

Is the Translational Diffusion of Organic Radicals Different from That of Closed-Shell Molecules?

MASAHIDE TERAZIMA*

Department of Chemistry, Graduate School of Science,
Kyoto University, Kyoto, 606-8502, Japan

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ABSTRACT

The translational diffusion of photochemically created intermediate radicals is measured by the transient grating technique. The diffusional behavior of these intermediates is different from that of stable molecules, which have already been investigated extensively. The investigation of the diffusion of these species will provide an opportunity to reveal the unique intermolecular interaction between the intermediates and matrix. This information will be valuable for understanding photochemistry in solutions.

1. Introduction

During many chemical reactions in solution, unstable intermediate species diffuse and encounter other molecules to produce secondary or final products. Hence, the diffusion of the intermediate is one of the key factors in controlling chemical reactions. Indeed, the diffusion coefficient (D) of intermediate species is involved in most of the theories of chemical reactions.^{1,2} Considering the importance of D , it is rather surprising that there is very little data on the D of unstable species. For many cases, D of intermediate species in the theories was replaced by D of a stable molecule with a similar size and shape or D calculated by a diffusion theory which can predict D of stable molecules to analyze the reaction. However, we actually do not know whether this replacement is correct or not. The diffusion is also important in identifying the intermolecular interaction between the diffusing species and the matrix. Is the intermolecular interaction between radicals and solvent so much different from that between analogous closed-shell molecules and the solvent to alter the molecular movement? To what degree do D and the intermolecular interaction depend on the electronic state? Answers to these interesting questions have not been clear yet.

The scarcity of the data is due only to the experimental difficulty in measuring D of transient species because usually it takes a long time—several minutes or hours or even days—for the measurement of D using traditional techniques. Here I will present D of intermediate radicals and persistent radicals we have recently measured and compare them to D of the analogous closed-shell molecules.

Several methods have already been used to detect the diffusion of radicals. EPR tomography is a direct detection method that measures the spatial broadening of the radical concentration profile, which was initially set to be localized in a sample tube.^{3,4} Since spatial broadening by diffusion even on the millimeter scale requires several minutes, this method is applicable only to stable radicals which persist for an order of minutes. Another interesting technique is the so-called photochemical space intermittency, which was originally developed by Noyes.^{5,6} In this method, the steady-state concentration of photochemically produced radicals which are destroyed by a second-order process is measured under various spatially inhomogeneous illuminations of light and dark areas. Since the second-order recombination of the radical depends on the (local) concentration, the relative size of the individual illumination area and D of the radicals affect the reaction efficiency. By analyzing the radical concentration, it is possible to measure the average distance that a radical diffuses during its lifetime. The method was applied to several reaction systems.^{7,8} Although this method is a prominent technique, D has to be obtained indirectly by a curve-fitting of the experimental data with many parameters, such as the reaction rate, the quantum yield of the reaction, and so on, which are sometimes very difficult to obtain accurately. Furthermore, the possible diffraction of light at the edge of the pattern was always neglected. Due to this complicated procedure, the uncertainty of D obtained with this method could be very great, and it has not been determined whether the diffusional behavior of radicals is different from that of the stable closed-shell molecules or not.

Recently, we have extensively used the transient grating (TG) technique to investigate photochemical reactions in solution.^{9–11} On the topic of the diffusion, we found that the diffusion process is determined not only by the molecular shape or size but also by the electronic state.¹² A notable example is the comparison of D with transient radicals and their parent molecules. In this Account, I summarize D of radicals we have measured so far and discuss the origin of the anomalous diffusion of the radicals. The data in this Account will be valuable in predicting D of unstable species in many chemical reaction analyses, as well as revealing a microscopic intermolecular interaction between the transient radicals and the solvent.

2. Methods

In the TG method, two coherent light beams are crossed at a sample to produce the interference pattern of the light intensity (Figure 1).^{9–11,13,14} If a photochemical reaction takes place in a bright region of the grating pattern, the reactants disappear, and intermediate species or products are created. Since the presence of different chemical species results in a different refractive index and absor-

Masahide Terazima received his Ph.D from Kyoto University in 1987. He joined the faculty of Tohoku University in 1986. Currently he is a member of the faculty of Kyoto University (1990–).

* Fax: +81-75-753-4000. Tel.: +81-75-753-4026. E-mail: mterazima@kuchem.kyoto-u.ac.jp.

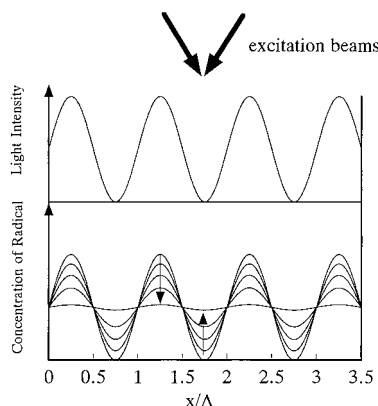


FIGURE 1. Spatial modulation of the radical concentration (bottom) induced by the interference pattern between two excitation beams (top) (x is a spatial coordinate, and Λ is the fringe spacing) The amplitude of the modulation decreases with time due to the translational diffusion of the chemical species along the x coordinate. The time evolution from the initial concentration profile is indicated by the arrows ($Dq^2t = 0, 0.2, 0.5, 1.0,$ and 3.0).

bance, photochemical reactions by the optical interference pattern lead to a spatially modulated refractive index or absorbance grating. When another probe beam is introduced in that region, satisfying Bragg's condition, a part of the probe light is diffracted as the TG signal. The signal intensity is proportional to the square of the spatial variations in the refractive index (δn) and absorption (δk) under a weak diffraction condition.¹⁵ In this Account, we used a nonresonant condition to any optical absorption for the probe light; i.e., δk is negligible.

The TG signal intensity reflects the spatial modulation of the chemical species. Hence, the intensity becomes weaker as the reactant and the product become spatially uniform in the grating region, which is accomplished by the translational diffusion (or back reaction from the intermediate to the reactant if the reaction is reversible). In Figure 1, the spatial profiles of the radical concentration modulation are shown at several times from $t = 0$.

For example, let us consider a simple photochemical reaction of $R_i \rightarrow P_j$, where R_i and P_j represent the precursor and intermediate species (or product), respectively. If a reaction takes place instantaneously and the products decay back to reactants or are converted to other products which do not give rise to a TG signal, the time dependence of the TG signal is expressed by

$$I_{\text{TG}}(t) = \alpha \{ \delta n_{\text{th}} \exp(-D_{\text{th}}q^2t) + \delta n_i \exp(-D_iq^2t) - \delta n_j \exp(-D_jq^2t + kt) \}^2 \quad (1)$$

where α is a constant, q is the grating wavenumber, k_j is the disappearance rate of P_j , D_{th} is the thermal diffusivity, $D_{i(j)}$ is the diffusion constant of the species, and $\delta n_{i(j)}$ is the peak-to-null difference in the refractive index at $t = 0$. The first term of eq 1 represents the decay of the thermal grating, which is created by the thermal energy associated with the nonradiative transition from the excited states. The second and the third terms, respectively, correspond to the smearing out processes of the reactant R_i and the product P_j . In many cases, the decay

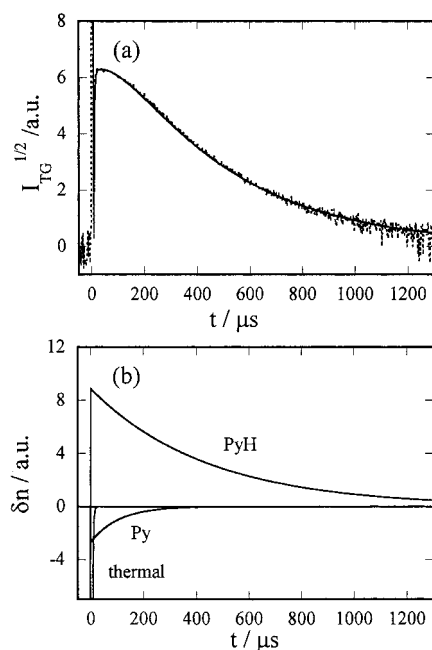


FIGURE 2. (a) Observed TG signal after photoexcitation of pyrazine in 2-propanol (dotted lines) and the best-fitted curves obtained with eq 2 (solid lines). (b) Signals due to the thermal grating (thermal), pyrazine (Py), and pyrazinyl radical (PyH) in the signal of (a).

rate constants of the TG signal are plotted against q^2 , and D is determined from the slope. In this way, the effect of a successive reaction (k_j) can be eliminated.

This TG method for measuring D has the following merits over the conventional techniques:

(A) High sensitivity, which is important for studying the dynamics without disturbance by the solute–solute interaction or for reducing the disappearance rate of the radicals, which is usually the second-order kinetics.

(B) Short-time measurement: since the TG signal monitors the spatial movement among a micrometer scale in distance of the fringes, it requires only a short time for the measurement. Owing to this merit, D of short-lived species can be studied.

(C) Small volume of sample.

(D) In an anisotropic medium, the anisotropic diffusion constant can be selectively measured.

(E) This TG method is a direct measurement. For determining D , only kinetic analysis of the TG signal is needed. We do not require any molecular photophysical or photochemical parameters, which are frequently required in fluorescence quenching experiments or the photochemical space intermittency method.

3. Radicals by Hydrogen Abstraction Reactions

A typical TG signal in a chemical reaction system is shown in Figure 2 for a pyrazine (Py)/2-propanol chemical system.¹⁶ First, the strong TG signal was assigned to the thermal grating which decayed to the baseline with a time constant of $2D_{\text{th}}q^2$. After reaching the baseline, it shows a growth–decay curve. Apparently, the slower component was due to the change of the chemical species. The dip between the thermal grating and the species grating is a

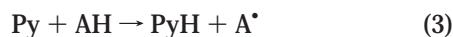
consequence of the interference effect between these components. Since the thermal grating is the pure phase grating with the negative sign, the species grating should consist of a phase grating with the positive sign for the stronger component. After the thermal grating, the square root of the TG signal was well expressed by a biexponential function with different signs of the preexponential factors:

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

where subscripts s and f stand for the slow and fast components, respectively, and $a_f < 0 < a_s$, $|a_s| > |a_f|$.

The chemical species which gave rise to the rise and decay components were assigned to Py and pyrazinyl radical (PyH) created by the photoinduced hydrogen abstraction reaction on the following grounds:

(1) PyH and 2-propanoyl radical are created from Py in 2-propanol solution efficiently by the hydrogen abstraction from the excited triplet state:



where AH is 2-propanol, and A^* is the alcoholic radical.

(2) The slow decay component became weaker and decayed faster under the air-saturated condition. The slower decay must be due to a species which is quenched by oxygen and created from the T_1 state of the precursor molecule.

(3) The created radicals, as well as the parent molecules (Py and 2-propanol), have absorption bands at shorter wavelengths than that of the He–Ne laser. Therefore, all of δn_i and δn_j should be positive.

(4) Py has much stronger absorption bands in the near-UV region compared with that of 2-propanol. Therefore, the depletion of Py should form a larger phase grating than that of 2-propanol.

(5) The TG experiment on acetone/2-propanol, which produces the 2-hydroxypropyl radical, exclusively showed that the TG signal was relatively weak and that the diffusional motion of this radical was much faster than that of the species which showed the slow decay.¹⁷ We believe that the 2-propanol and 2-hydroxypropyl radical did not appear in this TG signal because of the smaller extinction coefficients in shorter wavelength and a possible reverse hydrogen abstraction reaction.¹⁸

(6) A transient absorption measurement revealed that an absorption band of PyH lasted for a duration on the order of tens of milliseconds. The linear relationship between the decay rates and q^2 with a small intercept to the ordinate ensures that D can be determined from the slope (Figure 3). Recently, we found that this linear relation holds on a time scale of a few microseconds, too.¹⁹ Therefore, the signal cannot be due to any secondary radicals or secondary products from PyH.

(7) More directly, D of Py was measured by an independent method, involving NMR and Taylor dispersion.^{20,21} D from these measurements agreed well with D of the rise component from the q^2 plot.

D of Py and PyH are determined to be 1.2×10^{-9} and $0.38 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively, from the slopes of the q^2

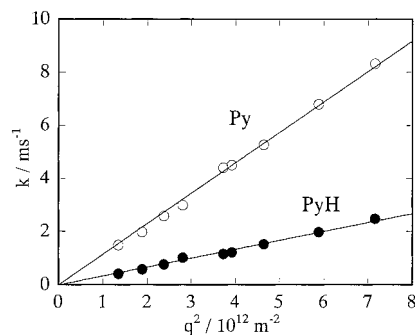


FIGURE 3. q^2 plot of the decay rate constant (k) of the species grating signals observed after photoexcitation of Py in 2-propanol.

plot (Figure 3). Many theories deal with the diffusion processes in solutions. For example, the Stokes–Einstein (SE) relation, one of the most frequently used and also the basis for many modified theories, is written as^{1,2}

$$D_{\text{SE}} = kT/f \quad (4)$$

$$f = 6\pi\eta r \{ (1 + 2\eta/\beta r) / (1 + 3\eta/\beta r) \}$$

where f is the friction coefficient, η is the viscosity, r is the radius of the solute, and β is the coefficient for boundary condition (which is 0 for slip boundary and ∞ for stick boundary conditions). This theory treats a spherical molecule in solvents which can be considered as a continuum. Many modifications based on the SE relationship have been proposed, such as the Spornol–Wirtz equation. We found that the theoretically calculated D based on the Spornol–Wirtz equation reproduces the experimentally observed D for stable (parent) molecules in many cases.²² Based on the SE equation, it is rather surprising to find the large difference in D between Py and PyH because the shapes and sizes of both molecules are very similar.

In other hydrogen abstraction reaction systems, as well as other photochemical reaction systems, similar TG signals were observed.²² Based on the same analysis, we found that *the radicals created by the hydrogen abstraction reactions diffuse generally slower than the parent molecules with similar volumes* (Table 1). In the following subsections, factors which may control the radical diffusion process will be examined.

(a) Size Dependence. Studies on various solutes revealed that the ratios (R) of D 's of the radical (D_r) to those of the parent molecules (D_p) depend on the molecular size (Table 1); for example, $R = D_r/D_p$ is about 0.3 for pyrazine (volume 0.13 nm^3) and about 0.8 for biquinoline (volume 0.61 nm^3).²² Their D values are plotted against the inverse of the molecular radius (Figure 4). For the parent molecules, D becomes smaller as the size of the molecules becomes larger.

The slower diffusion of the radicals may be explained by an attractive intermolecular interaction between the radicals and solvents. If a specific solute–solvent interaction is attractive, the solute is crowded by the solvent molecules which increase the friction and ultimately bring down the solute diffusion. If the molecule is small, the

Table 1. Diffusion Coefficients ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) of Organic Radicals (D_r) Created by Photochemical Reactions and Their Analogous Closed-Shell Molecules (D_p) in Solutions at 21 °C unless Otherwise Specified^a

solute	solvent	D_p	D_r	remarks	ref	
pyrazine	2-propanol	1.2	0.38		16, 43	
		0.92		21		
	ethanol	1.6	0.74		16, 20	
benzophenone	2-propanol	1.48	0.33		21	
		0.68		22		
		0.57		21		
	ethanol	0.80	0.49		17, 20	
		0.80	0.43	anion (+NaOH)	5	
	benzene	benzene	0.95	0.87		21
			1.28		+BzOH	43
MCH		1.34		21		
acetophenone	ethanol	1.53	0.96	+BzOH	17, 20	
		1.36			21	
	ethanol	1.36	0.58		22	
		1.37	0.52	anion (+NaOH)	32	
	methanol	1.78	1.25		32	
		1.91	1.15	anion (+NaOH)	32	
	benzoquinone	2-propanol	0.89	0.33		32
			0.89	0.28	anion (+NaOH)	32
		E/W (1/9)	0.55	0.46		25
		2-propanol	0.98	0.36		22
0.94					21	
benzaldehyde	ethanol	1.6	0.57		22	
		1.44		21		
	E/W (1/9)	0.76	0.61		25	
	2-propanol	0.99	0.37		22	
		0.93			21	
	ethanol	1.6	0.58		22	
		1.39			21	
acetophenone	ethanol	1.52	0.48	anion (+NaOH)	32	
		0.93	0.34		22	
	2-propanol	0.76			21	
2,2-biquinoline	ethanol	1.3	0.58		22	
		1.24		21		
	2-propanol	0.45	0.34		22	
		0.84	0.58		22	
TMPD	ethanol	1.8	0.91		28	
BISP	ethanol	0.57	0.46		29, 30	
		1.14	0.71		29, 30	
DPDAz	CHX	1.3	0.47		36, 43	
			3.3		36, 43	
	methanol	2.5			36	
HCDPDaz	benzene	1.1	0.49	carbene	37	
HBrDPDAz	benzene		0.68	carbene	37	
			0.90	carbonyl oxide	37	
HMeDPDAz	benzene		1.0	carbonyl oxide	37	
dibenzyl ketone	hexane	3.3	4.1		33	
		0.78	0.95		33	
	ethanol	0.92	1.1		33	
		0.57	0.64		33	
	2-propanol		0.64		33	
	CHX		1.1	25 °C	8	
benzyl radical	ethanol	0.79	0.87		38	
		3.08	2.93		21	
	HX		2.93		21	
OH-TEMPO	ethanol	0.57	0.65		38	
		0.84	0.88		38	
Ox-TEMPO	ethanol				38	
					38	
	water		1.7	25 °C	4	
	decaline		0.176		3b	
DPPH	squalene		0.023		3b	
			0.53		38	
	ethanol	0.54	0.53		38	
1-propyl radical	CHX	0.66			38	
			0.80	25 °C	7	
	cyclohexyl radical	CHX		0.40	25 °C	8
				0.72	26 °C	44
di- <i>tert</i> -butyl nitroxide	water				44	

^a The radicals are electrically neutral radicals unless otherwise specified. Abbreviations: AcN, acetonitrile; BISP, 1',3',3'-trimethylspiro-8-nitro(2*H*-1-benzopyran-2',2'-indoline); BzOH, benzhydrol; CHX, cyclohexane; E/W, ethanol–water mixture; DPPH, 2,2-diphenyl-1-picrylhydrazyl hydrate (analogous closed-shell molecule is 1,1-diphenyl-2-picrylhydrazine); DPDAz, diphenyldiazomethane; HCDPDaz, 2,2',4,4',6,6'-hexachlorodiphenyldiazomethane; HBrDPDAz, 2,2',4,4',6,6'-hexabromodiphenyldiazomethane; MCH, methylcyclohexane; OH-TEMPO, 4-hydroxy-2,2,6,6,-tetramethyl-1-piperidinyloxy (analogous closed-shell molecule is 2,2,6,6,-tetramethyl-4-piperidinol); Ox-TEMPO, 4-oxo-2,2,6,6,-tetramethyl-1-piperidinyloxy (analogous closed-shell molecule is triethylamine); TEMPO, 2,2,6,6,-tetramethyl-1-piperidinyloxy (analogous closed-shell molecule is 2,2,6,6,-tetramethylpiperidine); TMPD, *N,N,N,N*-tetramethyl-*p*-phenylenediamine. The “+” sign in the “remarks” section indicates that another reagent is added in the solution.

friction should affect the dynamics very sensitively. Compared with the hydrodynamic force from the solvents, the

force could be very large for small molecules. On the other hand, if the molecules are large, the friction of hydrody-

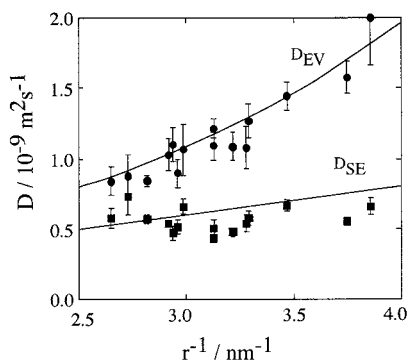


FIGURE 4. Size dependence of D of the hydrogen abstracted radicals (■) and their parent molecules (●) in ethanol. The solid lines represent D calculated by eq 4 (D_{SE}) and eq 5 (D_{EV}).

namics from the solvent is already very large and the additional friction cannot disturb the movement seriously. The above consideration predicts that if the radical size is larger, the diffusion should be similar to that of the parent molecule, which agrees exactly with the observed results shown in Figure 4.

(b) Temperature Dependence. The temperature dependence of D_p and D_r for some chemical systems was investigated in alcoholic solvents.²³ All the results revealed that D can be expressed by the Arrhenius relation with a single activation energy (E_D):

$$D = D_0 \exp(-E_D/kT)$$

Generally, the E_D values of the radicals were smaller than those of the parent molecules. Even among the parent molecules, E_D seemed to be dependent on the molecular size. Below in this section, we show that the size dependence of D_r as well as E_D can be consistently explained on the basis of an empirical equation by Evans et al.²⁴

The size-dependent E_D was observed and studied by Evans and co-workers,²⁴ and they derived an empirical equation to predict the size effect as

$$D_{EV} = AT/\eta^p \quad (5)$$

where

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

$$p = c/r_A + d$$

r_A is the radius of the (stable) solute, and a , b , c , and d are parameters to fit the experimental data. Using this equation, the activation energy of the diffusion is given by

$$E_D = E_\eta(c/r_A + d) \quad (6)$$

where E_η is the activation energy of the viscosity when we fit the temperature dependence of the viscosity by the Arrhenius equation. This relation reasonably reproduced the observed solute size dependence of E_D of the parent molecules satisfactorily.²³

Interestingly, the radical dependence of E_D and also the difference between E_D of the parent molecules and

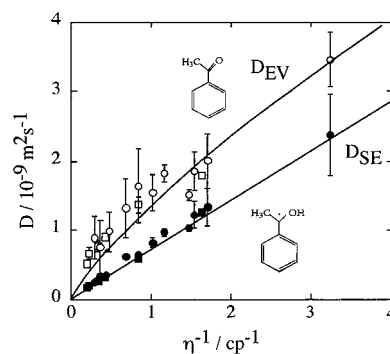


FIGURE 5. Viscosity dependence of D of the acetophenone ketyl radicals (closed symbols) and acetophenone (open symbols). Polar solvents and nonpolar solvents are represented by the squares and circles, respectively.

radicals can be explained by the above equations, if we assume that the slow diffusion of the radicals can be treated as an apparent expansion of the radical size by V_0 from the parent size. From the fitting of E_D of the radicals, we found that $V_0 = 0.8 \text{ nm}^3$ in 2-propanol reproduced the size dependence of E_D of the radicals well.²³ In this analysis, the slow diffusion of the radicals is explained in terms of the larger effective volume. Of course, the molecular volumes cannot be so largely expanded by the reactions. The increase of the effective volume should be interpreted as the enhanced intermolecular interaction as we will discuss later (section 8). A point emphasized here is that, using these empirical equations, we may be able to predict D_r of many radicals at any temperature.

(c) Solvent Effect. The solvent dependence of the radical diffusion was investigated for several systems.^{17,25} For example, D of benzophenone ketyl radical (BPK) was smaller than that of benzophenone (BP) in a variety of solvents (Figure 5). Again, D of the parents measured by Taylor dispersion agrees well with our data.^{20,21} Interestingly D of the parents curved when we plotted that data against the inverse of the viscosity. This curved nature is already well known for stable molecules.^{24,26} More interestingly, D of radicals is almost proportional to the inverse of the viscosity, which is exactly predicted by the SE relation. This dependence suggests that the radical movement is still governed mainly by the hydrodynamic force of the solvent molecules.

Among the solvents we investigated, water is a unique solvent for the radical diffusion.²⁵ For example, D_r of acetophenone ketyl radical is much smaller than D_p in ethanol. However, with increasing water content in the solvent, D_r becomes closer to D_p (Table 1). This effect was interpreted in terms of the hydrophobic hydration.

The solvent density dependence of D of transient radicals from pyrazine, benzophenone, and quinoxaline was measured in supercritical fluids (SCF) of trifluoromethane and CO_2 using the hydrogen abstraction reaction from triethylamine.²⁷ It was found that D_r is almost proportional to T/η and that, even in SCF, D values of the radicals are smaller than those of the stable molecules with similar sizes and shapes. It is interesting to note that the ratio of D values between the radical and the parent,

$R = D_r/D_p$, is larger than that determined in the liquid phase (e.g., $R = 0.33$ in ethanol and 2-propanol for pyrazinyl radical, while $R = 0.6$ in CF_3H), and it is not sensitive to the density.²⁷ This fact means that the cause of the slow diffusion of the radicals is not effective in a lower density region.

4. Ionic Radicals

Slow diffusion was also observed for ionic radicals using a photoionization reaction of *N,N,N,N*-tetramethyl-*p*-phenylenediamine (TMPD).²⁸ The TG signal probed at 633 nm mainly consists of the amplitude grating (δk term). The temporal profile of the species grating component was analyzed by a single-exponential function, and we assigned the signal to the species grating of the TMPD cation radical (TMPD⁺). By changing the probe wavelength, the diffusions of TMPD and TMPD⁺ were observed. From the slopes of the decay rate constants vs q^2 plots, the diffusion constants of TMPD and TMPD⁺ were determined to be 1.8 and 0.91 $\text{m}^2 \text{s}^{-1}$, respectively. Again, the diffusion of the cation radical was slower than that of the parent molecule.

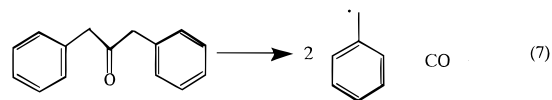
Spiropyrans are prototypes of photochromic molecules. They are transformed to a charge-separated merocyanine form, which is an unstable species in many matrixes (although it is not a radical). The D values of a spiropyran (SP) (1',3',3'-trimethylspiro-8-nitro(2*H*-1-benzopyran-2',2'-indoline) and the merocyanine form were investigated by the TG method at two different probe wavelengths. The D value of the transient (colored) form was found to be smaller than that of the original (colorless) form.²⁹ Recently, using an optical heterodyne detection of the TG signal, the signals from both species were separately observed, and the D values of the SP and merocyanine forms in ethanol were determined to be 0.57×10^{-9} and $0.46 \times 10^{-9} \text{m}^2 \text{s}^{-1}$.³⁰ The change of D was explained in terms of the photoinduced electric dipole moment.

We selectively created the neutral and charged radicals under a similar condition by adjusting the pH of the solution.³² The selective creation was confirmed by the transient absorption technique. The D values of the neutral and charged radicals and their parents are simultaneously determined (Table 1). We found that the D values of the neutral and charged radicals are very similar. The solvent effects of the D values of the neutral and charged radicals are also very similar in various solvents.³² Furthermore, activation energies of the neutral and charged radicals are also found to be very similar. These very similar behaviors between the neutral and charged radicals suggest that the intermolecular interactions between the radicals and solvents are closely related to the electronic interaction.

5. Radicals by Bond Dissociation Reactions

D of benzyl radical (BR) created by the photodissociation reaction of dibenzyl ketone (DBK) was measured in several organic solvents.³³ In this case, the self-termination reaction of BR cannot be neglected compared with $D_r q^2$ under

the experimental conditions. If the reaction proceeds by



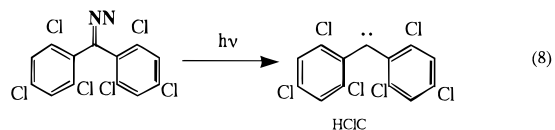
the second-order kinetics with a rate comparable to that of the diffusion, the temporal profile can no longer be expressed by eq 1. Even in such a case, as long as $D_r q^2$ is larger than $k_2 C(0)$ (k_2 is the second-order reaction rate constant, $C(0)$ is the initial concentration of the radical), the second-order kinetics can be approximated by the first-order kinetics with a rate constant of $2k_2 C(0)$. Therefore, the TG signal due to BR can be fitted by a single-exponential function with a rate constant of $D_r q^2 + 2k_2 C(0)$. From the analysis of the TG signal, D values of BR, DBK, and CO were determined separately.

Interestingly, it is found that D of BR is slightly larger than that of DBK. The ratio R is about 1.25, which is expected from the ratio of the molecular volume of BR to that of DBK and the SE equation. Indeed, D of BR is close to that of toluene. Therefore, we concluded that the diffusion of BR is not slower than that of the analogous closed-shell molecule.

Recently, we succeeded in measuring D of the 4-aminophenylthiyl radical, which is created by the photodissociation reaction of bis(*p*-aminobenzene)disulfide.³⁴ It is found that the diffusion constant of this radical is also similar to or even slightly larger than that of *p*-chloroaniline, which is an analogous molecule of the closed shell.

6. Carbenes and Radicals from Carbenes

One of the interesting unstable intermediates in chemistry is a family of biradicals. As an example, we tried to measure D of a carbene created by the photolysis from the diazo compounds. Unfortunately, however, most of the carbenes are converted to other species too quickly to be measured even by the TG method. Recently, relatively stable carbenes have been synthesized, such as 2,2',4,4',6,6'-hexabromodiphenyl carbene (HBrC) after the photolysis of 2,2',4,4',6,6'-hexabromodiphenyldiazomethane (HBrM), 2,2',4,4',6,6'-hexachlorodiphenyl carbene (HCIC) from the analogous diazomethane, and so on.³⁵ The main



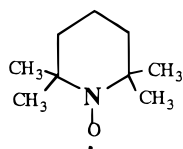
path of the decay in the degassed benzene solution may be the dimerization reaction with a half-life of ca. 20 ms–1 s,³⁵ which is sufficiently longer than the time period of the grating measurement. In this reaction system, diazomethanes, carbenes, and nitrogen molecule (N_2) can contribute to the signal. The results show that the D values of the carbenes are even smaller than those of the corresponding radicals.^{36,37} D of HBrC is larger than that of HCIC, which implies that the diffusion process depends on the substituents.

Under the air-saturated condition, the carbenes are converted to carbonyl oxides, and D of the carbonyl oxide was also measurable. The D values of the carbonyl oxides are slightly smaller than those of the parent diazomethanes; carbonyl oxide from HBrC has $R = 0.82$, and that from HMeC is $R = 0.91$.³⁷ The ratio of the diffusion constants implies that the diffusions of the carbonyl oxides are close to those of the radicals rather than the carbenes.

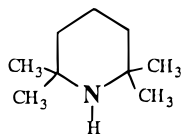
7. Stable Radicals

In contrast to the chemically unstable transient radicals, D values of chemically stable radicals have been measured by EPR tomography.^{3,4} However, comparison of D values of chemically stable radicals with those of their analogous closed-shell molecules has never been tried. We investigated D of chemically stable radicals as well as their analogous closed-shell molecules by the Taylor dispersion method in various solvents.³⁸ In alcoholic solvents, D values of some stable radicals (such as TEMPO and its derivatives) are slightly smaller than those of the closed-shell molecules. However, the difference is very small compared with that observed for the transient radicals. Even in alcoholic solvents, D of a large stable radical (DPPH) is almost identical to that of the closed-shell analogue. In nonpolar solvents, D values of free radicals and their analogous molecules are almost the same.

Independently, D of some stable radicals were investigated by Donkers and Leaist.²¹ They also found that D values of some stable radicals in aqueous solution are very similar to those for anions (nonradical molecules).



2,2,6,6-tetramethyl-1-piperidinyloxy



2,2,6,6-tetramethylpiperidine

8. Radical Diffusion

An interesting and important question is, “why do many transient radicals diffuse slower than the parent molecules?” In section 3b, we treated the radical diffusion as if the apparent molecular volumes of the radicals are expanded. However, rather than the molecular size expansion or formation of a complex between the radical and solvent, we consider that the answer to this question may be an enhanced attractive intermolecular interaction between the radicals and solvent molecules.

Recently, Bagchi and co-workers studied the diffusion processes as a function of solute–solvent interactions.^{39,40} They found that the diffusion becomes slower with an increase of the attractive intermolecular interaction. D of the solute was found to be very sensitive to the interaction. Using large attractive and repulsive interactions, they observed superstick and subslip limits of the diffusion constant, respectively.

What is the origin of the enhanced intermolecular interaction? (We have denied a participation of the hydrogen bonding as the origin before.) Recently, Morita

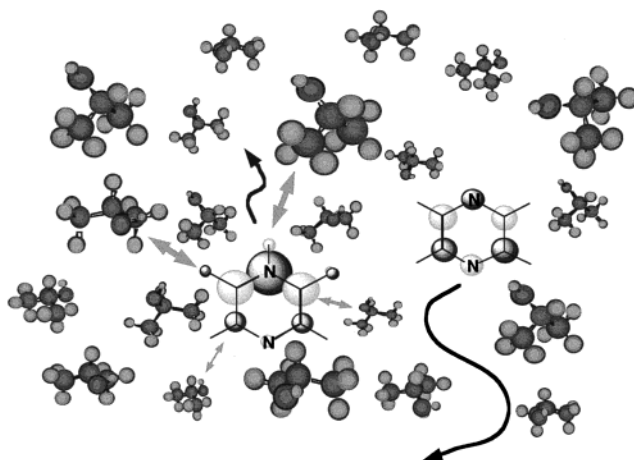


FIGURE 6. Illustration showing that slow radical diffusion is due to the attractive intermolecular interaction (arrows) between the radicals and the solvent (2-propanol). The attractive intermolecular interaction is caused by an enhanced charge sensitivity of the radicals. The radius of the circle at each atom of two molecules (left, PyH and right, Py) represents the amplitude of the region vector of the response kernel. The color of the circles indicates the sign of the amplitude.

and Kato reported an ab initio molecular orbital (MO) calculation of the response kernel which represents the response of the intermolecular charge polarization by external electrostatic field for pyrazinyl radical (PyH) and pyrazine (Py).⁴¹ The results revealed that the charge sensitivity of PyH is greatly enhanced compared with that of Py. The enhanced sensitivity will cause the enhanced intermolecular interaction (Figure 6). Indeed, molecular dynamics (MD) simulations incorporated in the charge response kernel showed that PyH diffuses about one-third as fast as Py.⁴² The D values of PyH and Py calculated by this method (after corrected for the viscosity) reproduced D of PyH and Py obtained simultaneously. The MO calculation showed that not only PyH but also BPK has an enhanced charge sensitivity compared with that of BP. The ratio of the sensitivity values between BPK and BP (0.57) is close to the ratio of D values, $R = 0.61$, observed experimentally. Interestingly, those researchers observed that the charge sensitivity of BR is close to that of toluene, which is consistent with the experimental observation described in section 5.

These theoretical studies support the view that the slow diffusion of the radicals originates from enhanced attractive intermolecular interaction. However, we have to admit that the MD simulation cannot explain all the experimental results we found. We hope that the slow diffusion of the transient radicals will be fully explored in the future.

Concluding Remarks

In this Account, the diffusion processes of transient radicals and stable radicals in solution are compared with those of the closed-shell molecules with similar shapes and sizes. Some of them, in particular the D values of the stable radicals, are close to those of the closed-shell analogues, but most of the transient radicals diffuse slower than the closed-shell molecules. The slower diffusion is attributed to the enhanced intermolecular interaction.

Determination of the diffusion constant could become a new method for probing the solute–solvent interaction. An interesting target of a future study for the translational diffusion process of transient species may be the diffusion of the excited molecules to answer the question, “can the electronic excitation change the diffusion process?” This point should be clarified in the future.

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