Diffusion processes of the intermediate radicals created by the photochemical reactions of ketones in alcoholic solvents are investigated by using the transient grating (TG) method. The electrically neutral radicals and the anion radicals of acetophenone, benzaldehyde, xanthone, benzophenone and benzil were created selectively by controlling the concentration of sodium hydroxide (NaOH) in alcoholic solvents. The translational diffusion constants \((D)\) of the anion radicals, the neutral radicals, and the parent stable molecules can be successfully measured under the same conditions by this method. It is found that both the neutral and anion radicals diffuse slower than the parent molecules. Values of \(D\) of the anion radicals, the neutral radicals and the parent molecules are compared in detail in wide ranges of solvent viscosities, solute sizes and temperatures. Under any conditions, \(D\) values of the charged radicals are similar to those of the neutral radicals. A possible origin of such a similarity is discussed in terms of the intermolecular charge polarizabilities of the radicals.

1 Introduction

Diffusion constants \((D)\) have been measured by several methods and analyzed based on various theories.\(^1\) Values of \(D\) are often described by the equation derived from the hydrodynamic theory such as the Stokes–Einstein (SE) equation or many other empirical modifications of the SE equation.\(^2\) Experimentally determined \(D\) values for molecules without any intermolecular interaction can be reproduced reasonably well based on these equations. Interesting cases arise when intermolecular interaction plays an important role in the dynamics. The translational diffusion process of molecules is sensitive to the environment around the solute molecule, and information of the intermolecular interaction, the solvation structure and the existence of microscopic aggregation, etc., may be extracted from the studies of the diffusion process.

For example, there are three interesting cases for diffusing species; ionic molecules (atoms), hydrogen bonded systems, and transient radicals. Mobilities \((\mu)\) or conductivities \((\lambda)\) of ions have been measured by several methods to elucidate solvation structures and charge effects on mobilities.\(^3,4\) The mobilities of ions can be transformed to the diffusion constants by the Nernst relationship.\(^1,5\) Generally, \(D\) values of ions are smaller than those of neutral molecules of similar sizes in the same solvent and at the same temperature.\(^5\) This is due to the strong intermolecular interaction between the charge of ions and solvent molecules by Coulombic forces. With decreasing molecular size, this effect becomes stronger and the difference between the \(D\) values of ions and stable molecules will increase. Two models are well known to interpret this size dependence of ionic mobilities. One is the excess size model,\(^6\) which is based on an increase of the molecular radius by the solvation structure of ions. The other is the dielectric friction model\(^5\) which is based on a friction which arises when the polarization of solvents follows the movement of the charges of ions. Both of two models can explain the size dependence of the \(D\) of the ion qualitatively. Boyd,\(^6\) Zwanzig\(^7\) and Hubbard–Onsager\(^8\) proposed equations to estimate the contribution of the dielectric friction by the continuous fluid theory. These equations can reproduce the experimental \(D\) values qualitatively, but not quantitatively. Recently, Bagchi and co-workers succeeded in reproducing the experimental \(D\) values quantitatively by a theory based on the dielectric friction.\(^9\)

The influence of the solute–solvent interaction through hydrogen bonding was reported recently by Chan and Chan,\(^10\) and Tomina 

Radicals are another interesting system for diffusion studies as well as for elucidating the mechanism\(^12\) and dynamics\(^13\) of chemical reactions. Unfortunately, until recently, only a few \(D\) values of radicals have been reported\(^14\) because of the technical difficulty. However, recently, we succeeded in measuring the \(D\) values of many intermediate radicals which appear during photochemical reactions by the transient grating (TG) method.\(^15\)–\(^18\) It was found that the transient neutral radicals created by photoinduced hydrogen abstraction reactions of ketones, quinones and \(N\)-heteroaromatic molecules diffuse much slower than their parent molecules.\(^15\)–\(^18\) We further investigated the viscosity \((\eta)\) dependence,\(^16\) the solute radius \((r)\) dependence\(^11\) and the temperature \((T)\) dependence of the \(D\) values of such radicals. The differences in \(D\) between the radicals and the parent molecules become larger with increasing \(\eta, 1/r\) or \(1/T\). These tendencies are similar to those of ions.\(^3\) We could reproduce such dependences by using the excess size model with a volume increase of \(5–8 \times 10^2\ \AA^3.\(^18\) This apparent volume expansion was interpreted in that the radicals interact with surrounding molecules strongly. This model is similar to that used for \(D\) of ions. However, since these electrically neutral radicals do not have charges, the source of the radical–solvent interaction is not immediately clear. Considering that not all of the radicals diffuse more slowly than closed shell molecules [e.g. benzyl radicals,\(^16\) \(2,2,5,5\text{-tetramethyl-1-piperidinylxoy} (\text{TEMPO})\) or some other stable radicals\(^20\)], we cannot attribute the origin of the radical–solvent interaction to only the presence of the unpaired electron. Since the slow diffusion of radicals was observed not only in polar solvents but also in non-polar solvents and in aprotic solvents,\(^16\) hydrogen bonding between the OH or NH group of the radical and the solvents cannot be the origin of the slow diffusion. Therefore, contrary to ions or hydrogen bonding systems, the origin of the slow diffusion remains unclear.

A natural extension of this research is the study of the diffusion of ion radicals, which have an unpaired electron and a
charge. In this case, since the motion of the radicals can be detected as electronic current, experimental measurement is easier. Indeed, the mobilities of the photochemically produced intermediate radical cations and anions probed by the time of flight (TOF) technique have been reported by Houser and Jar-nagin.\textsuperscript{21} Freeman and co-workers,\textsuperscript{22} and Albrecht and co-workers.\textsuperscript{23} They found that \( D \) of the ion radicals are smaller than those of neutral molecules of similar shapes and sizes. Freeman and co-workers attributed the origin of the slow diffusion to the electrostrictive drag by the charged species and dimerization for some compounds.\textsuperscript{22} Albrecht and co-workers found that \( D \) of the charged radicals can be well reproduced by the SE equation.\textsuperscript{23} This result, in good agreement with the SE relation, is similar to that found for the neutral radicals we have studied. However, even if one wishes to extract the effect of the charge or the unpaired electron by comparison of \( D \) of the charged radicals determined by this method with those of closed shell molecules, one has to use \( D \) of closed shell molecules measured by other methods under different conditions. Because \( D \) is very sensitive to environment and experimental conditions, accurate comparisons are very difficult. However, if we use the TG method, \( D \) values of stable molecules can be measured simultaneously with those of the transient species.\textsuperscript{24} For example, Terazima \textit{et al.} have determined \( D \) of a cation radical and its parent molecule, \( N,N,N',N'-\text{tetramethyl-p-phenylenediamine (TMPD)} \), by the TG method under exactly the same conditions.\textsuperscript{24} The result showed that the TMPD cation radical diffuses only half as quickly as the TMPD parent molecule in ethanol. However, the contribution of the charge and the unpaired electron could not be separated from this measurement. It would be very useful, if \( D \) values of closed shell molecules, neutral radicals, and ion radicals of similar shapes and sizes can be measured under the same condition.

In this work, we performed TG experiments along this line. Values of \( D \) of parent molecules, neutral radicals and anion radicals of ketones are determined by the TG method under the same conditions and compared. To create the neutral radicals, we employed hydrogen abstraction reactions. Charged radicals can be created from the neutral radicals by subsequent reactions. For example, the photochemical process of acetophenone (AP) is described in Scheme 1.\textsuperscript{25}

The lowest excited triplet (\( T_1 \)) state of AP is created by the intersystem crossing from the lowest excited singlet (\( S_1 \)) state by UV irradiation within an excitation laser pulse width (ca. 10 ns). The neutral radical is created from the \( S_1 \) state of AP by hydrogen abstraction (process b). The neutral radical and the anion radical are in equilibrium (process c). Therefore, one can create the anion radical or the neutral radical selectively by controlling the pH (pOH) of the solution. In aqueous solution such selective creation of the AP anion radical has been reported and the p\( K_a \) was determined to be 9.9.\textsuperscript{26} Here we create the anion radicals or the neutral radicals of acetophenone, benzaldehyde, xanthone, benzophenone and benzil in alcoholic solvents by controlling the concentration of sodium hydroxide (NaOH). Values of \( D \) of the anion radicals, the neutral ketyl radical and the parent stable molecules are measured under the same conditions and compared. The role of the charge and unpaired electron in diffusion is discussed on the basis of the obtained results.

\section{Experimental}

The experimental arrangement for the TG technique has been described elsewhere in detail.\textsuperscript{15,20,24,27} Briefly, an excitation laser pulse from an excimer laser [XeCl (308 nm); Lumonics Hyper-400] was split into two beams and crossed inside a 10 mm path quartz sample cell. The laser power at the crossing point was measured by a pyroelectric joulemeter (Molecron J3-09) and was typically ca. 0.3 mJ cm\(^{-2}\). Solute molecules in the cell were excited by the interference pattern between these beams (optical grating). The excited molecules release the heat by non-radiative relaxation and the temperature of the sample is modulated (thermal grating). A part of the excited molecules react and the concentrations of the reactant and product was also modulated, giving rise to the species grating. The thermal grating and the species grating disappear by heat conduction and mass diffusion, respectively. Therefore, these processes can be measured from the time profile of the light intensity of the diffracted probe beam (TG signal). The TG signal was detected by a photomultiplier tube (Hamamatsu R-928) after isolation with a pinhole and a glass filter (Toshiba R-62) and recorded with a digital oscilloscope (Tektronix 2430A). The time profile of the TG signal was analyzed with a microcomputer. The signal was averaged by a digital oscilloscope and a microcomputer to improve the S/N ratio. The fringe spacing \( A \) was roughly estimated from the crossing angle \( \theta \) and then calibrated from the decay of the thermal grating signal of a benzene solution containing a trace of Methyl Red.\textsuperscript{28} The temperature of the sample solution was controlled by flowing temperature-regulated methanol around a cell holder with a temperature control system (Lauda RSD6D).

For the transient absorption (TA) measurement, the sample was excited by the excimer laser (ca. 5 mJ cm\(^{-2}\)) and probed by a 100 W Xe lamp. The probe light was monochromated with a Spex model 1704 monochromater and detected by the photomultiplier.

Spectroscopic grade solvents (methanol, ethanol, propan-2-ol, butan-1-ol and pentan-1-ol) and solute (acetophenone, benzaldehyde, xanthone, benzophenone and benzil) were purchased from Nacalai Tesque and used without further purification. Typical concentrations of the solutes were ca. \(10^{-2}\) M. Sample solutions were deoxygenated by the nitrogen bubbling method and flowed by a peristaltic pump (Atto SJ-1211) to avoid the effect of reaction products in the signal.

The van der Waals volumes \( V_w \) of the molecules were obtained from the atomic increments method given by Edward.\textsuperscript{29} The radii of the molecules, \( r \), were calculated from \( V_w \) using the relation \( r = (3V_w/(4\pi))^{1/3} \).

\section{Results}

\subsection{Assignment of the TG signal}

The time profile of the TG signal after the photoexcitation of AP in ethanol is shown in Fig. 1(a). The time profile of the root square of the TG signal \( I_{TG(t)^{1/2}} \) can be fitted well with a sum of three exponential functions.

\[ I_{TG(t)^{1/2}} = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) = a_3 \exp(-k_3 t) \]  

where, \( k_1 > k_2 > k_3 \) are the decay constants and \( a_1 > a_2 > a_3 > 0 \) are the pre-exponential factors. The solid line in Fig. 1(a) is the line fitted by using the non-linear least-squares.
method with eqn. (1) and the profiles of the three components are shown in Fig. 1(b). The method for assignment of each exponential component of the TG signal to its origin has been described previously in detail.\textsuperscript{15,20,24,27} The TG signal intensity is proportional to a sum of the square of the refractive index change and the absorbance change induced by the optical grating.\textsuperscript{10} In this reaction system, absorption bands of any species are on the far blue side from the probe wavelength (633 nm).\textsuperscript{28,31} Thus, the TG intensity is proportional to only the square of the refractive index change. The thermal effect (thermal grating) and the creation or depletions of chemical species (species grating) can contribute to the refractive index change. The time profiles of the signals due to the thermal grating and the species grating are given by solving Fourier’s thermal diffusion equation and Fick’s reaction–diffusion equation, respectively.\textsuperscript{15} Since in the observation time range of the TG signal, the creation and termination reaction of the radicals can be neglected as shown later, the time dependence of the TG signal is given by\textsuperscript{13–20,24}

$$I_{TG}(t)^{1/2} = \delta n_0^0 \exp(-D_{th} q^2 t) - \sum \delta n_p^0 \exp(-D_p q^2 t) + \sum \delta n_k^0 \exp(-D_k q^2 t)$$

(2)

where, $q$ is the grating vector [$q = 2\pi/A$, ($A$; fringe length)], the first term of eqn. (2) represents the thermal grating and $\delta n_0^0$ is the initial refractive index change just after the excitation. $\delta n_p^0$ and $\delta n_k^0$ are the initial refractive index changes by the species grating of the parent molecules and the radicals, respectively. $D_{th}$ is the thermal diffusion coefficient of the solvent and $D_p$, $D_k$ are the diffusion constants of the parent molecules and the radicals, respectively.

Generally, as the refractive index decreases with increasing temperature, $\delta n_0^0$ is negative. Because the heat conduction process is a faster process than the mass diffusion process, $D_{th}$ is about 100 times larger than $D_p$ or $D_k$. Therefore, component 1 in the TG signal obtained [Fig. 1(b)] is assigned to thermal grating. Comparing eqn. (2) with eqn. (1), $D_{th}$ is given by $k_1 = D_{th} q^2$. The obtained value is close to the literature values.\textsuperscript{26}

As both the parent molecules and the radicals in this system have absorption bands at shorter wavelengths than that of the probe beam, both $\delta n_p^0$ and $\delta n_k^0$ are expected to be positive from Kramers–Kronig relationship. Therefore, the sign of the parent molecule component is negative, which is the same as the sign of the thermal grating term. On the basis of this reasoning, component 2 in the TG signal [Fig. 1(b)] is assigned to the signal from the parent molecule. On the other hand, the radical’s contribution in the TG signal should be positive. Component 3 in Fig. 1(b) should be due to the radical. It has been reported that the electrically neutral radical is created by photoexcitation of AP in a pure alcoholic solvent.\textsuperscript{17} In this reaction system, four chemical species (AP, AP ketyl radical, ethanol, hydroxyethyl radical) could contribute to the signal. However, since the absorption coefficient of ethanol and hydroxyethyl radical are smaller than those of AP and the ketyl radical, the TG signal due to ethanol and the hydroxyethyl radical could not be detected. Therefore, we assign component 2 to the species grating of AP and component 3 to that of the AP ketyl radical. Then, $D_p$ and $D_k$ are the diffusion constants of AP and the AP ketyl radical, respectively.

Next, we performed a similar measurement for AP in ethanol which contains sodium hydroxide. Fig. 2(a) shows the time profile of the TG signal of AP ethanol + 0.01 M NaOH. The shape of this signal is slightly different from that given in Fig. 1(a). This time profile can also be fitted by eqn. (1) very well [solid line in Fig. 2(a)]. The three exponential components are shown in Fig. 2(b). Comparing Fig. 2(b) with Fig. 1(b), we find that the intensity of component 3 is enhanced relative to the other components. The enhancement suggests that the transient in pure ethanol is different from that in ethanol + NaOH. In an aqueous solution, it was reported that the anion radical is created in an alkaline solution, while the electrically neutral radical is created in pure water.\textsuperscript{28} In the next section, we use the transient absorption technique to identify the intermediates in ethanol and ethanol + NaOH.
3.2 Transient absorption measurements

We examine the intermediates created in pure ethanol and ethanol + NaOH by the transient absorption (TA) method. Fig. 3(a) shows the TA spectra with a 10 μs time delay after excitation in pure water and in NaOH + water. The observed TA spectrum in pure water [filled circles in Fig. 3(a)] is assigned to the AP neutral radical [reported TA spectrum26] is shown by the solid line in Fig. 3(a). Upon adding NaOH to that solution, the TA spectrum changes and it becomes similar to the reported spectrum of the AP anion radical [dotted line in Fig. 3(a)].26 Hayon et al. have reported pK₄ values of AP, benzophenone and benzil as 9.9, 9.25 and 5.5, respectively.26

The TA spectra observed in pure ethanol and NaOH + ethanol are shown in Fig. 3(b). The TA spectrum in pure ethanol [filled circles in Fig. 3(b)] is close to the reported spectrum of the AP neutral radical in ethanol (solid line).31 The TA spectrum in AP–NaOH + ethanol [open squares in Fig. 3(b)] is similar to the spectrum of the AP anion radical in water26 [dotted line in Fig. 3(a), (b)]. Therefore, we assigned this spectrum to the AP anion radical.

Based on these observations, we conclude that the electrically neutral radicals and the anion radicals can be created selectively by controlling the concentration of NaOH in alcoholic solvents. Fig. 4 shows the intensities of the TA signals at 450 nm and the intensities of the TG signals at various concentrations of NaOH in ethanol. Both of the intensities steeply change at pOH ≈ −log [NaOH] = 3–4. Under dilute conditions (NaOH < ca. 10⁻⁴ M), the neutral radical is created. If the concentration of NaOH is > ca. 10⁻³ M, the anion radical is dominant in ethanol. Since the spectra do not depend on the monitoring time (10 μs to a few ms), the neutral radical and the anion radical of AP are in equilibrium within 10 μs after the creation (Scheme 1) in water and in ethanol. The pK₄ value of this equilibrium is pK₄ = 3–4 in ethanol (pK₄ = 14 − 9.9 = 4.1 in water26). According to this result, component 3 in the TG signal in pure ethanol [Fig. 1(b)] is assigned to the AP neutral radical and that in ethanol + 0.01 M NaOH [Fig. 2(b)] to the AP anion radical.

The created radicals are relatively stable and their TA signals are observable for tens of milliseconds after excitation (1–5 mJ cm⁻²). The TA signals show second-order decay which should be due to the self-termination reaction of the radicals.26,33 Under a weak excitation laser power for the TG measurement (ca. 0.3 mJ cm⁻²), the intensities of the TA signals are almost constant and the shapes of the TA spectra do not change within the time range for the TG measurement (a few milliseconds). Therefore, it is evident that the created radicals do not react with the solvent or the parent molecules, and the time profile of the TG signal (Fig. 1 and 2) can be analyzed simply by the diffusion process of each species.

3.3 Comparison of values of D for neutral radicals with anion radicals

The decay rate constants k₁, k₂ obtained by the fitting of the TG signals at various fringe spacings are plotted vs. the square of the grating vector q in Fig. 5. Based on the assignment given above and from eqn. (1) and (2), the following relationships are obtained.

\[ k_2 = D_p q^2 \]  
(3a)

\[ k_3 = D_k q^2 \]  
(3b)

The TG signal decays not only by the diffusion process but also by any reaction processes. In this case, the decay rate of the TG signal is accelerated by the reaction, and more detailed consideration is necessary for the analysis as we have reported for the benzyl radical case.19 However, the linear relationship between the decay rate constants and q² with small intercepts with the ordinate (Fig. 5) and also the slow radical decays measured by the TA method ensure that D can be determined from the slope of the plot. The values obtained for D of the parent molecule, the neutral radical and the anion radical in ethanol are listed in Table 1. The value of D for AP in ethanol is the same as that in ethanol + NaOH within experimental error. This suggests that the effect of addition of 0.01 M NaOH on diffusion is negligibly small. The main source of the experimental error comes from the fitting error of the double-exponential function and the fact that the D values of the parent molecules have large errors.34 Recently, Donkers and Leaist have reported D of AP by using the Taylor dispersion (TD) method as \(1.24 \times 10^{-9}\) and

![Fig. 3](image-url)  
(a) Transient absorption spectra at a 10 μs time delay after the excitation of AP in water (○) and AP in water + 0.01 M NaOH (□). (b) Transient absorption spectra of AP in pure ethanol (○) and AP in ethanol + 0.01 M NaOH (□). Spectra of the neutral radical of AP (solid line) and the anion radical of AP (dotted line) from ref. 26 (in water), 31 (in ethanol) are shown in both figures for comparison.  
![Fig. 4](image-url)  
Plot of the signal intensity of the transient absorption at 450 nm (top) and that of the transient grating (bottom) at a 100 μs delay after the excitation against the concentration of NaOH in AP–ethanol + NaOH.
Fig. 5 Relationship between the decay rate constants (k) of each component of the TG signal and q². ●, ○ denote the parent molecule (AP), the neutral radical of AP in ethanol, respectively. ■, □ denote the parent molecule (AP), and the anion radical of AP in ethanol + 0.01 M NaOH, respectively.

$0.76 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ in ethanol and propan-2-ol, respectively.\textsuperscript{35} Our values from the TG method are close to their values from the TD method with relative errors of 10 and 17% in ethanol and propan-2-ol, respectively.

The solvent viscosity depends on the concentration of electrolytes. In diluted solution (<1 M), the Jones–Dole equation describes the concentration dependence of the viscosity well.\textsuperscript{36}

$$\eta/\eta^0 = 1 + AC^{1/2} + BC$$  \hspace{1cm} (4)

where η and η₀ are the viscosities of the electrolyte solution and the pure solvent, respectively. Parameter A expresses the ion–ion interaction and is zero when the solvent is neutral; C is the concentration (m) of the solute while B is the coefficient of the solvent viscosity, which indicates the ion–solvent interaction. Values of B for Na⁺ and OH⁻ have been reported as 0.086 and 0.112 dm³ mol⁻¹, respectively, in water.\textsuperscript{37} Generally, B depends mainly on the ion volume and does not change much with variation of solvent.\textsuperscript{38} We estimated the viscosity change of the solution by the addition of NaOH from eqn. (4). Using B data in water, we obtained $\eta/\eta^0 = 1.002$ at 0.01 M NaOH. Since, roughly, D is inversely proportional to the viscosity, this small change of the viscosity is within the experimental error of this work. Therefore, the viscosity change upon the addition of NaOH (0.01 M) is negligible and D of the neutral radical and the anion radical can be compared directly.

Both D of the neutral radical and anion radical of AP are smaller than that of the parent molecule. Previously, the reduction of D of neutral radicals relative to the parent molecules was explained in terms of intermolecular interactions between the radicals and the solvent molecules. In this case, we suspect that the intermolecular interactions between both the neutral and anion radical and the solvent molecules are similarly strong. Before this study, we expected the values of D of anion radicals to be smaller than those of neutral radicals because the anion radical has both charge and an unpaired electron, both of which can affect the diffusion process. However, this is not the case, although a slight difference between D of neutral radicals and the anion radicals is just detectable beyond experimental error (Table 1). This slight difference may be due to the contribution of the charge to the diffusion process or possible ion pair formation between the anion and sodium cation. However, previous EPR studies showed that the ion pairs of ketals tend to dissociate in alcohol.\textsuperscript{39} Another possibility is that the anion radicals are associatively active and form dimers.\textsuperscript{40} In this case, D of the anion radical dimer is expected to be $ca. 1.25 = 2^{1/2}$ times larger than that of monomer.\textsuperscript{23,36} Since D is inversely proportional to the radius of the solute.

It is interesting that this charge effect on D of the anion radical is much smaller compared with the reported charge effect on D of the ions of similar sizes.\textsuperscript{1,3,2} The charge effect on diffusion in the anion radical may be reduced by some factors. This phenomenon could be related to the origin of the anomalously slow diffusion of radicals. In later sections, we discuss the solvent viscosity, solute size and temperature dependence of D of neutral and anion radicals to clarify this behavior.

### 3.4 Solvent viscosity, solute size and temperature dependence of D

Contrary to our initial expectation, the diffusion of the AP anion radical is similar to that of the neutral radical. In order to examine further the cause of the effects of the charge and unpaired electron on the diffusion process, we investigate D under various conditions. According to the SE equation, D is proportional to temperature (T) and inversely proportional to the viscosity of solvent (η) and radius of solute (r). Dependences of D of these species on solvent viscosity, solute size and temperature are discussed below.

In order to monitor the effect of viscosity, we measured the TG signal of AP in methanol, propan-2-ol, butan-1-ol and pentan-1-ol. The time profiles of the TG signals in various solvents are similar to that in ethanol and D can be determined by the same method as before. Values of D of the parent molecules, the neutral radicals and the anion radicals in these solvents are listed in Table 1 and plotted vs. η⁻¹ in Fig. 6.

To monitor the effect of molecular size, benzaldehyde, xanthone, benzenophenone and benzil were studied with their neutral radicals and anion radicals being created by the same method as for AP. The time profiles of the TG signals of such solutes are quite similar to that of AP in both pure ethanol and ethanol + 0.01 M NaOH. The obtained D values of these species are listed in Table 2 and plotted vs. 1/r in Fig. 7. Values of D of the parent molecules are close to the literature values [1.39, 0.90 and 0.95] × 10⁻⁹ m² s⁻¹ for benzaldehyde, xanthone and benzenophenone, respectively] within ±15%.\textsuperscript{35} From Fig. 6 and 7, it is evident that the D values of the anion

<table>
<thead>
<tr>
<th>Solvent</th>
<th>AP in pure solvent</th>
<th>neutral radical</th>
<th>AP in solution + 0.01 M NaOH</th>
<th>anion radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>1.36 ± 0.11</td>
<td>0.58 ± 0.01</td>
<td>1.37 ± 0.10</td>
<td>0.52 ± 0.03</td>
</tr>
<tr>
<td>methanol</td>
<td>1.78 ± 0.05</td>
<td>1.25 ± 0.04</td>
<td>1.91 ± 0.12</td>
<td>1.15 ± 0.02</td>
</tr>
<tr>
<td>propan-2-ol</td>
<td>0.89 ± 0.03</td>
<td>0.33 ± 0.01</td>
<td>0.89 ± 0.05</td>
<td>0.28 ± 0.02</td>
</tr>
<tr>
<td>butan-1-ol</td>
<td>0.77 ± 0.08</td>
<td>0.26 ± 0.01</td>
<td>0.80 ± 0.20</td>
<td>0.19 ± 0.03</td>
</tr>
<tr>
<td>pentan-1-ol</td>
<td>0.66 ± 0.09</td>
<td>0.19 ± 0.01</td>
<td>0.63 ± 0.06</td>
<td>0.14 ± 0.05</td>
</tr>
</tbody>
</table>

radicals of all solutes in all solvents in this work are close to those of the neutral radicals. Therefore the reduction of the charge effect on \( D \) seems to be general for the intermediate ketyl radicals created by the hydrogen abstraction reaction.

We compare the experimental \( D \) values of these species with theoretical calculations where \( D \) is described by the Stokes law

\[
D = \frac{k_B T}{f}
\]

where \( f \) is the friction of the solute molecules in the solvent.

![Fig. 6](image) Viscosity dependence of \( D \) of AP in alcohols (●), the neutral radical of AP in alcohols (○), AP in alcohol + 0.01 M NaOH (■), the anion radical of AP in alcohol + 0.01 M NaOH (□). Solvents are 1, pentan-1-ol; 2, tert-butanol; 3, propan-2-ol; 4, ethanol and 5, methanol. Solid line and dotted line are \( D \) calculated from eqn. (7) and (8), respectively.

![Fig. 7](image) The solute size dependence of \( D \) of parent molecules in ethanol (●), neutral radicals in ethanol (○), AP in alcohol + 0.01 M NaOH (■), the anion radical of AP in alcohol + 0.01 M NaOH (□). Solute ketones are 1, benzil; 2, benzophenone; 3, xanthone; 4, acetophenone and 5, benzaldehyde. Solid line and dotted line are \( D \) calculated from eqn. (7) and (8), respectively.

The solute size dependence of \( D \) of all solutes in all solvents in this work are close to those of the neutral radicals. Therefore the reduction of the charge effect on \( D \) seems to be general for the intermediate ketyl radicals created by the hydrogen abstraction reaction.

We compare the experimental \( D \) values of these species with theoretical calculations where \( D \) is described by the Stokes law

\[
D = \frac{k_B T}{f}
\]

where \( f \) is the friction of the solute molecules in the solvent.

Fig. 6 Viscosity dependence of \( D \) of AP in alcohols (●), the neutral radical of AP in alcohols (○), AP in alcohol + 0.01 M NaOH (■), the anion radical of AP in alcohol + 0.01 M NaOH (□). Solvents are 1, pentan-1-ol; 2, tert-butanol; 3, propan-2-ol; 4, ethanol and 5, methanol. Solid line and dotted line are \( D \) calculated from eqn. (7) and (8), respectively.

\[
\text{Eqn. (6) and (7) are well known as the Stokes–Einstein (SE) formula, which gives one of the most fundamental equations for } D. \text{ Constant } a \text{ in eqn. (7) indicates the boundary condition of the friction between the solute and solvent. For the stick boundary condition, } a = 6, \text{ and for the slip boundary condition, } a = 4. \text{ The calculated } D \text{ of the SE equation (} D_{SE} \text{) generally reproduce experimental } D \text{ well when the sizes of solute molecules are sufficiently large. However, if the volume of a solute molecule is small or close to the solvent volume, } D_{SE} \text{ underestimates the experimentally observed } D \text{ because the continuous fluid approximation for the solvent is no longer valid.}

\[
\text{Some modifications of the SE equation have been proposed.}^5 \text{ Evans and co-workers proposed an empirical equation, which is given by}^{41}
\]

\[
f_{EV} = \frac{k_B \exp(a/r_A + b)}{k_B \exp(a/r_A + b)}
\]

where \( a, b, c \) and \( d \) are constants, which were determined by Evans and co-workers as \( a = 5.973 \text{ Å}, b = -7.3401, c = -0.8636 \text{ Å} \) and \( d = 1.0741. \) In a series of our previous studies, we have shown that the calculated \( D \) values from this equation (\( D_{EV} \)) agree very well with the \( D \) values of the parent molecules. On the other hand, the \( D \) values of radicals are closer to \( D_{SE} \) under the stick condition.\text{15–18 Fig. 6 and 7 show plots of } D_{EV} \text{ and } D_{SE} \text{ (stick boundary). As can be seen, } D \text{ values of the parent molecules are close to } D_{EV} \text{ and } D \text{ of both the neutral and anion radicals are close to } D_{SE}. \text{ It is interesting that the experimental data indicate that the difference in } D \text{ between the parent molecules and the anion radicals increases with increasing } \eta \text{ and/or decreasing } r. \text{ This tendency is what we observed before in neutral radicals.}

\[
\text{Table 2 Size dependence of the diffusion constants (}\text{[D]} \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\text{) of the parent molecules, the neutral radicals and the anion radicals in ethanol and ethanol + 0.01 M NaOH}
\]

<table>
<thead>
<tr>
<th>solute</th>
<th>( D ) in ethanol</th>
<th>( D ) in ethanol + 0.01 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>1.60 ± 0.05</td>
<td>1.52 ± 0.02</td>
</tr>
<tr>
<td>xanthone</td>
<td>0.90 ± 0.05</td>
<td>0.87 ± 0.04</td>
</tr>
<tr>
<td>benzophenone</td>
<td>0.80 ± 0.05</td>
<td>0.80 ± 0.10</td>
</tr>
<tr>
<td>benzil</td>
<td>0.77 ± 0.05</td>
<td>0.70 ± 0.10</td>
</tr>
</tbody>
</table>
that an Arrhenius-type relation holds for this system. Deter-
exponential factor. The log
where \( E \) is the diffusion activation energy and \( D_0 \) is the pre-
several solutions can be generalized by the following Arrhenius-type equa-
tion.

\[
D = D_0 \exp\left(-\frac{E_D}{k_B T}\right)
\]

(9)

where \( E_D \) is the diffusion activation energy and \( D_0 \) is the pre-
exponential factor. The log \( D \) vs. \( 1/T \) plots of Fig. 7 indicate
that an Arrhenius-type relation holds for this system. Determined \( E_D \) and \( D_0 \) values are listed in Table 3. It is of note that,
although \( D \) of the parent molecules and neutral (or anion) radicals are very different, \( D_0 \) of these species are very similar.
On the other hand, \( E_D \) of both types of radical are larger than those of the parent molecules. This behavior can be again reproduced by calculation from eqn. (7) and (8), both qualitatively and quantitatively (Fig. 8). Again this is similar to the case of the neutral radicals reported before.\(^{18} \) In that paper, we explained the temperature dependence by the excess size model. The activation energy of the anion radical is almost the same as that of the neutral radical. The charge in the radical does not change the activation energy of diffusion. We consider a possible origin of this fact below.

4 Discussion

4.1 Comparison of \( D \) between ionic radicals and stable ions

In the previous section, we compared \( D \) of charged radicals with those of neutral radicals. This comparison will provide information of the charge effect on the radicals. In order to discuss the charge effect on the radicals and also that on the closed shell molecules, \( D \) of stable ions are compared with those of the closed shell molecules. A large number of studies have been made on the diffusion process of metal ions.\(^{3} \) As the metal ions become small, the effect of the Coulombic force becomes remarkably large and values of \( D \) of metal ions become much smaller than \( D_{SE} \). This effect has been explained by the formation of a complex with a large number of solvent molecules.\(^{4} \) Since the sizes of the metal ions are too small for the hydrodynamic theory based on the continuous fluid model, it would not be appropriate to use such data for comparison with our samples. Values of \( D \) of larger non-metallic ions have been measured by the ionic conductance method for some tetraalkylammonium ions and the values are compared with values of \( D \) of some tetraalkyltins by the Trylor dispersion technique.\(^{5} \) The results show that the ionic mobility is slower than that of non-ionic molecules and such differences were analyzed by the dielectric friction model.

The effect of the dielectric friction is given by

\[
f = f_0 + R \eta / r^3
\]

(11)

where \( f_0 \) is the hydrodynamic friction and the \( R / r^3 \) term is the dielectric friction. Generally, \( f_0 \) is calculated from the Einstein's formula [eqn. (7)]. According to the theory by Zwanzig, \( R \) is given by

\[
R_Z = \frac{A e^2 (\varepsilon_0 - \varepsilon_e) R_D}{(g_0 (2g_0 + e_0))}
\]

Based on the Hubbard–Onsager (HO) theory, \( R \) is written as

\[
R_{HO} = \frac{A e^2 (\varepsilon_0 - \varepsilon_e) R_D}{(g_0)}
\]

(13)

where, \( \varepsilon_0 \) and \( \varepsilon_e \) are the static and optical dielectric constants, respectively, \( \varepsilon \) is the charge of the proton and \( \tau_p \) is Debye's relaxation time. Constant \( A \) has a value of 3/8 for the stick boundary condition and 3/4 for the slip boundary condition of eqn. (12), 17/280 for the stick boundary condition and 1/15 for the slip boundary condition of eqn. (13).

Evans and co-workers\(^{6} \) experimentally determined \( R \) of some tetraalkylammonium ions in several solvents by comparison of \( D \) of non-ionic molecules. The experimentally obtained values of \( D \) of the ionic molecules studied by Evans and co-workers\(^{6} \) are plotted vs. \( 1/r \) and \( 1/\eta \) in Fig. 9 along with our data. Both \( D_{SE} \) and \( D_{EV} \) calculated from eqn. (7) and (8) are plotted. It is evident from the figures that values of \( D \) of the ions are close to \( D_{SE} \) under the stick condition, similarly to

![Fig. 9](image-url)

| Table 3 Activation energy for diffusion (\( E_D \)) and the pre-exponential factor (\( D_0 \)) \( D = D_0 \exp\left(-\frac{E_D}{k_B T}\right) \) of AP, the neutral radical and the anion radical obtained by the Arrhenius plot of \( D \) (Fig. 8) in ethanol and ethanol + 0.01 M NaOH |
|-----------------|-----------------|-----------------|
| parent molecule | in ethanol       | neutral radical  |
|                  | in ethanol + 0.01 M NaOH | in ethanol + 0.01 M NaOH |
| D_0/10^{-7} m^2 s^{-1} | E_D/kcal mol^{-1} | D_0/10^{-7} m^2 s^{-1} | E_D/kcal mol^{-1} |
|-----------------|-----------------|-----------------|
| parent molecule | in ethanol       | neutral radical  |
|                  | in ethanol + 0.01 M NaOH | in ethanol + 0.01 M NaOH |
| 2.0 ± 0.1       | 2.97 ± 0.04     | 2.88 ± 0.05     |
| 1.7 ± 0.2       | 3.52 ± 0.06     | 3.56 ± 0.03     |

\(^{4} \) 1 cal = 4.184 J.
radicals. This agreement indicates that the diffusion of the stable ions is expressed by the stick boundary condition of the hydrodynamic model rather than the dielectric model. (The agreement of $D$ of the non-ionic molecule with $D_{\text{EV}}$ is expected since eqn. (8) was empirically determined from these data.)

4.2 Models for slow diffusion

For a detailed comparison of $D$ values of neutral radicals, anion radicals and stable ions, the size dependence of diffusion of the three types of species are plotted in Fig. 9(b). Although $D_{\text{SE}}$ [straight solid line in Fig. 9(b)] reproduce $D$ of three species, some differences are notable; $D$ decreases in the order: stable ions, neutral radicals, anion radicals.

We have explained the diffusion process of the neutral radicals based on the excess volume model.\cite{16,17} In this model, the equation derived by Evans and co-workers\cite{18,19} was modified as if the molecular volume of the radical was expanded. An equation from this model is given by\cite{20}

$$f_v = k_b^{-1} \exp \left[\frac{a}{(r^2 + 3V_0/4\pi)^{3/2}} - b \right] \sigma(\exp(3V_0/4\pi r^2) + d)$$

(14)

where $V_0$ is the apparent excess volume of the radical. In a series of investigations on radical diffusion, we have succeeded in reproducing the size, viscosity and temperature dependences of $D$ of the radical by this model with $V_0 = 5 \times 10^{-6}$ $\text{m}^3$. Although values of $D$ calculated from this model ($D_\text{H}$) are close to $D_{\text{SE}}$, the size dependence of the diffusion activation energies of radicals agrees better with the calculation based on this model rather than on the SE equation.\cite{21} Values of $D_{\text{SE}}$ are proportional to $1/r$ [straight line in Fig. 9(b)] while the slope of $D_\text{SE}$ on $1/r$ is gentler [dotted line in Fig. 9(b)]. Values of $D_{\text{SE}}$ are close to $D$ of the neutral and anion radicals but those of the stable ions are slightly larger than $D_V$.

Felderhof showed that the HO theory for ionic mobility needs to be corrected and performed more careful numerical studies based on dielectric friction theory.\cite{22} In a similar manner, Ibuki and Nakahara tested the dielectric friction theory for ion mobility in polar solvents. They found that the HO theory is better than the Zwanzig theory to describe the motion of an ionic species and proposed an approximate HO theory.

4.3 Intermolecular interactions of neutral and anion radicals

One of the main interesting findings in this research is that $D$ values of neutral radicals are quite close to those of the anion radicals and ions. This fact indicates that the friction of the neutral radicals (whatever its origin), and the dielectric friction of ions are not additive. It is interesting that $D$ values of ions, neutral radicals and ionic radicals are close to $D_{\text{SE}}$ under the stick boundary condition under a variety of conditions of solvent, temperature and molecular size (although slight differences are apparent). This fact may suggest that $D_{\text{SE}}$ at the stick boundary condition could be the lowest limit of $D$. If the boundary condition is already completely stick-like for the neutral radicals and ions, the condition cannot be ‘more stick-like’ even if a charge is attached to the neutral radical or if an unpaired electron is attached to the ion. Another possible explanation for the similar $D$ values of neutral and ionic radicals may be related to the origin of the slow diffusion of the neutral radicals. We will come back to this point later in this section.

What is the origin of the slow diffusion of the neutral radicals? To answer this the fact that $D$ of the neutral radicals and that of the stable ions are very similar over wide ranges of viscosities and molecular sizes (Fig. 9) may be a clue. It suggests that the solute-solvent intermolecular interaction of ions and neutral radicals could be similar, more specifically, similar to the electrostatic interaction. Of course, neutral radicals have no overall charge, but if the charge densities of the radicals are polarized significantly and/or the radicals have large dipole moments, they can interact with the solvent molecules by electrostatic interaction. This effect may be the origin of the slow diffusion of the radicals.

Now and Zwanzig proposed a theory of the dielectric friction for a dipolar molecule,\cite{23,24} and subsequently, many theories have been proposed to account for the dielectric friction to the rotation of polar solutes in polar solvents\cite{25} or reorientation of polar solute molecules interacting with polar solvents.\cite{26} No theory to explain the dielectric friction effect of a polar solute to the translational diffusion have been reported. However, by analogy with the rotation process, it is natural to consider that the diffusion process of the polar solute should be influenced by the dielectric friction. In fact from the dynamic Stokes shift measurement, Maroncelli and co-workers concluded that, even in non-polar solvents, the dielectric friction can be notable by the interaction with the quadrupole moment of the solvent.\cite{27} Moreover, Okazaki et al. found that a merocyanine form of a benzisopropryn, which has a large dipole moment (ca. 12 D) diffuses slower than the non-charge-separated spiro-form not only in ethanol but also in cyclohexane.\cite{28} These observations suggest that the dielectric friction is not so small as predicted from eqn. (12), (13), and the corrected HO equations even in non-polar solvents.

If electrostatic interaction is the main origin of the slow diffusion of the radicals (such as due to dielectric friction), the radicals should be more polar than the parent molecules. We calculated and compared the polarizabilities and the dipole moments of the radicals and the parent molecules by using a semi-empirical molecular orbital (MO) calculation with modified neglect of diatomic overlap (MND0) method.\cite{29} However, the calculated dipole moments of the ketyl radicals of AP and benzophenone (1.6, 1.4 D, respectively) are smaller than those of the parent molecules of AP and benzophenone (2.7 and 2.5 D, respectively). Furthermore, the polarizabilities of the radicals and the parent molecules are found to be similar.\cite{30} Therefore, we could not find any significant differences in the molecular orbital character between the radicals and their parent molecules by simple MO calculations.

A possible explanation of the slow diffusion of radicals was given very recently by Morita and Kato.\cite{31} They investigated electric properties of radicals created by the hydrogen abstraction reactions by ab initio MO calculations, and found that the sensitivities of the intramolecular charge polarization induced by an external electrostatic field are remarkably enhanced in the some radicals, though this sensitivity does not

\[ D_{\text{SE}} \approx 3.33564 \times 10^{-30} \text{C m.} \]
appear in the usual polarizability calculated by the MO calculation we used.\textsuperscript{50} According to their analysis, such an enhancement is due to the $\sigma$-$\pi$ mixing that facilitates the deformation of the $\pi$-electron orbital of aromatic radicals. They suggested that this particular sensitivity of aromatic radicals could be the origin of the anomalous slow diffusion of the radicals. Their theoretical suggestion seems to be consistent with our finding that the friction of neutral radicals is similar to that of ions.

Their calculations show that the charge sensitivity depends on the molecular structure. When a charge is attached to the neutral radical, the structure should be changed and the $\sigma$-$\pi$ mixing, which is the origin of the enhanced charge sensitivity, could diminish. In that case, only the intermolecular interaction by the electric charge (not the charge sensitivity) causes the slow diffusion of the ionic radicals like that of stable ions. This exclusive mechanism of the slow diffusion of neutral and ionic radicals may answer to the question as to why the effect of the charge and the unpaired electron is not additive.

5 Conclusion

The translational diffusion constants ($D$) of electrically neutral ketyl radicals, anion radicals and parent molecules were measured by the transient grating (TG) method in alcoholic solutions. The neutral radicals and the anion radicals could be created selectively by controlling the concentration of sodium hydroxide not only in aqueous solution but also in alcoholic solutions. The presence and the decay kinetics are examined by transient absorption and the time profile of the TG signal is interpreted in terms of the mass diffusion of these species. It was found that both the neutral and anion radicals diffuse more slowly than the parent molecules. Values of $D$ of the anion radicals are compared to those of the neutral radicals for studying the effect of the charge and the unpaired electron on the diffusion process. We measured the solvent viscosity dependence, the solute size dependence and the temperature dependence of $D$. These $D$ values are compared with the values calculated based on the Stokes–Einstein equation ($D_{\text{MO}}$) and the equation proposed by Evans and co-workers ($D_{\text{Evans}}$). Values of $D$ of the parent molecules are close to $D_{\text{Evans}}$, while $D$ of both types of radicals are close to $D_{\text{MO}}$. $D$ values of anion radicals are close to that of the neutral radicals over a wide range of solvent viscosity, solute size and temperatures. Comparing this result with reported $D$ values of stable ions, we found that the diffusion of neutral radicals, ionic radicals and ions are similar. For a more careful comparison, we calculated $D$ values using the dielectric friction model, which is corrected by the Hubbard–Onsager equation ($D_{\text{MO}}$). The $D$ values of the radicals are close to $D_{\text{Evans}}$. On the other hand, the $D$ values of ions are closer to $D_{\text{MO}}$ than $D_{\text{Evans}}$. At present, we think that the slow diffusion of the radicals and ions may be due to a similar origin, which may be solute–solvent electrostatic interaction. Recently, Morita and Kato reported that the sensitivities of the intramolecular charge polarization of the radicals are enhanced remarkably by an external electrostatic field. They proposed that such an enhancement is the origin of the anomalously slow diffusion of radicals. Their proposal is consistent with our explanation.

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