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Translational diffusion process of charged radicals: *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine and its cation radical

Masahide Terazima *, Toshiya Okazaki, Noboru Hirota

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

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Abstract

The translational diffusion coefficients (*D*) of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) and its cation radical were measured by the transient grating method. The *D* value of the free cation radical is about twofold smaller than that of the neutral molecule. The *D* values of both species were calculated on the basis of the Stokes–Einstein (SE) relation, the Spernol–Wirtz modification of the SE relation and the Hubbart–Onsager theory. The calculations and comparisons with previously determined *D* values of neutral radicals suggest that, contrary to the intuitive picture of the diffusion of charged species, it may be the unpaired electron and not the charge that mainly governs diffusion.

Keywords: Translational diffusion process; Charged radical; Transient grating method

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1. Introduction

The rates and mechanisms of many chemical reactions in solution are influenced by diffusion processes through encounter rates. When the diffusion process becomes the rate-determining step, such reactions are said to be diffusion controlled. In such reactions, measurements of the diffusion coefficients (*D*) of the intermediate species are crucial for the analysis of the reaction schemes and kinetics [1–3]. Recently, we have demonstrated that the transient grating (TG) technique is a direct, convenient and accurate method for the determination of the *D* values of reactive transient species in solution [4–8]. We have successfully applied this method to photoinduced hydrogen abstraction reactions, and have found that the *D* values of the transient radicals are much smaller than those of the parent molecules, although the molecular volumes are very similar [5,6,8]. From extensive studies on various neutral radicals, we now believe that the unpaired electron plays an important role in the radical diffusion process. In this study, we investigate the diffusion process of a charged radical in an alcoholic solvent by the TG method. In addition to elucidating the fundamental process of diffusion of the transient species generally, the result is important in the analysis of the kinetics of electron transfer systems, in which spatial movements of charged species control the dynamics.

There have been many theoretical and experimental studies on the diffusion processes of ionic species [9–22]. On the basis of these investigations, it is commonly believed that long- range electrostatic interaction is important for the diffusion process in a solution containing charged species. The diffusion should be described by the hydrodynamic friction as well as the dielectric friction. However, we have observed the slow diffusive character of neutral radicals, and it is of interest to compare the effect of the charge with that of the unpaired electron for the diffusion of a charged radical.

Traditionally, the *D* values of charged species have been determined by conductivity measurements. For example, Freeman and coworkers [13–15,18] have reported the *D* values of charged species over a wide range of conditions, from normal liquids to low density gases. They have found that the *D* values of cations are about threefold smaller than those of the neutral molecules in alkanes [14,18]. However, since this method can only be applied to a charged species, it is rather difficult to compare directly the *D* values of charged species with those of the parent neutral molecules under the same experimental conditions. Furthermore, so far, only the effect of charge has been considered to be of importance in diffusion and the possible contribution of the unpaired electron has been neglected. The measurement of the *D* values of ionic radicals with relatively large sizes, which are usually important in chemical reactions, is rare.

In this study, we measure directly the *D* values of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) and its

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* Corresponding author.

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cation radical simultaneously by the TG method. The choice of this species is based on the relatively stable character of the charged form and the extensive studies on its photoionization [23–32]. Because of the low ionization potential in polar solvents, TMPD is a popular solute for the investigation of photoionization. For example, Hirata et al. [31,32] have extensively studied the ionization process in various solvents using a transient absorption method. According to their results, TMPD is ionized by a one-photon process to produce a geminate pair consisting of a TMPD cation radical and an electron. After the geminate pair recombination process in the nanosecond range, the solvated electron is scavenged by the solvent and/or impurity in the solution. The TMPD free cation radical survives for a long time in alcoholic solvents [23,26,31].

From the results of our experiments, the comparison with calculated D values and the observations of previous investigations on neutral radicals, we suggest that the diffusion of the TMPD cation is more strongly affected by the unpaired electron than by the charge of the cation.

2. Experimental details

Details of the TG experimental method have been published elsewhere [4–8]. We briefly describe the essential step for the measurement. The third harmonic of an Nd:YAG laser (Spectra Physics DC-11; $\lambda = 355$ nm) was used for the photoexcitation of TMPD in ethanol. Typically, the excitation laser power for the TG measurement was less than 0.1 mJ per pulse. After crossing two beams from the excimer laser in the sample solution, the time dependence of the grating signal, probed by an He–Ne or Ar ion laser (Uniphase 2213), was monitored with a photomultiplier (Hamamatsu R928). Various probe beam wavelengths from the Ar ion laser were selected by a monochromator. The observed TG signal was averaged by a digital oscilloscope (Tektronix 2430A) and the data were then transferred to a microcomputer for data processing. The repetition rate of the excitation pulse was typically approximately 3 Hz. The sample solution was deoxygenated by nitrogen bubbling. The irradiated volume was so small (typically about 4×10^{-3} cm^3) compared with the entire volume of the sample solution (approximately 4 cm^3) that the accumulation of the reaction product was not serious. The fringe spacing (Λ) was calculated from the decay of the thermal grating signal of a methyl red–benzene solution using the thermal diffusion constant of benzene described in Ref. [5].

For transient absorption measurements, the sample solution was irradiated by an Nd:YAG laser and probed by the light from a 900 W Xe lamp. The probe light was monochromated with a Spex model 1704 spectrometer and detected by a photomultiplier. The time dependence was recorded with a digital oscilloscope.

Nuclear magnetic resonance (NMR) self-diffusion measurements were carried out on a JEOL JNMEX270-W spectrometer at a proton resonance frequency of 270 MHz. The sample was contained in a 5 mm sample tube. A homospoil coil of the spectrometer was used to generate the magnetic field gradient pulses and the observed amplitude of the spin echo signal was analysed by the relation

$$I_{\mathrm{NMR}} \propto \exp[-\gamma^2 G^2 \delta^2 D(\Delta - \delta/3)]$$

where γ is the magnetogyric ratio of the proton, G is the magnetic field gradient, δ is the gradient duration and Δ is the interval between the r.f. and gradient pulses. The parameters used to determine D in this equation were calibrated using the D value of water ($D = 2.54 \times 10^{-9}$ m^2 s^{-1} at 30 °C) under the same experimental conditions.

Spectrograde ethanol was used as received. The typical concentration of the solutions was 5 mM.

3. Results

After photoexcitation to the excited singlet state, TMPD relaxes to the ionizing state and then forms a TMPD cation radical [23–32]. During the non-radiative processes on relaxation, TMPD releases excess energy as heat to the matrix. Hence the spatial modulation of the excitation light, which is introduced by the interference between the two excitation beams, induces the same modulation pattern of temperature (thermal grating signal) and cation species (population grating signal of the cation) and an antiphase (180° phase shifted) modulation of the parent molecules (population grating signal of TMPD). Each component diffracts the probe beam as the TG signal to a phase matched direction. The thermal grating and population grating signals are destroyed by the thermal diffusion and mass diffusion respectively.

Fig. 1 shows a typical temporal profile of the TG signal after photoexcitation of TMPD in ethanol probed with an He–

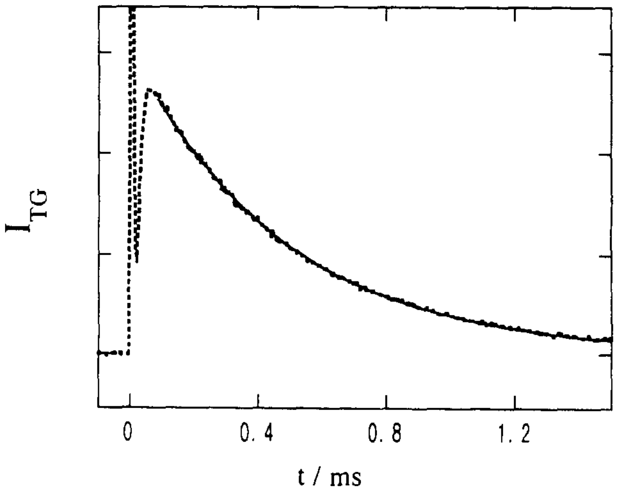

Fig. 1. Temporal profile of the TG signal after photoexcitation of TMPD in ethanol probed at 633 nm. The main part of the signal on the fast time scale comes from the thermal grating and the slower component is due to the TMPD cation radical. The dotted line is the experimentally observed result and the full line is the curve calculated using Eq. (2).

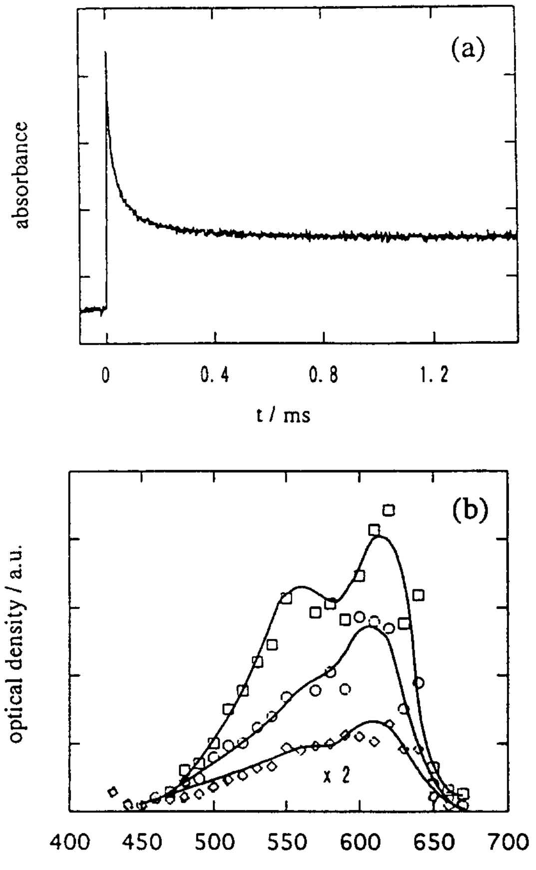

Fig. 2. (a) Temporal profile of the transient absorption signal probed at 633 nm. The transient absorption spectra at 5, 30 and 300 μs after photoexcitation are shown in (b).

Ne laser. The initial strong signal is due to the contribution of the thermal grating, which decays with a time constant of $D_{th}q^2$ (D_{th} is the thermal diffusion coefficient; $q=2\pi/\Lambda$ is the wavevector of the grating). The signal takes a minimum value at a certain time and then rises again. After the second peak of the signal, it decays again and the decay curve is well characterized by a single exponential function. Since the time constant of the decay is about 2–3 orders of magnitude smaller than the thermal diffusion time, the signal should be due to the population grating and the decay is caused by mass diffusion in the solution.

In order to identify the chemical species involved in the population grating signal, we measured the transient absorption on the time scale of the TG measurement. The photoexcitation of the sample induces a rather strong transient absorption in the 550–650 nm range. The signal first decays rapidly with a time constant of 0.2 μs^{-1} and then with a second- order decay. The signal intensity then remains almost constant in our TG observation time scale (Fig. 2(a)). The spectra at 5, 30 and 300 μs after excitation are almost identical and are very similar to the previously reported spectrum of the TMPD cation [23–27]. The first decay in the early time range, the subsequent second-order decay and the long- lived nature of the charged species are consistent with previous observations [31]. After the photoionization of TMPD, the geminate ion pair is generated and is then transformed to a loose or solvent-separated ion pair. The ion pair is separated into free ions by the thermal fluctuation of the surrounding molecules. The solvated electron should be scavenged on a time scale of several hundred nanoseconds [31]. Therefore the electron has already disappeared at our observation time and is not observed in our spectrum. On the basis of these facts, we conclude that the possible chemical species giving rise to the TG signal are TMPD itself and the free cation radical.

When the intermediate species is stable on the time scale of the TG measurement, the time dependence of the diffracted signal, $I_{TG}(t)$, induced by fringes with wavevector q, can be calculated from the diffusion equation and the theory of optical gratings. The result is given by [5]

$$\begin{aligned} I_{TG}(t) = \alpha[& \delta n_{th}^0 \exp(-D_{th}q^2t) - \delta n_{TMPD}^0 \\ & \exp(-D_{TMPD}q^2t) + \delta n_+^0 \\ & \exp(-D_+q^2t)]^2 + \beta[-\delta k_{TMPD}^0 \\ & \exp(-D_{TMPD}q^2t) + \delta k_+^0 \\ & \exp(-D_+q^2t)]^2 \end{aligned} \qquad (1)$$

where a thick grating in a weak signal limit is assumed, and α and β are constants which depend on the laser intensities of the probe and excitation beams and the experimental configuration. δn_{TMPD}^0 and δn_+^0 are the refractive index changes due to TMPD and the light-induced cation species respectively, δk is the extinction coefficient change due to these species and D_{TMPD} and D_+ are the mass diffusion coefficients of these species.

To analyse the observed signal, we made the following assumption: the refractive index and absorption changes due to the depletion of TMPD (δn_{TMPD}^0 and δk_{TMPD}^0) are negligible compared with the δn_+^0 and δk_+^0 terms at the He–Ne laser wavelength. This assumption is rationalized by the fact that the He–Ne laser wavelength is approximately at the peak of the absorption band of the TMPD cation (approximately 630 nm), while the absorption of TMPD is far from the probe wavelength in energy. Indeed, the dip between the thermal grating signal and the population grating signal (Fig. 1) indicates that the δn_+^0 and δk_+^0 terms in Eq. (1) contribute to the TG signal ($\delta n_+^0 > 0$ and $\delta n_{th}^0 < 0$ at this wavelength), and the observed single exponential decay is consistent with only one species involved in the signal.

On the basis of this assumption, after the complete decay of the thermal grating signal, the time dependence of the TG signal should be expressed by

$$I_{TG}(t) = [\alpha(\delta n_+^0)^2 + \beta(\delta k_+^0] \exp(-2D_+q^2t) \qquad (2)$$

The decay rate constant of $I_{TG}^{1/2}(t)$ is D_+q^2, and a plot of this quantity against q^2 is shown in Fig. 3. The plot gives a straight line with a small intercept, which is consistent with the long-lived nature of the cation. From the slope, D_+ is determined as 0.91×10^{-9} m^2 s^{-1}.

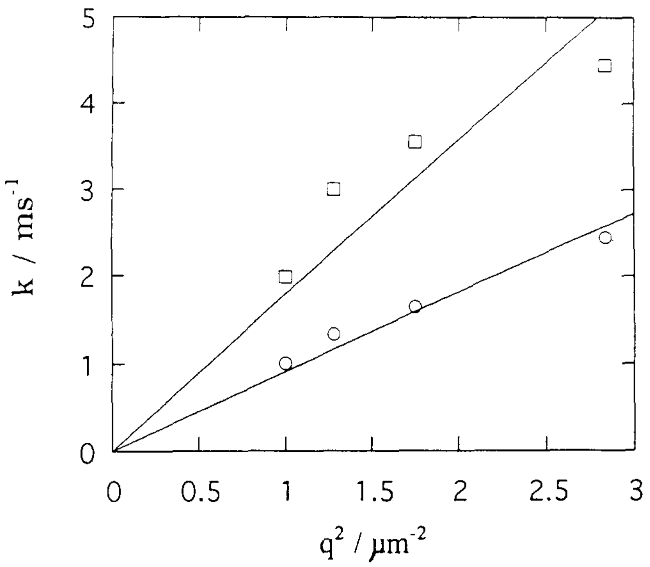

Fig. 3. Plot of the decay rate constants (k) of the TG signal vs. the square of the wavevector of the grating (q^2). Squares denote the decay rate of the TG signal due to TMPD probed at 515 nm and the circles denote the decay rate of the TG signal due to the TMPD cation probed at 633 nm. The slopes give the D values of the species.

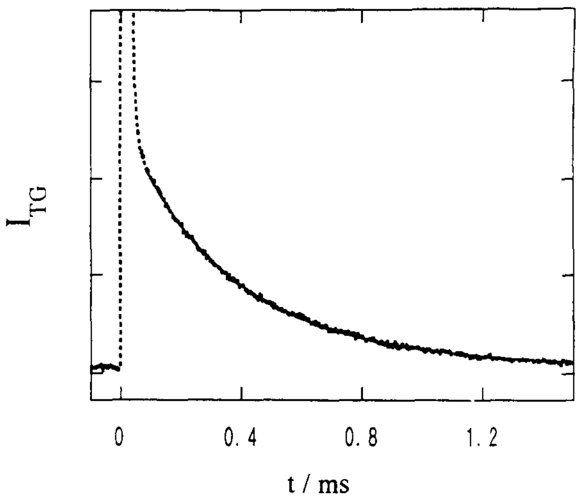

Fig. 4. The observed TG signal probed at 515 nm (dotted curve). The best-fit curve using Eq. (4) is shown by the full line.

The reason why we could not observe the population grating signal due to neutral TMPD in the above experiment is that the refractive index and/or absorption changes are negligible at the He–Ne laser wavelength. Therefore, to determine D_{TMPD}, we used an Ar ion laser to probe the grating. At a shorter wavelength than 633 nm, we expect that the strong absorption band of TMPD should contribute to the signal. Fig. 4 shows the TG signal probed at 515 nm. At this wavelength, the contribution of $\delta k_+{}^0$ decreases (Fig. 2) and, as a consequence, the TG signal intensity decreases. At the same time, the decay curve deviates slightly from a single exponential function. Since the absorption of TMPD is still negligible at this wavelength, we can neglect the δk terms from both TMPD and cation compared with the δn terms. Therefore the TG signal after complete decay of the thermal grating signal is expressed by

$$I_{TG}(t)=\alpha[-\delta n_{TMPD}{}^0\exp(-D_{TMPD}q^2t)+\delta n_+{}^0\exp(-D_+q^2t)]^2 \quad (3)$$

It should be noted that the dip between the thermal grating and population grating signals disappears at this probe wavelength. This disappearance is because, at 515 nm, the sign of $\delta n_+{}^0$ changes to negative which is now the same as δn_{th}. (Note that $\delta n_{TMPD}{}^0$ is still positive at this wavelength.) The observed temporal profile of the TG signal can be fitted well with a double exponential function with the same signs for the pre-exponential factors

$$I_{TG}{}^{1/2}=a_s\exp(-k_st)+a_f\exp(-k_ft) \quad (4)$$

where subscripts s and f denote the slow and fast components respectively. We found that the decay rate constant of the long- lived component (k_s) is close to D_+q^2 determined from the He–Ne probe experiment. Therefore the shorter lived component should be due to TMPD. Indeed, when the probe beam wavelength is shifted further to the blue (488 nm), the relative contribution of this component increases. Again this is expected because $\delta n_{TMPD}{}^0$ should increase as the wavelength approaches the absorption band of TMPD. Fig. 3 also shows the k_f vs. q^2 plot probed at 515 nm. The slope (D_{TMPD}) is 1.8×10^{-9} m^2 s^{-1}. This value is about twofold larger than D_+.

To support the adequacy of the above analysis by an independent method, we measured D_{TMPD} by the NMR technique. D_{TMPD} in ethanol-d_6 is 1.5×10^{-9} m^2 s^{-1}, which is close to the value determined by the TG method. Hereafter in this paper, we will use D_{TMPD} and D_+ determined by the TG experiment because they were measured under exactly the same experimental conditions.

4. Discussion

The results of our measurements show that the cation diffuses about twofold slower than the neutral molecule. First, we examine whether this difference can be explained by translational diffusion theories in solution. Frequently, the diffusion coefficient in solution is related to the fluid properties through the Stokes–Einstein (SE) relation [3]

$$D=kT/a\pi r\eta \quad (5)$$

where r is the radius of the diffusing molecule, η is the viscosity of the solution and $a=4$ in the slipping boundary limit and $a=6$ in the sticking boundary limit. However, this relationship usually underestimates D, and various modifications have been proposed. In previous investigations, the semi-empirical modification by Spernol and Wirtz [33] (D_{SW}) was found to reproduce well the experimentally observed D values [34]. We also found that the values estimated by this relation agree reasonably well with the D values

Table 1
Diffusion coefficients (D) of TMPD and its cation radical, and the calculated values using the Stokes–Einstein (SE) relation, the Spernol–Wirtz (SW) equation and the Hubbard–Onsager (HO) theory

	$D(10^{-9}\ \mathrm{m^2\ s^{-1}})$
TMPD	1.8
TMPD$^+$	0.91
Calculated	
SE	0.905 [a], 0.603 [b]
SW	1.99 [a], 1.33 [b]
HO	0.664 [a], 0.504 [b]

[a] Slip boundary condition.
[b] Stick boundary condition.

of various aromatic compounds in alcoholic solutions [6,8]. D_{SW} is given by [33]

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

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

where the subscripts M and A represent the solute and the solvent respectively. The reduced temperatures, T_M^r and T_A^r, which are parameters of the intermolecular interactions, are calculated by

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

using the freezing (T_X^f) and boiling (T_X^b) points of the solute ($X \equiv M$) or the solvent ($X \equiv A$). f_{SW} is sometimes called the microscopic friction.

In this work, the radii of the solutes were calculated from the molecular geometries and the van der Waals' radii. The radii of the solvents were determined using the same method as Spernol and Wirtz [33] from the density, molecular weight and the free volume (74%). The viscosities of the solvents were taken from Ref. [35]. The calculated values of D_{SE} and D_{SW} are listed in Table 1 for $a = 4$ and $a = 6$. Interestingly, we find that D_{SW} is in good agreement with D_{TMPD}, while D_+ is close to D_{SE}.

In the above treatment, only the hydrodynamic friction is considered, and the effect of the electrostatic field exerted by the ion is neglected. However, in the diffusion of a charged molecule, the additional friction between the moving ion and the solvent dipoles should be taken into account. Several theories which contain this dielectric friction within a continuum model have been proposed [9–12,16,21]. Of these, in the theory by Hubbard and Onsager (HO), both types of friction are treated together simultaneously in the electrohydrodynamic equation [10,11]. The applicability of HO theory to the D values of charged atoms or small molecules has been tested in many ways. It has been found that HO theory successfully explains the D values obtained from the limiting ionic conductance [16,21]. We have applied HO theory to calculate D_+. The HO equation in a dielectric solution of viscosity η and pressure p is given by

$$\eta\nabla^2 v = \nabla p - (1/2)[E_0 \times (\nabla \times P^*) + E_0(\nabla P^*)]$$

where E_0 and P^* are the electrostatic field due to the presence of the ion and the polarization deficiency by orientational relaxation of the flowing solvent dipoles respectively. The numerical solution has been given in terms of a function of dimensionless quantity of

$$x = f/\eta R_{HO} \tag{7}$$

where f is the friction coefficient and R_{HO} is the HO radius given by

$$R_{HO} = \left\{ \frac{e^2}{16\pi\eta\epsilon_0^2} [((\epsilon_0 - \epsilon_\infty)\tau_D) \right\}^{1/4} \tag{8}$$

Ibuki and Nakahara [16] expanded x as a function of a parameter r/R_{HO} as

$$x = y(r/R_{HO}) + \sum_n a_n (R_{HO}/r)^n \tag{9}$$

We used the following parameters to calculate D_+ in ethanol; $y = 4\pi$, $a_1 = -2.7866$, $a_2 = 8.6216$, $a_3 = -3.3425$ and $a_4 = 0.39550$ for the slipping boundary condition and $y = 6\pi$, $a_1 = -2.2145$, $a_2 = 6.9579$, $a_3 = -2.7296$ and $a_4 = 0.33780$ for the sticking boundary condition [16].

The calculated D_{HO} values are listed in Table 1. Qualitatively, the similar values of D_{HO} and D_{SE} result from the relatively large size of the molecule. In HO theory, the ion is treated as an inpenetrable sphere with a charge at the centre. Hence the effect of charge becomes negligible for a large molecule. Despite the several assumptions of this theory, the similar values of D_{HO} and D_{SE} suggest that the charge does not play a major role in the diffusion process of this molecule through dielectric friction.

There are two reasons why we believe that the effect of the unpaired electron is stronger than that of the charge. First, the calculated D_{SE} value closely reproduces the observed D_+ value. This situation is very similar to that previously observed for neutral radicals [5,6,8]. For a TMPD radical without charge, i.e. a neutral TMPD radical in solution, our empirical relation predicts that the expected D value of this neutral radical should be close to D_{SE}; in other words, the effect of charge could be negligible in D. The second reason originates from the experimentally obtained molecular size dependence of $D_{\mathrm{parent}}/D_{\mathrm{radical}}$. In previous work [8], we found that $D_{\mathrm{parent}}/D_{\mathrm{radical}}$ depends on the molecular size. The ratio of D_{TMPD} to D_+, $D_{TMPD}/D_+ \sim 2$, is equal to that expected from the size dependence of the ratio for neutral radicals. Considering these observations, we suggest that the charge of the TMPD cation radical is not an important factor in determining the diffusion in alcoholic solvents.

Freeman and coworkers [13–15,18] have investigated the diffusion of cation radicals in γ-irradiated liquids from measurements of the conductivity. They have found that the D values of the cations are about threefold smaller than those of the neutral molecules in alkanes [13,18]. The large reduction of the mobility was explained in terms of the larger effective radii of the ions than of the neutral molecules. They attributed the cause of the larger size to the electrostriction effect of the charged radicals, i.e. they proposed that the solvent molecules are clustered around the ions due to an electrostatic effect [13,18]. The basic idea of the clustering model is very similar to our model proposed for neutral radical diffusion [5,6,8]. In a series of studies using this model, we have successfully explained the slow diffusion of radicals as well as the anomalous solute size dependence and temperature dependence of D_{radical}. The only difference is that, in the neutral radical case, we believe that the high polarizability due to the unpaired electron of the radical may be the main cause of aggregation. Our observations here, together with previous investigations on neutral radicals, suggest that, in diffusion, the unpaired electron is more important than the charge even in the charged radical of TMPD. At this stage, we are unaware whether this conclusion holds for other charged radicals in general. From theoretical studies on the diffusion of charged atoms or small molecules, it is well established that the charge leads to a decrease in diffusion due to dielectric friction. Considering these traditional arguments, it would perhaps be better to say that the diffusion of a cation radical with a relatively large size could be controlled by the unpaired electron. Further experimental and theoretical investigations are needed for a complete understanding of the diffusion processes of charged radicals.

5. Conclusions

The TG signal probed at 633 nm after photoexcitation of TMPD–ethanol solution is composed of the thermal grating and population grating due to the cation radical. From the time profile of the signal, the translational diffusion coefficient (D_+) of the TMPD cation radical can be determined. At a shorter probe wavelength, TMPD and its cation radical contribute to the population grating signal, from which the D value of TMPD can be measured. The observed D_+ value is about twofold smaller than that of TMPD. The large reduction in diffusivity is attributed to solvent clustering around the cation radical. From a comparison with previous results on neutral radicals, we suggest that the attractive force between the radical and the surrounding molecules leads to aggregation which makes the translational diffusion of the radical slower than that of the parent molecule.

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