

Transient Radical Diffusion in Photoinduced Hydrogen Abstraction Reactions of Benzophenone Probed by the Transient Grating Method

Masahide Terazima,* Koichi Okamoto, and Noboru Hirota*

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, 606, Japan

Received: July 1, 1993*

The transient grating method is used for investigating the diffusion dynamics of the transient radicals created by photoinduced hydrogen abstraction reactions of benzophenone (BP) in various solvents, acetone in 2-propanol, and acetaldehyde in ethanol. The diffusion coefficients (D) of the BP ketyl radical and BP are obtained simultaneously. In acetone/2-propanol and acetaldehyde/ethanol systems, only the signals due to intermediate radicals are observed. The D values of the transient radicals are two to three times smaller than those of BP. The measured D s of the radicals usually show good agreement with the theoretically calculated values on the basis of the Stokes-Einstein (SE) relationship, whereas the SE relation underestimates D for stable parent molecules and the values are reproduced by the modified SE equation by Spornol and Wirtz. The smaller D values suggest the existence of a specific radical-molecule interaction.

1. Introduction

Diffusion plays an essential role in chemical reactions. Movements of radicals created in the reaction process determine the fate of the radical (rate and efficiency of the reaction) as well as many physical properties of the radical and products (e.g., CIDEP, CIDNP, magnetic field effect).¹⁻³

However, compared with the extensive studies made on the diffusion processes of neutral stable molecules, radical diffusion processes in reaction systems have not been well studied. The main reason is the experimental difficulty in tracing the movements of radicals in space, especially of transient radicals. For example, Noyes has developed the photochemical space intermittency (PSI) method⁴ to measure D (diffusion coefficient) of unstable radicals,⁴⁻⁷ but it requires various parameters on the reactions and the experimental conditions, most of which are difficult to be obtained accurately.⁴ As another example, the decay of the transient absorption signals is sometimes analyzed for studying the fast dynamics of radicals.⁸ This technique, however, also requires several parameters that could contain certain unambiguities.

Recently we have demonstrated that the transient grating (TG) method with a pulsed laser can probe the movement of transient radicals conveniently with high accuracy.⁹ The TG method has several merits over other methods in measuring D of transient radicals. First, since the TG signal decays with smearing out the fringes created by two coherent light beams, it takes only a short time to measure D compared with the conventional methods, which monitor the molecular movement in a macroscopic distance. This merit allows us to study a diffusion process of a short-lived species. Second, this method is so sensitive that it can probe a trace amount of the species of interest. It also makes this method suitable to study the transient radicals, which could be created only in a limited amount even by a strong pulsed laser. Third, even though it has good time resolution, it still probes the diffusion process at several to hundreds of microseconds after the creation of the radicals. Thus we can safely neglect the effect of the initial conditions of the radicals such as the spin multiplicity of the precursor or a specific short-range radical-radical interaction such as the "cage effect". In other words, we can study the diffusion processes of radicals surrounded by solvent molecules. (Of course this could be one of the demerits, if we want to study the radical dynamics just after the reaction.) Finally, the TG method can trace the diffusion of not only the radicals but also

SCHEME I



their parent molecules. Therefore we can compare D s of radicals and of parent molecules under exactly the same conditions.

In the previous work, the TG method has been applied to investigate the diffusion of the intermediate radicals produced by a hydrogen abstraction reaction of pyrazine in 2-propanol (Scheme I).⁹ Surprisingly, we found that the pyrazinyl radical has D four times smaller than that of the parent molecule, pyrazine, although the difference in the molecular volume between pyrazine and pyrazinyl radical is just one hydrogen atom. We have interpreted the large difference in terms of a specific radical-solvent interaction in solution. In order to establish the generality of this method and to seek the origin of the radical-solvent interaction, we need more data on the D s of other transient radicals in various solvents.

In this work, we show that the TG method can be applicable to study other hydrogen abstraction reactions by taking as an example benzophenone (BP) under various conditions. BP is a prototype of carbonyl compounds and its photophysical and photochemical properties have been investigated extensively by many means as described in a later section. The diffusional motion of the intermediate radical in the reaction is important to elucidate the mechanism of the reaction. We can successfully detect the diffusion processes of the intermediate radicals and the parent molecules as the TG signals. We find that D s of the transient radicals are smaller than that of BP but agree well with the calculated values from the Stokes-Einstein relation. We investigate the solvent dependence of D s of the transient radicals to obtain information about the radical-solvent interaction.

2. Experimental Section

Experimental arrangement for the TG method has been published elsewhere.¹⁰ Briefly, excitation laser light at 308 nm was generated by an excimer laser (Lumonics Hyper-400) with XeCl operation. The laser beam was shaped to have a nearly Gaussian intensity profile with lenses and a spatial filter. Since the coherent time of the excimer laser is much shorter than that of the pulse width, the two beams should be carefully adjusted in time. The laser beam was split into two equal intensity beams with a beam splitter and crossed inside a 10-mm-path quartz

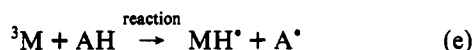
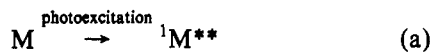
* Abstract published in *Advance ACS Abstracts*, November 1, 1993.

sample cell at an ambient temperature (23 °C). First, the fringe spacing Λ was roughly estimated from the crossing angle θ and then Λ was calibrated from the decay of the thermal grating signal by using the thermal diffusion constant of benzene ($10.1 \times 10^{-8} \text{ m}^2/\text{s}$).¹¹ The repetition rate of the excitation pulse was typically $\sim 3 \text{ Hz}$ to prevent heating as well as building up of photochemical products. A He-Ne laser was brought into the crossing region at the Bragg angle for a probe beam. The diffracted signal was detected by a photomultiplier (Hamamatsu R-928) and averaged by a digital oscilloscope (Tektronix 2430A) and a microcomputer.

Spectrograde solvents (2-propanol, ethanol, benzene, hexane, cyclohexane, methylcyclohexane, acetonitrile) were used as received. Benzophenone (Wako Chemical Co.) was purified by vacuum sublimation. Sample solutions were deoxygenated by the nitrogen bubbling method just before the measurement. Fresh samples were used after every ~ 1000 shot irradiations.

3. Method

The principle for the measurement of D of the transient radicals was reported previously.⁹ Here only the essential points needed for analyzing the TG signal are described. The transient grating is created as a sinusoidal bright-dark pattern in the sample solution by crossing two coherent beams with an angle θ .¹² At the bright position of the fringes, a reactant (M) is excited to the excited singlet state ($^1M^{**}$). In carbonyl compounds like BP, the intersystem crossing (isc) from the S_1 state to the lowest excited triplet (T_1) state (3M) takes place very efficiently and 3M abstracts a hydrogen atom from another reactant (AH).



As a result, new species MH^* and A^* are created and reactants M and AH are consumed in the bright region. Since the optical properties of MH^* and A^* are different from those of M and AH, the photochemical reaction induces gratings: the phase grating (modulation of the refractive index) and/or the amplitude grating (modulation of the extinction coefficient). Also the radiationless transitions in processes (b), (c), and (d) produce the thermal grating, which is composed of only a change of the refractive index δn_{th} . Since the refractive index decreases with increasing temperature, δn_{th} should be negative. These gratings diffract the probe beam in the direction that satisfies the Bragg condition.

The time dependence of the TG signal ($I_{TG}(t)$) due to these gratings is given by⁹

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

where α , β , A , B , and C are constants that depend on the laser intensities of the probe and excitation beams as well as the experimental configuration, δn_{th}^0 is the refractive index change due to the creation of the species $i = A^*$ and MH^* ($j = AH$ and M), $\delta k_{i(j)}^0$ is the extinction coefficient change due to the creation of the i (j) species, D_{th} is the thermal diffusion coefficient in the solution, $D_{i(j)}$ is the mass diffusion coefficient of species i (j), q is the magnitude of the wave vector of the grating ($q = 2\pi/\Lambda$), and k_i is the first-order disappearance rate constant of the

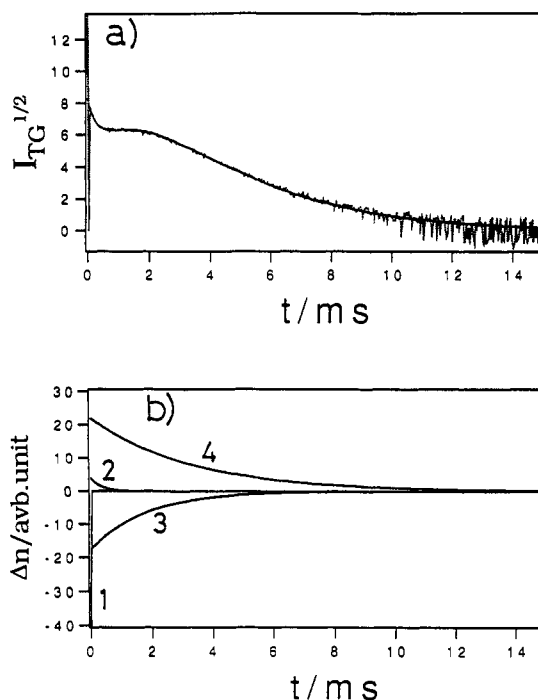


Figure 1. (a) Typical temporal profile of the TG signal ($I_{TG}^{1/2}$) after the photoexcitation of benzophenone in 2-propanol under the nitrogen-bubbled condition (dotted line) and the best-fitted curve by eq 2 after the complete decay of the thermal grating signal (solid line). (b) Phase grating contributions to the signal in (a) as given by the fitting procedure described in the text. The assignments of these component are (1) the thermal grating, (2) unidentified fast diffusing species, (3) benzophenone, and (4) benzophenone ketyl radical.

intermediate radicals i by subsequent reactions. It is important to note that the contributions of the reactant (j) and the radicals (i) have opposite signs. This gives a starting clue to determine the diffusing species from the temporal profile of the TG signal.

In the derivation of eq 1, we have made several assumptions on the TG experiment (the thick grating and the weak signal condition etc.) as well as on the reaction system (the dynamics of the molecules in solution is expressed by Fick's law and the disappearance of the radicals follows the first-order kinetics). When the subsequent reaction is not described by the first-order kinetics (which is the case in many reactions), the above equation should be modified.¹³ However, since the intermediate radicals we examine in this work live long enough compared with the observation times as shown later, eq 1 is applicable to describe the time dependence of the TG signal. To distinguish the intrinsic lifetime of the radicals from the smearing out time among the fringes, the time dependence of the TG signal is measured as a function of q^2 .

4. Results and Analysis

4.1. Time Dependence of the TG Signal. Benzophenone in Alcohols. A typical TG signal observed after the photoexcitation of BP in 2-propanol (2-PrOH) at room temperature is shown in Figure 1a. The TG signal due to the thermal grating, which originated from the vibrational relaxation (b) and the isc process (c), is first dominant. The signal decays due to the thermal diffusion process among the fringes with a rate constant determined by D_{th} and the fringe spacing. Reaching the baseline once, it rises rapidly to a certain intensity and then decays. The temporal profile of the decay is not simple; the slow signal first decays and then slightly rises and finally decays to the baseline. Since these slow processes have time constants almost 2–3 orders of magnitude slower than that of the thermal grating, the time developments of these components must reflect the molecular diffusion dynamics in solution. It is important to note that the

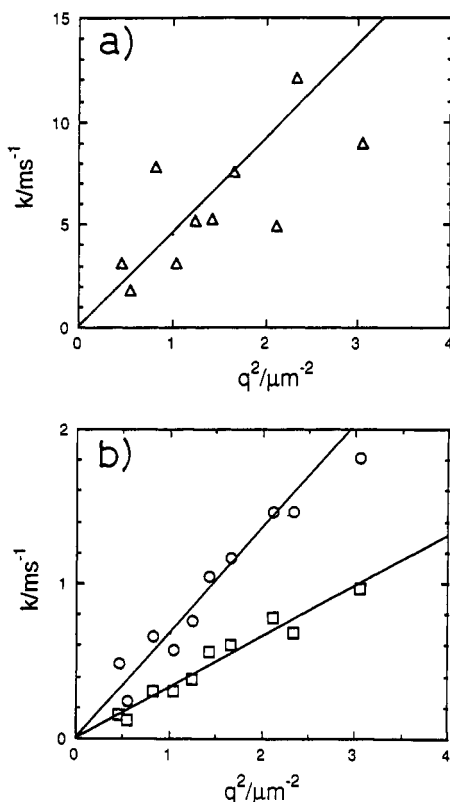


Figure 2. (a) Plot of the decay rate constants k_f vs q^2 and (b) those of k_i and k_s vs q^2 of benzophenone/2-propanol reaction system.

signal drops to the baseline once. This fact, together with that the thermal grating is composed of only the pure phase grating with negative δn ($\delta n_{th} < 0$), leads to a conclusion that the grating of the slow response is due to the pure phase grating and the most dominant component has positive δn . Therefore, the general equation (1) is simplified to have $\delta k = 0$.

After the contribution of the thermal grating becomes negligible, we find that the time dependence of the root square of the TG signal ($I_{TG}^{1/2}$) is fitted well by a sum of three exponential functions with different signs of pre-exponential factors.

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

where subscripts s, i, and f stand for the slow, intermediate, and fast components, respectively. By the least-square fitting, each contribution to the TG signal is separated out and shown in Figure 1b. First, the contribution of the thermal grating decays rapidly with the rate constant determined by D_{th} . The initial decay in the slow component is represented by the first term in eq 2 with $a_f > 0$. Then the rise is due to the intermediate component with $a_i < 0$. The slowest component with $a_s > 0$ is dominant at longer t .

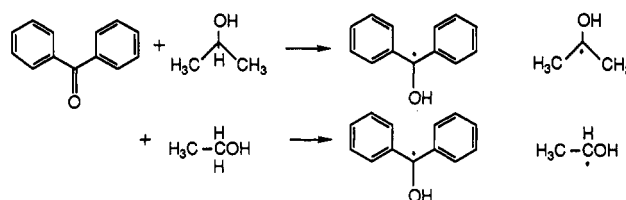
All of the rate constants depend on the fringe spacing Λ . Figure 2 shows the q^2 dependence of k_s , k_i , and k_f . The relatively large scattering of the data points for k_f is due to the weakness of the fast component. Each slope of the plot gives D of each chemical species. Although the intercepts, which represent the intrinsic lifetimes of the species, should have nonzero values for transient radicals, all plots indicate very small intercepts. We assume the intercepts to be zero for determining the slopes by the least-square method. We estimate that the error introduced by this assumption is within 5% typically. The error due to other sources will be discussed later. The D s for the diffusing species are determined to be $D_f = 4.56 \times 10^{-9} \text{ m}^2/\text{s}$, $D_i = 0.678 \times 10^{-9} \text{ m}^2/\text{s}$, and $D_s = 0.326 \times 10^{-9} \text{ m}^2/\text{s}$. When an air-saturated solution is used as the sample, the TG signal due to mass diffusion becomes weaker and also decays faster than in the nitrogen-saturated solution.

TABLE I: Diffusion Coefficients of the Transient Radicals (the First Column in the D_{exp} Section) and Their Parent Molecules (the Second Column) Measured by the Transient Grating Method (D_{exp})^a

solute	solvent	$D_{exp}/10^{-9} \text{ m}^2 \text{ s}^{-1}$		$D_{SE}/10^{-9} \text{ m}^2 \text{ s}^{-1}$		$D_{SW}/10^{-9} \text{ m}^2 \text{ s}^{-1}$
benzophenone	ethanol	0.55	1.0	5.3	0.48	0.94
	2-propanol	0.33	0.68	4.6	0.24	0.49
+ DMA	benzene	0.85	2.5		0.88	1.67
+ TEA		0.97		4.9		
+ CHD		0.89				
+ DMA	cyclohexane	0.64	1.5		0.59	1.14
+ TEA		0.55		5.4		
+ CHD		0.62	1.9			
+ TEA	methylcyclohexane	0.75		8.0	0.78	1.40
+ CHD		0.92	2.2			
+ TEA	hexane	1.53		11.	1.78	4.30
+ CHD		1.60	3.6			
+ CHD	acetonitrile	1.07			1.49	2.67
acetoaldehyde	ethanol	0.70			0.71	1.14
acetone	2-propanol	0.62			0.33	0.56
pyrazine ^b	2-propanol	0.31	1.3		0.33	1.06

^a The D values in the third column are those of unidentified species. Calculated values by the SE equation (D_{SE}) and by the SW equation (D_{SW}) are also listed. ^b Reference 9.

SCHEME II



In ethanol, the rise part in the slow component becomes less obvious, but the basic features of the time development are the same as in 2-propanol solvent. The determined D s in these solutions are summarized in Table I.

Photophysical processes of the excited states of BP have been studied extensively.¹⁴ The created photoexcited S_1 state is relaxed to the T_1 state within ~ 30 ps with the quantum yield of unity.¹⁴ Even under the deoxygenated condition without any chemical quencher, the triplet state decays to the ground state within an order of tens of microseconds. However, the TG signal of the slow component is observed for as long as tens of milliseconds with relatively small q . Therefore the slow component of the TG signal apparently represents the mass diffusion not of the excited states but of a chemical species produced by a photochemical reaction. According to the photochemical investigations of BP,¹⁵ the triplet-state BP is deactivated to the ground state or abstracts a hydrogen from alcohols to form transient radicals of diphenylhydroxymethyl radical (benzophenone ketyl radical (BPK^{\bullet})) and A^{\bullet} is the 2-hydroxypropyl radical (HP^{\bullet}) or hydroxyethyl radical (HE^{\bullet}) in the case of 2-propanol or ethanol, respectively (Scheme II).¹⁵ Therefore the diffusion of BP, alcohols (2-propanol or ethanol), BPK^{\bullet} , A^{\bullet} , and reaction products from BPK^{\bullet} and A^{\bullet} could be involved in the TG signal. According to the (transient) absorption studies,¹⁵ all of these species have their absorption bands at shorter wavelengths than that of the He-Ne laser. A theoretical consideration on the refractive index associated with the absorption bands states that the refractive index change due to these species should be positive ($\delta n_{ij} > 0$).¹⁶ Because of the depletion of the parent molecules (BP and AH), these reactants create a negative phase grating, and the formation of the radicals or the stable products creates a positive phase grating. Therefore, it seems reasonable to consider that the slow and fast components are originated from the radical species and the intermediate one is attributed to the grating of the parent molecules. For further

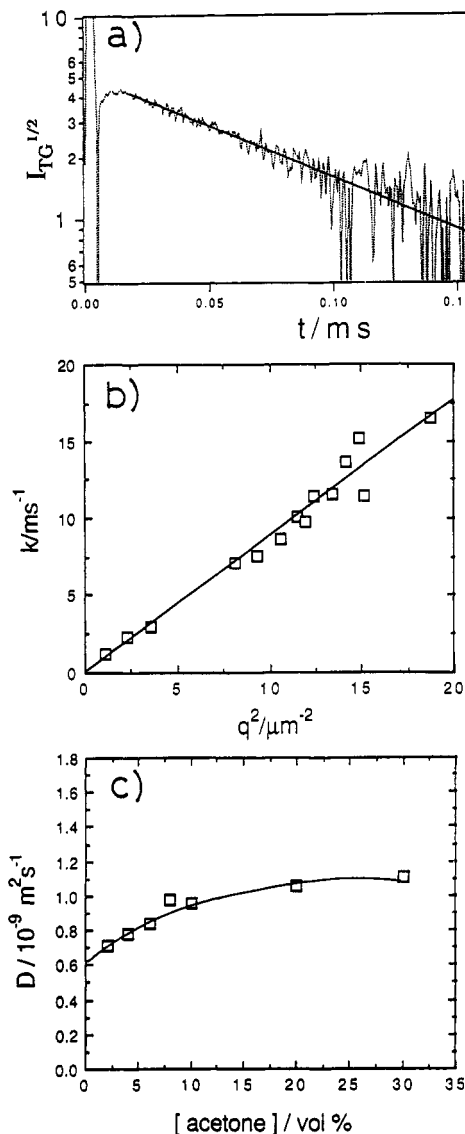
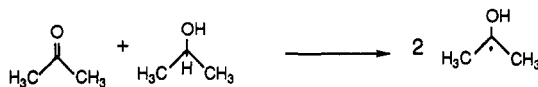


Figure 3. (a) Typical temporal profile of the TG signal ($\log(I_{TG}^{1/2})$) after the photoexcitation of acetone in 2-propanol under the nitrogen-bubbled condition (dotted line) and the best-fitted curves by eq 2 after the complete decay of the thermal grating signal (solid line). (b) Plot of the decay rate constants (k) vs q^2 . (c) The dependence of the diffusion coefficient of 2-hydroxypropyl radical on the concentration of acetone ([acetone]). The solid line is a guide for eyes.

SCHEME III

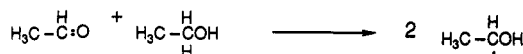


identification of the chemical species in the TG signal, it is required to have more information on the nature of each species. For this purpose, reactions of acetone and acetoaldehyde are studied.

4.2. Reactions of Acetone and Aldehyde in Alcohols. According to the time-resolved EPR (TREPR) investigations on the photochemical reaction of acetone in 2-propanol, the S_1 state of acetone after the photoexcitation is converted to the T_1 state promptly and then it abstracts a hydrogen from 2-propanol efficiently to produce two identical HPr^\bullet (Scheme III).¹⁷ Since only three chemicals are involved, this system could be more suitable for studying the diffusion process of HPr^\bullet than other reaction systems.

Figure 3 shows a typical TG signal after the photoexcitation of acetone in 2-propanol (5 vol %) under nitrogen-bubbled condition. Similar to the case of BP, a strong TG signal due to the thermal grating first appears and it decays to the baseline.

SCHEME IV



Then it rises again followed by a slow decay. The slow component is relatively weak compared with the BP case. The dip that reaches the baseline indicates that the slow component is due to the pure phase grating with a positive sign. The time dependence of $I_{TG}^{1/2}$ is expressed well by a single exponential function:

$$I_{TG}^{1/2}(t) = a \exp(-kt) \quad (3)$$

Under the air-saturated condition, the signal intensity diminishes and the decay of the signal becomes faster.

In this case, the assignment of the chemical species is straightforward. First, the chemical species that can contribute to the positive phase grating is HPr^\bullet or reaction products from HPr^\bullet . Second, the effect of oxygen suggests that this species is chemically unstable with respect to oxygen. The main product from HPr^\bullet is the dimerized compound, tetramethylethylene glycol (pinacol), which is stable against oxygen. Therefore the most plausible assignment for the diffusing species in the TG signal is HPr^\bullet . The other chemical species, acetone and 2-propanol, cannot contribute to the TG signal because of the small extinction coefficients.

The possibility of the contribution of the reaction product is further eliminated as follows. First of all, since the dimerized product does not have a π electron, the absorption bands should be located far from the visible and near-UV regions and the optical character must resemble that of 2-propanol. Then for the same reason the signal due to 2-propanol does not appear in the TG signal, the signal due to pinacol should not be observable. Second, the second-order rate constant of the dimerization reaction, $2\text{HPr}^\bullet \rightarrow (\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{OH})(\text{CH}_3)_2$, has been reported to be $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{17b} The concentration of the excited acetone under our experimental condition is roughly estimated to be $(1-5) \times 10^{-6} \text{ M}$ from the photon density of the excitation laser and the absorbance of the sample. Then the creation rate of the product is evaluated to be $(1-5) \times 10^{-3} \text{ s}^{-1}$. However, we could not observe any rising component of the TG signal in the microseconds time region. Finally, we extend the measurement to a relatively small spacing of the fringes ($q \geq 4 \mu\text{m}^{-1}$). At this q , the lifetime of the slow decay component is $\sim 70 \mu\text{s}$ and the single exponential fitting reproduces the data from $20 \mu\text{s}$ after the excitation, which indicates that the diffusing species are created at least within $20 \mu\text{s}$ from the laser irradiation. The TREPR measurements indicate that HPr^\bullet is the main radical species at least until $100 \mu\text{s}$ at room temperature.^{17d,e} On these three grounds, we exclude the participation of the reaction product in the slow TG signal. Also the above estimate is consistent with the small intercept value in the k vs q^2 plot (Figure 3b).

Because of the small extinction coefficient of acetone and weak TG signal, we must use relatively concentrated solution of acetone for the above measurement. Then the viscosity of the solution could be different from that of pure 2-propanol and the obtained D might not represent the true diffusion coefficient of HPr^\bullet in 2-propanol. In order to obtain D in a dilute solution, we examine the concentration dependence of the D (Figure 3c). As the concentration of acetone becomes dilute, D gradually decreases as expected from a relatively high viscosity of 2-propanol and a low viscosity of acetone. By extrapolation to $[\text{acetone}] = 0 \text{ M}$, $D = 0.62 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ is determined for HPr^\bullet .

To examine the diffusion process of HEt^\bullet , the TG signal is measured in the reaction system of acetoaldehyde in ethanol. After the excitation of acetoaldehyde, it abstracts a hydrogen from ethanol to produce two HEt^\bullet radicals (Scheme IV).¹⁸

The time profile of the TG signal is essentially the same as that of acetone. A single exponential function fits the decay from $20 \mu\text{s}$ after the laser excitation. Under the air-saturated condition,

the signal becomes weaker and decays faster. On the same grounds described for acetone in 2-propanol, we ascribe the chemical species to HET^* . Again, probably the small extinction coefficients of acetaldehyde and ethanol do not allow the corresponding TG signals to appear. From the extrapolation to $[\text{acetone}] = 0 \text{ M}$, the D value of HET^* in ethanol is obtained as listed in Table I.

4.3. Assignment of the Chemical Species of the BP System in Alcohols. After determining D s of HPr^* and HET^* , we are now in a position to identify the diffusing chemical species that appeared in the TG signal of BP/alcohols systems. Based on the facts that alcohols do not contribute to the TG signal, it is reasonable to ascribe the negative phase grating component to the depletion of the ground state of BP. Probably a larger extinction coefficient and longer wavelengths of the absorption bands of BP compared with those of alcohols make the BP component dominant in the TG signal. Therefore $D_1 = 0.678 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in 2-propanol and $1.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in ethanol represent the diffusion coefficient of BP.

The positive phase grating components (D_s and D_f) should be assigned to BPK^* or A^* or reaction products from these species. It has been widely known that the final products formed by this reaction are the dimerized species, benzopinacol and pinacol. As discussed in the previous section, the contribution of pinacol in the TG signal can be safely ignored. Also the contribution of tetraphenylethylene glycol (benzopinacol) can be eliminated for the following reasons. First, since this molecule does not have a strong absorption band in visible and near-UV regions, the phase change δn due to the creation of this species is expected to be small. Second, the second-order rate constant of $\text{BPK}^* \rightarrow (\text{Ph})_2\text{C}(\text{OH})\text{C}(\text{OH})(\text{Ph})_2$ is reported to be $k = 5.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.^{15b} Using the same estimation as that in section 4.1 (b), we obtain the decay rate of BPK^* to be $\sim 5.9 \times 10^1 \text{ s}^{-1}$, which is too small to create benzopinacol in our observing time. Support of this estimate is given by the transient absorption measurements. After the excimer laser irradiation of a deoxygenated BP/2-propanol solution, a relatively strong transient absorption with the peak maximum at 550 nm is observed. The spectrum resembles the reported transient absorption spectrum of BPK^* .¹⁵ The lifetime of the absorption is on the order of milliseconds, which confirms the long lifetime of BPK^* in Figure 2. Further, the fact that D of A^* measured in acetone/2-propanol or in acetone/ethanol is totally different from either D_s or D_f in both alcohols suggests that A^* does not appear in the TG signal. We believe that the TG signal of A^* is hidden under the relatively strong signal due to BPK^* because of the inherent weakness of the signal as described in the previous section. As a result, either D_s or D_f could represent the diffusion coefficient of the created radical, BPK^* . Since D_f is too large for the diffusion coefficient of a molecule having a volume of BPK^* , we believe that it is D_s that represent the D of BPK^* . The long lifetime of BPK^* is consistent with the small intercept of the k_s vs q^2 plot.

Additional evidence comes from the hydrogen donor dependence of the TG signal as described in the next section. Even using different donors, we obtain similar D s for the positive δn components. The radicals of the hydrogen donor molecules cannot be the origin of the slow component. At this time, we do not know the origin of D_f . The very fast diffusion of this species suggests that it could be a fragmented species.

4.4. Solvent Dependence of D of BPK^* . In order to study the solvent dependence of D of BPK^* , we measure D of BPK^* in various solvents. To produce BPK^* in nonreactive solvents, we add hydrogen donors, dimethylaniline (DMA), triethylamine (TEA), and 1,4-cyclohexadiene (CHD), in the solution (concentrations of these donors are $\sim 0.1 \text{ M}$ for DMA and TEA and 0.2 M for CHD). Without these donors, there is no observable slow component in the TG signal. This fact indicates that BP does not react with these solvents efficiently. After adding these

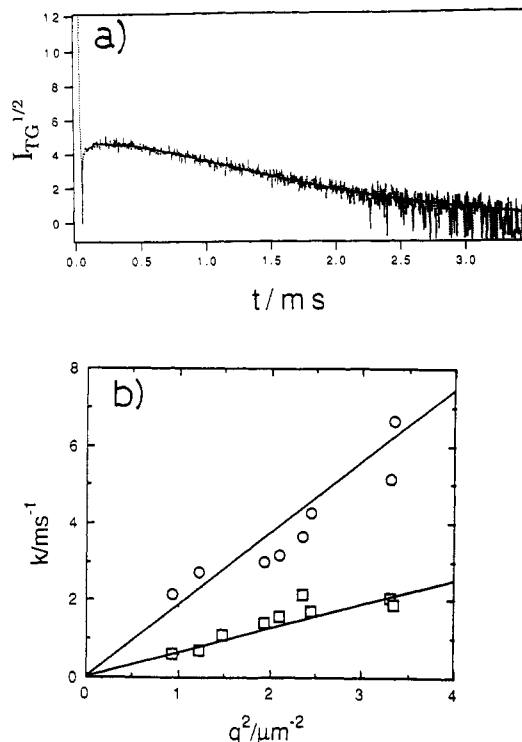


Figure 4. (a) Typical temporal profile of the TG signal ($I_{\text{TG}}^{1/2}$) after the photoexcitation of benzophenone in cyclohexane with CHD under the nitrogen-bubbled condition (dotted line) and the best-fitted curve by eq 2 after the complete decay of the thermal grating signal (solid line). (b) Plot of the decay rate constants (k) vs q^2 of BP in CHD.

donors, slow components are observed following the thermal grating signal.

The photoreaction of excited triplet BP has attracted many investigators for a long time and the reaction path and its mechanism have been studied extensively.^{15,19} The reaction yields of the hydrogen abstractions from amines are usually very high and the efficiency of the reaction has been considered to be due to the participation of the charge-transfer interaction between BP and the amines.¹⁹ Under certain conditions, it is known that the charge-transfer reaction takes place and benzophenone anion and the cation of the amines are created.¹⁹ However, the contributions of such species are minor in the solvents we use¹⁹ and the lifetimes of these species are usually relatively short ($\sim 50 \text{ ns}$ in benzene).²⁰ Therefore, we neglect the contribution of the charged species in this paper. Further, if BP anion contributes to the TG signal, the phase change δn due to the anion is expected to be negative, which is opposite to the case of BPK^* , because the absorption band of BP anion is on the longer wavelength side of that of He-Ne laser.²¹

The time development of the TG signal depends on the hydrogen donor and the solvent. For example, the TG signal after the photoexcitation of BP with CHD in cyclohexane is given in Figure 4a. The signal is composed of the rise and decay components, i.e., the sum of two exponentials (eq 2 with $a_f = 0$) with different signs of the preexponential factors $|a_s| > |a_i|$ and $a_s > 0 > a_i$. With DMA, the time dependence is similar. On the other hand, with TEA in cyclohexane, the TG signal shows two decay components, which is expressed by eq 2 with $a_f = 0$ and the same sign of the preexponential factors $a_s, a_i > 0$. In acetonitrile with CHD, the rise component becomes weak and the temporal profile is nearly expressed by a single exponential function.

From the slopes of the k vs q^2 plots (Figure 4b), the D values with these hydrogen donors in various solvents are obtained as listed in Table I. The D values are classified according to the identification of the diffusing species. It is noteworthy that usually the slowest component with $\delta n > 0$ appears in the TG signal including the alcohol solvents. The values of D_s correlate with

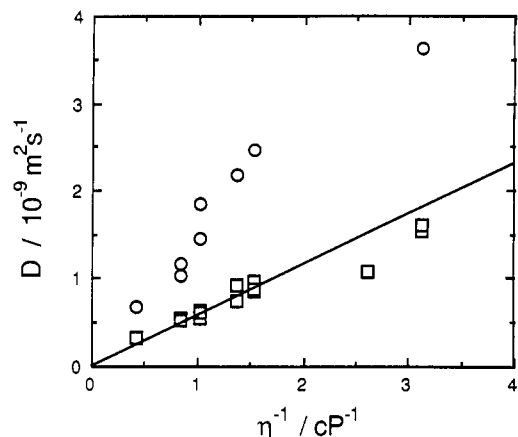


Figure 5. Viscosity dependence of D of BP (circles) and BPK* (squares) in various solvents. A solid line is the predicted D based on the Stokes-Einstein relation.

the viscosity of the solvent (Figure 5); namely, these values are inversely proportional to the viscosity of the solvents as predicted by the Stokes-Einstein relation (eq 4 in the next section). Therefore it is reasonable to consider that the species that gives rise to the slowest component in the nonalcoholic solvents is the same as that in alcoholic solvent, BPK*, that is, we ascribe the slowest component to the diffusion of BPK* on the basis of the identification in alcoholic solvents.

From the negative sign of the preexponential factor and the same argument as in the previous sections, the species that gives the fast rising component with CHD and DMA is attributed to BP. The assignment of the faster decaying component with TEA is not obvious. The identification of this species is left to a future study.

The important conclusion from the results is that D of BPK* is several times smaller than that of BP even in nonalcoholic solvents.

5. Discussion

As shown so far, we can successfully measure the translational diffusion coefficients of several transient radicals created by photoinduced hydrogen abstraction reactions of carbonyls in various solvents. The D values listed in Table I contain a certain amount of experimental errors. Sources of the uncertainty arise from several steps. First, the estimate of the fringe spacing or equivalently q could have an error. Second, the imperfection of the curve fitting to determine k introduces an additional error, in particular, for a weak signal. Third, we ignore small but possible contribution from a hidden species such as 2-propanol or ethanol. Fourth, we fix the intercept to zero in calculating the slope of the k vs q^2 plot as described in section 4.1(a). The total amount of the uncertainty due to these factors also depends on the reaction system. The estimated typical error in D_r and D_t originated from the scatter of the data and from the neglect of the finite intercept (for the radicals) is less than $\pm 10\%$ of the reported values in Table I. The error of D_t (the values in the third column in Table I) is estimated to be larger (about $\pm 20\%$), because of the weak intensity and relatively fast decay. Even after taking into consideration these errors, the results in Table I show that the diffusion of BPK* is two to three times slower than that of BP.

According to the Stokes-Einstein relationship for a diffusing molecule in a homogeneous nonviscous solution with viscosity η , D is calculated by²¹

$$D_{SE} = kT/6\pi\eta r(f/f_0) \quad (4)$$

where r denotes the radius of a spherical molecule and f/f_0 is a factor for correcting the deviation from the spherical shape. If this relation holds for the parent and radical, the D of the radical should be similar to that of the parent molecule, because the

TABLE II: Estimated Radii of the Molecules for the Calculation of D_{SE} and D_{SW} in Table I^a

	$r/\text{\AA}$		$r/\text{\AA}$
benzophenone	3.77	acetone	2.78
pyrazine	2.68	acetaldehyde	2.54
DMA	3.34	cyclohexane	3.16
TEA	3.44	benzene	3.08
CHD	3.03	hexane	3.37
2-propanol	2.82	methylcyclohexane	2.48
ethanol	2.58	acetonitrile	2.48

^a The calculation methods are described in the text.

volume difference between the radical and the parent molecule is just one hydrogen atom, which is negligible compared with the whole molecular size.

The small D s of the radicals may be attributed to an attractive interaction between the molecules in solution. Since we can neglect a possible radical-radical interaction, which might affect the molecular dynamics just after the creation of the radical pair, the radicals should be surrounded by the solvent molecules in our observing time scale. Thus, the large difference in D suggests that a specific attractive interaction between the radicals and solvents participates in the diffusion process. In such a case, the radicals diffuse accompanied by several solvent molecules and this makes the movement slow. One possibility for such an interaction is a hydrogen-bonding interaction. However, the observation that the radical diffusion is slower than that of the parent molecule even in nonpolar solvents such as cyclohexane excludes this possibility (Figure 5).

In Table I, we list the calculated D_{SE} from eq 4 and the molecular volume estimated from the molecular structure and the van der Waals radius of each atom. The radii of these molecules used for the calculation are listed in Table II. The data of viscosities of the solvents are taken from ref 22. According to numerous studies on the diffusion process in solution²³ and our previous work on the diffusion process of a dye molecule in various solvents,¹¹ D s calculated on the basis of the SE relation usually underestimate the measured values. This tendency is also seen in this study; D_{SE} is usually smaller than D s of the parent molecules. Several modifications of the SE equation to reproduce experimentally obtained D s have been proposed so far. A semiempirical modification proposed by Spornol and Wirtz²⁴ is recommended by several groups.^{25,26}

$$D_{SW} = kT/6\pi\eta f_{SW}$$

$$f_{SW} = \left(0.16 + 0.4 \frac{r_A}{r_B}\right) (0.9 + 0.4 T_A^r - 0.25 T_B^r) \quad (5)$$

where r_A and r_B respectively represent the radii of the solute (A) and the solvent (B). The reduced temperatures, T_A^r and T_B^r , 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 ($X = A$) or the solvent ($X = B$). We also found that D of the dye molecule can be reproduced well by the SW modified equation.¹¹

The radii of the liquid samples and solvents are calculated on the basis of the same method used by Spornol and Wirtz,²³ from the density, the molecular weight, and the free volume (74%).²⁷ The calculated values of D_{SW} listed in Table I agree well with the observed D for the parent molecules. Interestingly this situation is totally opposite for the radicals; that is, D s of the transient radicals are overestimated by D_{SW} but are in a good agreement with D_{SE} , which do not take into account any specific interaction between solute and solvent except the hydrodynamical force. It is noteworthy that D of both BP and BPK* are proportional to the viscosities of the solvents (Figure 5). This fact indicates that the slow diffusion process of the radical does not depend on or

at least is not sensitive to the solvation structure of the solution. The dynamics seems to be essentially determined by the hydrodynamics.

Burkhart and Wang have measured D of several alkyl radicals and benzyl radical by the PSI method.⁸ They have found that D s of alkyl radicals are smaller than those of the parent molecules, although that of benzyl radical is in good agreement with the calculated value by the SE equation. Schuh and Fischer have measured D of the *tert*-butyl radical in many solvents and concluded that the calculation based on the SE equation cannot reproduce the observed D . Our results are different from theirs.

Even in our case, the rule, smaller D s of radicals than those of parent molecules, does not hold for acetone/2-propanol and acetoaldehyde/ethanol systems. Although the diffusion process of the parent molecules cannot be observed in the TG signal, the self-diffusion coefficients of the alcohols have been measured ($D = 0.56 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for 2-propanol and $D = 0.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for ethanol). Comparing these values, we find D s of HPr[•] and HEt[•] are similar to those of 2-propanol and ethanol, respectively. At the same time, these values are close to that of acetone in 2-propanol and acetoaldehyde in ethanol estimated by the SW relation. The above results suggest that the relative diffusion coefficient of the radical compared with that of the parent molecule may depend significantly on the nature of the radical.

Further investigations are being made to clarify the origin of the difference in D s of the radicals and the parent molecules.

6. Summary

We have applied the TG method to investigating the diffusion dynamics of the transient radicals created by photoinduced hydrogen abstraction reactions of BP in various solvents. Together with the previous work, we have demonstrated that the TG method is sensitive enough to trace the mass diffusion processes of the transient radicals produced by hydrogen abstractions of several reactants (pyrazine, benzophenone, acetone, and acetoaldehyde) in alcoholic solvents.

The translational diffusion coefficients of the radicals are two to four times smaller than that of BP. The slow diffusion suggests an attractive radical-solvent interaction. To examine the effect of hydrogen bonding, we measure the diffusion coefficients in nonalcoholic solvents, which hardly have any hydrogen bonding. The results that the transient radicals move slower than those of the parent molecules even in the nonalcoholic solvents exclude the importance of hydrogen bonding for slow motion. Empirically, the D s of the stable molecules are reproduced well by the modified SE equation by Sperrin and Wirtz, whereas the D s of many radicals agree well with the values calculated by the original SE equation.

Acknowledgment. This work is supported by a Scientific Research Grant-in-Aid for the Priority Area of "Molecular Magnetism" (Area No. 228/04242102) provided by the Ministry of Education, Science and Culture of Japan.

References and Notes

- (1) Molin, Yu. N., Ed. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1984.
- (2) Adrian, F. J. *J. Chem. Phys.* **1971**, *54*, 3918.
- (3) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251.
- (4) Noyes, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 566; *J. Phys. Chem.* **1965**, *69*, 3182.
- (5) (a) Levison, S. A.; Noyes, R. M. *J. Am. Chem. Soc.* **1964**, *86*, 4525. (b) Burkhart, R. D. *J. Phys. Chem.* **1969**, *73*, 2703.
- (6) Burkhart, R. D.; Boynton, R. F.; Merrill, J. C. *J. Am. Chem. Soc.* **1971**, *93*, 5013.
- (7) Burkhart, R. D.; Wong, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7203.
- (8) (a) Scott, T. W.; Liu, S. N. *J. Phys. Chem.* **1989**, *93*, 1393. (b) Scott, T. W.; Doubleday, C., Jr. *Chem. Phys. Lett.* **1991**, *178*, 4.
- (9) Terazima, M.; Okamoto, K.; Hirota, N. *J. Chem. Phys.* **1993**, *98*, 6257.
- (10) Terazima, M.; Hirota, N. *J. Chem. Phys.* **1991**, *95*, 6490.
- (11) Terazima, M.; Okamoto, K.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 5188.
- (12) For example, Eichler, H. J.; Gutner, P.; Pohl, D. W. *Laser induced dynamic gratings*; Springer Verlag: New York, 1986.
- (13) Terazima, M.; Okamoto, K.; Hirota, N. To be published.
- (14) (a) Wilkinson, F. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; John Wiley & Sons: London, 1975; Vol. 2. (b) Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *Chem. Phys. Lett.* **1973**, *24*, 162.
- (15) (a) Bell, J. A.; Linschitz, H. *J. Am. Chem. Soc.* **1963**, *85*, 528. (b) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038. (c) Land, E. J. *Proc. R. Soc.* **1968**, *305A*, 457. (d) Hayon, E.; Ibat, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072. (e) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393. (f) Redmond, R. W.; Scaiano, J. C. *Chem. Phys. Lett.* **1990**, *166*, 20.
- (16) Lonhurst, R. S. *Geometrical and Physical Optics*, 2nd ed.; Wiley: New York, 1967.
- (17) (a) Porter, G.; Dogra, S. K.; Loutfy, R. O.; Sugamori, S. E.; Yip, R. W. *J. Chem. Soc. Faraday Trans. I* **1973**, 1462. (b) Lehn, M.; Fisher, H. *Int. J. Chem. Kinet.* **1983**, *15*, 733. (c) Basu, S.; Grant, A. I.; McLauchlan, K. A. *Chem. Phys. Lett.* **1983**, *94*, 517. (d) Tominaga, K.; Yamauchi, S.; Hirota, N. *J. Chem. Phys.* **1988**, *88*, 553. (e) Levstein, P. R.; van Willigen, H. *J. Chem. Phys.* **1991**, *95*, 900. (f) van Willigen, H.; Levstein, P. R.; Ebersole, M. H. *Chem. Rev.* **1993**, *93*, 173.
- (18) Tominaga, K.; Hirota, N. Unpublished results.
- (19) (a) Cohen, S. G.; Baumgarten, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 3471. (b) Cohen, S. G.; Cohen, J. I. *J. Am. Chem. Soc.* **1967**, *89*, 164; *J. Phys. Chem.* **1968**, *72*, 3782. (c) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040. (d) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141. (e) Arimitsu, S.; Masuhara, H.; Mataga, N. *J. Phys. Chem.* **1975**, *79*, 1255. (f) Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6452. (g) Devadoss, C.; Fessenden, R. W. *J. Phys. Chem.* **1990**, *94*, 4540. (h) Miyasaka, H.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 131. (i) Miyasaka, H.; Morita, K.; Kamada, K.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3385.
- (20) (a) Shida, T.; Nosaka, Y.; Kato, T. *J. Phys. Chem.* **1978**, *82*, 695. (b) Shida, T.; Iwata, S.; Imamura, M. *J. Phys. Chem.* **1974**, *78*, 741.
- (21) (a) Cussler, E. L. *Diffusion*; Cambridge University Press: Cambridge, 1984. (b) Tyrrell, H. J. V.; Harris, K. R. *Diffusion in liquids*; Butterworths: London, 1984.
- (22) Viswanath, D. S.; Natarajan, G. *DATA Book on the Viscosity of Liquids*; Hemisphere Pub. Co.: New York, 1989.
- (23) (a) Tominaga, T.; Matsumoto, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 533. (b) Evans, D. F.; Tominaga, T.; Davis, H. T. *J. Chem. Phys.* **1981**, *74*, 1298.
- (24) Sperrin, A.; Wirtz, K. Z. *Natureforsch.* **1953**, *89*, 522.
- (25) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.
- (26) Sandhu, H. S. *J. Magn. Reson.* **1975**, *17*, 34.
- (27) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 216.