios obtained by experimental $D$ are very close to 1.25 in all of the solvents (Table 1). Therefore, the diffusion process of BR created by the photodissociation of DBK is not like those of the transient radical we have previously investigated, but it is similar to that of a stable molecule. A possible origin of the difference between the previous radicals and BR is discussed in the next section.

$D$ of short-lived radicals have been scarcely reported because of the experimental difficulties. Exceptionally, Burkhat et al. measured $D$ of some alkyl radicals and BR created by photodissociation of alkanes and toluene, respectively, in cyclohexane by using the photochemical space intermittency (PCSI) method.[15] For the PCSI measurement, the sample solutions are illuminated by a "leopard" light–dark pattern of circular spot and the steady-state concentrations of radicals are detected as a function of

**TABLE 3: Diffusion Constants by the TG Method and Dipole Moments and Polarizabilities Calculated by the Semiempirical MO Method (MNDO) of BR, the Radicals Produced by Hydrogen Abstraction, and Each Parent Molecule (Scheme 2)**

| | | diffusion const/$10^{-9}$ m$^2$ s$^{-1}$ | | dipole moment/D | | polarizability/Å$^3$ | |
|---|---|---|---|---|---|---|---|
| | | parent | radical | parent | radical | parent | radical |
| benzyl | in ethanol | | 1.1[a] | 0.02[d] | 0.02 | 8.62[d] | 7.99 |
| | in 2-propanol | | 0.64[a] | | | | |
| α-OH-benzyl | in ethanol | 1.5[b] | 0.66[b] | 2.85 | 1.06 | 9.13 | 8.78 |
| | in 2-propanol | 0.99[b] | 0.37[b] | | | | |
| benzoquinone | in ethanol | 1.6[b] | 0.57[b] | 0.00 | 3.10 | 8.24 | 8.01 |
| pyrazine | in ethanol | 1.6[b] | 0.74[b] | 0.01 | 2.97 | 6.30 | 6.21 |
| benzophenone | in ethanol | 1.0[c] | 0.55[c] | 2.52 | 1.36 | 17.13 | 16.39 |
| acetophenone | in ethanol | 1.3[b] | 0.58[b] | 2.72 | 1.55 | 10.31 | 9.99 |

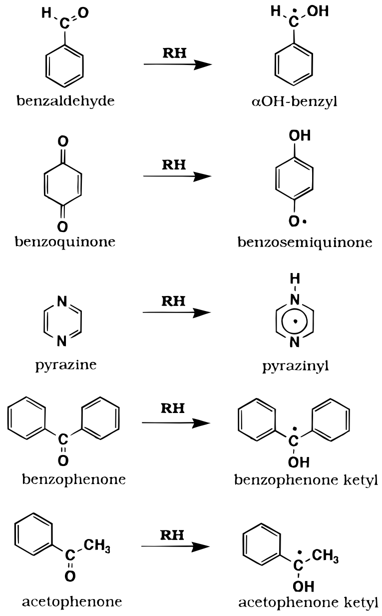
[a] This work. [b] References 20 and 59. [c] Reference 19. [d] Toluene is used as the parent molecule of BR.

the light intensity as well as of the total area illuminated. To estimate $D$ from the experimental data, one must know independently the quantum yield for the production of the radicals, the rate of absorption of the light, and the rate constant of the recombination of the radicals. Moreover, this method is based on some assumptions such as the reaction process of the radical is diffusion controlled and follow the Smoluchowski equation, etc. Considering the many assumptions and many ambiguous parameters used in the method, it is rather surprising that their value of $D_{BR}$ in cyclohexane ($D = 1.1 \times 10^{-9}$ m$^2$ s$^{-1}$) is close to our value ($D = 0.95 \times 10^{-9}$ m$^2$ s$^{-1}$).

**4.3. Properties of Benzyl Radical.** In a series of previous papers, we have reported the anomalously slow diffusion of many transient radicals created by the hydrogen abstraction reaction compared with the stable parent molecules with similar sizes and shapes in various solvents, while, in this paper, we found that $D$ of BR, which is also a transient radical, is similar to that of the stable molecule with a similar size and a shape such as toluene. The cause of the different diffusion behaviors between BR and the other radicals produced by hydrogen abstraction (RH$^\bullet$) is important to study because it will provide a clue to understand the diffusion process of the radicals in solution. There are three factors which might cause the difference: (a) distribution of the unpaired electron in the molecule, (b) hydrogen-bonding effect, and (c) electrostatic effect.

(a) Burkhart et al. have also found that some alkyl radicals diffuse slower than the parent molecules, while BR diffuses with a similar velocity as toluene. They attributed the species-dependent diffusion to the degree of the delocalization of the unpaired electron in the molecule. Since the unpaired electron of BR is delocalized to the phenyl ring by the $\pi$-electron resonance, the spin density on each atom of BR is reduced and the intermolecular interaction between the unpaired electron and other molecules could be weak. On the other hand, the unpaired electron of an alkyl radical is localized on several carbon atoms and the intermolecular interaction which comes from the unpaired electron could be enhanced. In order to examine this idea, we tried to see a correlation between the spin density distribution and $D$ of the transient radicals we have studied so far by the TG method. α-Hydroxybenzyl radical (BR-OH) is taken as example for the comparison with BR. $D$ of these species are listed in Table 3. $D$ of BR-OH in ethanol and 2-propanol are about 2 times smaller than the $D$ of BR. Furthermore, $D$ of BR-OH is smaller than the parent molecule (benzaldehyde), while $D$ of BR is similar to toluene. The spin density on each atom of BR was determined from an EPR measurement[46] and also from an MO calculation.[47] About 50% of the unpaired electron is localized on the α-carbon and the other is delocalized on the ortho and meta carbons in the phenyl ring. The hyperfine splitting of BR-OH[48] was also reported. More directly Ficher and co-workers compared the spin density distribution of BR with that of BR-OH.[49] They found that the spin density on the O atom of BR-OH is less than a few % and the spin density distribution of BR-OH is nearly the same as that of BR. Therefore, contrary to the very different diffusion constant, the spin density distribution of BR and BR-OH is very similar. We should conclude that the slow diffusion of BR-OH than BR cannot be attributed to the property of the unpaired electron distribution of the molecule.

**SCHEME 2**



(b) Next, we consider the effect of the hydrogen bonding. Recently, Tominaga et al. reported that the molecules which have $-$OH or $-$NH$_2$ substituent diffuse anomalously slowly in protic solvents due to the strong intermolecular interactions between the substituent and the solvents.[50] All of the RH$^\bullet$ we investigated have $-$OH or $-$NH substituent while BR does not. The hydrogen bonding could be the main origin of the slow diffusion of RH$^\bullet$. However, there is some evidence to exclude the participation of the hydrogen bonding in the radical diffusion as follows: (1) If the hydrogen bonding is the main cause of the slow diffusion of the radicals, the effect should be pronounced in a solvent which can make the hydrogen bond easily. In our previous studies, however, we found that the radicals diffuse slower than the parent molecules not only in protic solvents but also in nonpolar solvents such as benzene or cyclohexane.[19] (2) The $D$ of BPK is close to that of diphenyl methyl radical, which does not have an $-$OH group to form a hydrogen bond.[51] (3) The temperature dependence of $D$ of the radicals can be expressed by the Arrhenius relation with a single activation energy and it is close to that of the viscosity of the solvent.[21] The similarity indicates that the activation energy of the hydrogen bond is not involved in the diffusion process. (4) Our recent investigation on the substituent effect of several radicals indicates that $>\dot{C}{-}OH$ and $>\dot{N}H$ groups can make only a weak hydrogen bonding with solvents.[52] We conclude that the interaction of the hydrogen bonding cannot be the origin of the slow diffusion of the radicals.

(c) Finally, we consider the interaction of the electrostatic force. It is well established that the molecules with a large dipole, or a large polarizability, diffuse slowly by the electrostatic interaction with solvent molecules. This phenomenon has been explained by dielectric friction. This dielectric friction depends on the electrostatic property of the solvent and has been believed to be effective only in a polar solvent.[10−12] However, Maroncelli et al. proposed that even in a nonpolar solvent (no dipole moment), the dielectric friction can occur by the interaction with the quadrupole moment of the solvent from the dynamic Stokes shift measurement.[53] Recently, Okazaki et al. reported that *D* of the merocyanine form of benzospiropyran, which has a large dipole moment (about 12 D) are ∼2 times smaller than that of the spiro form in cyclohexane and ethanol,[54] although cyclohexane has no dipole and no quadrupole. We considered that the origin of a solute−nonpolar solvent electrostatic interaction could be due to the interaction between the solute and the intramolecular partial dipole of solvent (for example, C−H). As both BR and $RH^{\bullet}$ radicals have no charge, possible electrostatic forces of the radicals are due to dipole interaction and/or dispersion force. If the charge distributions of the radicals are quite different from those of the parent molecules and the radicals have large dipole moments and/or polarizabilities, the diffusion could be slower by the enhanced dielectric friction in polar and nonpolar solvents. We calculated that dipole moments and polarizabilities of BR, $RH^{\bullet}$, and parent molecules by using a semiempirical molecular orbital (MO) calculation with modified neglect of diatomic overlap (MNDO) method.[55] The results are listed in Table 3 (toluene is used as the parent molecule of BR). Actually, the dipole moments of benzoquinone and pyrazine are increased from 0 to 2.5−3 D by converting to the radicals. On the other hand, both BR and toluene have no dipole moment. The dipole moments of ketones decrease from 2.5−3 D (for parent molecules) to −1.5 D (for the radicals). Apparently, the slow diffusion of such radicals cannot be explained by the dipole interaction. The polarizabilities of the radicals and their parent molecules are similar. The charge distribution of both radicals and the parent molecules are similar, too.

We could not find any significant differences which can affect the molecular diffusion by the simple MO calculations. However, recently, Morita and Kato revealed a very prominent difference in the electric character between a transient radical (pyrazinyl radical) and the closed-shell molecules (pyrazine and benzene) by the ab initio MO method.[56] They calculated the charge sensitivity for each atom of the molecule by an external electric field and found that the intramolecular local polarizability of the pyrazinyl radical is much larger than that of pyrazine or benzene despite the fact that the usual polarizability under a uniform electronic field is very similar for these molecules. The normal-mode analysis of the local polarizability indicates that the charge sensitivity of the pyrazinyl radical is due to the $\sigma-\pi$ mixing that is caused by the deformation of the $\pi$ electron orbital. A similar enhanced local polarizability was observed for BPK but not for BR.[57] This weak local polarizability of BR comes from the stable $\pi$ electron resonance structure. Although the dynamic property such as the translational diffusion should be calculated by another method, e.g., MD simulation with taking into account this character, it is plausible that such an enhanced polarizability increases the friction during the molecular movement and slows down the diffusion process.

In a series of our studies, we have reported slow diffusion for many transient radicals in many solvents even in supercritical fluids.[58] Among the radicals so far studied, BR is only one radical that has *D* similar to that of the closed-shell molecule (toluene).

## 5. Conclusion

Diffusion processes of the benzyl radical (BR) created by the photodissociation from dibenzyl ketone (DBK) were studied by the transient grating (TG) method in several organic solvents (hexane, cyclohexane, ethanol, and 2-propanol). The observed TG signals can be well fitted by a sum of four exponential functions and they are attributed to the thermal grating signal and the species gratings due to CO, BR, and DBK. From the slope of the decay rate constants against $q^2$ plots, the thermal diffusion constants, and the diffusion constants (*D*) of CO and DBK are determined. The plot of the BR component has a finite intercept with the ordinate, which indicates that the subsequent chemical reaction cannot be neglected. By applying a short period approximation, we found that the slope and the intercept represent *D* of BR and the self-termination reaction rate constants ($2k_2$), respectively. *D* of CO, DBK, and BR are larger than those calculated by using the SE equation ($D_{SE}$) and closer to those calculated by an equation proposed by Evans et al. ($D_{EV}$). In all the solvents we examined, the ratios of *D* of BR to those of DBK are close to 1.25, which is expected from the difference of the molecular volumes of BR and DBK. Furthermore, *D* of BR is close to that of toluene. This result is very different from what is expected from the previous studies of the transient radicals created by the hydrogen abstraction reaction. We compare the property of BR with those of the radicals produced by hydrogen abstraction ($RH^{\bullet}$) to find a possible origin of the different diffusion process of BR and others. The spin densities, dipole moments, and the polarizabilities cannot explain the difference satisfactorily. Recently, Morita and Kato showed an enhancement of the intramolecular charge sensitivity to local electric field for $RH^{\bullet}$ based on the ab initio molecular orbital theory. This effect is not observed for BR because the $\sigma-\pi$ mixing, which is the origin of the particular sensitivity enhancement, is less effective due to the stability of $\pi$-electron orbital of BR. The intermolecular interaction between the radicals and solvents could be the origin of the anomalously slow diffusion process.

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